DOE-BES Principal Investigators' Meeting Physical Behavior of Materials

March 15-17, 2023, Virtual Meeting Program and Abstracts





U.S. Department of Energy Office of Science – Basic Energy Sciences Division of Materials Sciences and Engineering



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FOREWORD

This booklet presents the collection of extended abstracts submitted to VIII'th Physical Behavior of Materials Principal Investigators meeting. This virtual meeting is sponsored by Division of Materials Sciences and Engineering (MSE) of Department of Energy, Office of Basic Energy Sciences (BES), and is held on March 15-17, 2023.

The purpose of Principal Investigators meeting is to bring together all the principal investigators and their co-PIs who are supported by the Physical Behavior of Materials program to share the latest exciting scientific knowledge and discoveries, facilitate exchange of ideas and promote collaborations. For BES and the participating investigators, the meeting serves the purpose of providing an overview and assessment of the whole program, which helps BES to identify new research areas and chart future directions for the program. This meeting brings together leading experts in topical areas of research supported by our program and is designed to stimulate and inspire new ideas.

The Physical Behavior of Materials program supports transformative and innovative research activities at the crossroads of materials science and condensed-matter physics. The primary mission of the program is to support both fundamental and use-inspired basic scientific research, to advance our knowledge of materials' behavior. The primary scientific interests of the program include electronic, electromagnetic, magnetic, and thermal behavior of materials, including novel light-matter interactions and quantum-information science projects that are relevant to BES mission. The program has a rich portfolio in many ground breaking, exciting, and high-risk high-reward projects in both experimental and theoretical areas.

The 2023 Principal Investigators meeting is being held virtually. The meeting format has been modified to include shortened oral presentations, short "poster talks", and special sessions to introduce "new projects" recently added to the Physical Behavior of Materials program. This meeting brings together over 100 scientists, and is organized to include 26 regular presentations, 40 virtual poster talks, and 16 new project introductions.

We appreciate the contributions of all Physical Behavior of Materials investigators for sharing their exciting ideas and latest findings. We are also grateful to the outstanding support of Tia Moua of the Oak Ridge Institute for Science and Education, and Teresa Crockett of MSE.

> Refik Kortan, Ph.D. Athena S. Sefat, Ph.D. Program Managers, Physical Behavior of Materials Program Division of Materials Sciences and Engineering Office of Basic Energy Sciences Department of Energy March 2023

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11:50-12:10	"Disorder in Topological Semimetals" Kirstin Alberi, <i>National Renewable Energy Laboratory</i>
12:10-12:30	"Emergent properties of magnons coupled to microwave photons" Benjamin Jungfleisch, <i>University of Delaware</i>
12:30-12:50	"Multiphoton Quantum Simulation through the Control of Electromagnetic Near-Fields in Photonic Networks" Omar Magana-Loaiza, LSU

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13:15-13:20	"Complex chalcogenides under pressure" Janice Musfeldt, University of Tennessee
13:20-13:25	"Investigating Excitonic Properties through Photon Correlation in Quantum Optical Materials" Moungi Bawendi, <i>Massachusetts Institute of Technology</i>
13:25-13:30	"Nanoscale Free-Electron Lasing" Karl Berggren, Massachusetts Institute of Technology
13:30-13:35	"Nanoscale Quantum Sensing and Imaging of Topological Magnets" Chunhui Du, University of California, San Diego
13:35-13:40	"Mid-Infrared Colloidal Quantum Dots LEDs" Philippe Guyot-Sionnest, <i>University of Chicago</i>

Session III: Spin Behavior of Materials, Moderator: Chia-Ling Chien

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14:00-14:20	"Optical, Electrical and Magnetic Studies of Hybrid Organic-Inorganic Perovskite Semiconductors" Valy Vardeny, University of Utah
14:20-14:40	"Understanding and enhancing Rashba Splitting in doped 2D organic- inorganic halide perovskites: towards efficient spintronics and IR photodetectors" Luisa Whittaker-Brooks, <i>University of Utah</i>
14:40-15:00	"Complex magnetism and emergent phenomena in correlated electron materials and heterostructures" Hariharan Srikanth, <i>University of South Florida</i>

15:00-15:24 Break

Session IV: Poster Presentations I, Moderator: Michael Flatte

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15:32-15:40	"Light-Matter Quantum Control: Coherence and Dynamics" Jigang Wang, Ames National Laboratory
15:40-15:48	"A Nonlinear Approach to Weyl Transport" Kenneth Burch, <i>Boston College</i>
15:48-15:56	"Photon-mediated interactions in superconducting circuits as a new tool to study emergent phenomena far from equilibrium" Hakan Tureci, <i>Princeton University</i>
15:56-16:04	"Coherent control of strongly interacting spins in the solid-state" Jeffrey Thompson, <i>Princeton University</i>
16:04-16:12	"Atomistic and Mesoscopic Study of Metallic Glasses" Takeshi Egami, <i>Oak Ridge National Laboratory</i>
16:12-16:20	"Metamaterials as a Platform for the Development of Novel Materials for Energy Applications" Willie Padilla, <i>Duke University</i>
16:20-16:28	"Study of Materials and Interface Properties for High-Efficiency Spin Injection" Jing Shi, University of California, Riverside
16:28-16:36	"Pure Spin Current Phenomena in Magnetic and Quantum Materials" Chia-Ling Chien, <i>Johns Hopkins University</i>
16:36-16:44	"Spin Functionality Through Complex Oxide Heteroepitaxy" Yuri Suzuki, Stanford University
16:44-16:52	"Elucidating Chirality-induced Magnetism and Magnetoelectric Functionalities in Layered Chiral Hybrid Metal Halide Perovskite" Dali Sun, North Carolina State University
16:52-17:00	"Unique optical excitations in topological insulators " Stephanie Law, University of Delaware

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11:20-11:40	"The synthesis 2D Janus vdW crystals and novel quantum phenomena arising from mirror-symmetry breaking" Sefaattin Tongay, Arizona State University
11:40-12:00	"Electron transfer in heterostructures based on two-dimensional materials" Hui Zhao, University of Kansas
12:00-12:20	"Spin Transport in group IV materials and 2D membranes" Hanan Dery, <i>University of Rochester</i>

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12:30-12:35	"Optically controlled quantum phase transitions at Van der Waals interfaces" Lian Li, West Virginia University
12:35-12:40	"Quantum Transduction with Abundant Elements for Cleaner Energy" Michael Flatte, University of Iowa
12:40-12:45	"Optical Information Processing Through Jointly-Optimized Diffractive Surfaces and Electronic Neural Networks" Aydogan Ozcan, University of California, Los Angeles

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13:45-14:05	" Shining Light on Intrinsic Anion and Cation Instabilities in Hybrid Perovskites" Masaru Kuno, <i>University of Notre Dame</i>
14:05-14:25	"Discovery of Goniopolar Metals with Zero-field Hall and Nernst Effect" Joseph Heremans, <i>Ohio State University</i>
14:25-14:45	"Properties, Electrochemical Activity, and Stability of Solid Oxide Cell Fuel-Electrode Materials" Scott Barnett, Northwestern University

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15:16-15:24	"Characterization of Functional Nanomachines" Michael Crommie, <i>Lawrence Berkeley National Lab</i>
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- 16:12-16:20 "Photoelectrochemistry of Halide Perovskites: from Stability to Chirality"" Yiying Wu, *Ohio State University*
- 16:20-16:28 "Microscopic understanding of growth, substrate engineering, and proximity coupling in two-dimensional organic/inorganic hybrid systems" Pengpeng Zhang, *Michigan State University*
- 16:28-16:36 "Semiconductor nanoshell quantum dots for energy conversion applications" Mikhail Zamkov, *Bowling Green University*
- 16:36-16:44 "Control of Light-Matter Interactions in Hybrid Structured Environments with Novel Nanomaterials of Different Dimensionalities" Anton Malko, *University of Texas, Dallas*
- 16:44-16:52 "Excitons in Low-Dimensional Perovskites" William Tisdale, *Massachusetts Institute of Technology*
- 16:52-17:00 "Electron Spin Polarization in Large Electric Fields" Vanessa Sih, *Michigan University*

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11:40-12:00	"Overcoming optical selection rules in materials by extreme localization of light" Hayk Harutyunyan, <i>Emory University</i>
12:00-12:20	"Measurement of Near-Field Thermal Radiation Between Flat Surfaces with a Nanogap" Zhuomin Zhang, <i>Georgia Institute of Technology</i>
12:20-12:40	"Collective Energy Transport of Excitons in Two-dimensional Materials" Stephen Cronin, <i>University of Southern California</i>
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12:45-12:50	"Understanding the Role of Defects to Accelerate Wadsley-Roth Niobates for Long-Duration Energy Storage" Morgan Stefik, <i>University of South Carolina</i> ,

- 12:50-12:55 "Electron Hydrodynamics in 3D Quantum Materials" Fazel Tafti, *Boston College*
- 12:55-13:00 "Probing and Understanding the Spatial and Energy Distributions of Plasmonic Hot Carriers via Single-Molecule" Kun Wang, *Mississippi State University*
- 13:00-13:05 "Molecular Insights for Fine-Tuned Hydrogen Interaction Control: MXenes as a Model System" Patrick Ward, *Savannah River National Laboratory*

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13:45-14:05	"Exploring the Impact of the Local Environment on Charge Transfer States at Molecular Donor-Acceptor Heterojunctions" Barry Rand, <i>Princeton University</i>
14:05-14:25	"Tailoring Photophysical Energy Transfer for Selective Separations of Critical Lanthanides" Andrew Ferguson, <i>National Renewable Energy Laboratory</i>
14:25-14:45	"Design, synthesis, and atomic scale characterization of rare-earth based supramolecular nanographene and nanoribbons" Saw Hla, <i>Argonne National Laboratory</i>

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15:24-15:32	"Opening New Frontiers of Near-Zero-Index (NZI) Optics: from Photonic Time Crystals to Non-Reciprocity and Novel Localization Regimes" Alexandra Boltasseva, <i>Purdue University</i>
15:32-15:40	"Plasmonic Photoconductive Nanostructures for High-Power Terahertz Wave Generation" Mona Jarrahi, University of California, Los Angeles
15:40-15:48	"Uncovering and Surmounting Loss Mechanisms in Nitride Light Emitters" Chris Van de Walle, University of California, Santa Barbara
15:48-15:56	"Response of Gallium Oxide to Pressure, Temperature, and Alloying"

Matthew McCluskey, Washington State University

- 15:56-16:04 "Fundamental Studies on Heat Conduction in Polymers" Svetlana Boriskina, *Massachusetts Institute of Technology*
- 16:04-16:12 "Extreme Thermoelectric Behavior in Low-Dimensional Oxide Conductors" Joshua Cohn, University of Miami
- 16:12-16:20 "Probing Coherence in Nanoscale Energy Transport with High Spatial-Temporal Resolution" Bolin Liao, University of California, Santa Barbara
- 16:20-16:28 "Singlet and Triplet Exciton Interaction and Dynamics in Molecular Crystals" Ivan Biaggio, *Lehigh University*
- 16:28-16:36 "Novel Physical Behaviors Driven by Magnetostructural Phase Transitions" Shane Stadler, *Louisiana State University*
- 16:36-16:44 "Weyl Semimetals for High-Thermopower Transverse Thermoelectric Transport" Sarah Watzman, *University of Cincinnati*
- 16:44-16:52 "Orienting Strained Interfaces designed to Direct Energy Flow Bodies" Dongkyu Lee, *University of South Carolina, Columbia*
- 16:52-17:00 Closeout, PBM program managers



Construction and Quantum States of Single and Yin-Yang Flat Bands Feng Liu University of Utah

Program Scope

This project, titled "Construction and Quantum States of Single and Yin-Yang Flat Bands", encompasses a comprehensive study of physical mechanisms that lead to formation of exotic many-body quantum electronic states associated with topological flat bands (FBs) in lattice models and FB materials. It consists of three correlated research topics: (1) Orbital design of 2D/3D single and yin-yang flat bands and search of FB materials; (2) Complete population inversion between yin-yang FBs; (3) Fractional excitonic insulator state. The common theme of the proposed research is to improve our fundamental understanding of topological FBs, demonstrate novel and exotic many-body quantum phases arising from single and yin-yang FBs, and discover new classes of topological FB materials.

Our theoretical/computational project will employ a multiscale approach, combining several stateof-the-art theoretical and computational techniques, ranging from single-particle first-principles density-functional-theory (DFT) electronic structure calculations to tight-binding (TB) model Hamiltonian calculations and analyses, and to calculations and solutions of many-body Hamiltonian. Specifically, open-source package of DFT method combined with many-body GW and Bethe-Salpeter equation (e.g. Berkley-GW) and our newly developed in-house package of exact diagonalization (ED) method for solving many-body TB Hamiltonian will be used to study various excitonic states arising from photoexcitation, including fractional excitations, between yin-yang FBs. Topological properties of single-particle electronic states will be analyzed using conventional methods of calculating (spin) Chern numbers, while topology and fractional statistics of many-body quantum states will be analyzed using ED calculations of spectral flow, quasi-hole excitation and particle-cut entanglement spectra.

Our studies will significantly improve our fundamental understanding of the nature and underpinning of many-body quantum states in association with single and yin-yang FBs, in terms of lattice symmetry and dimension, electron-electron Coulomb vs. exchange interaction and screening, and fractional statistics of band population. Both the continuations and new initiatives of the proposed research will significantly not only improve our fundamental understanding of the construction of topological FBs and realization of FBs-enabled many-body quantum states, but also expand the scope of topological FB materials and FB physics. They will provide useful guidelines for future experimental efforts in synthesis and characterization of new 2D and 3D topological FB materials. They will also have direct technological impact on advancing quantum materials and devices for energy applications, to fulfill the mission of the Department of Energy.

Recent Progress

During the last two years, we have published 25 journal papers fully or partially supported by this DOE grant, including 5 Physical Review Letters, 6 Nano Letters, and one invited review arttcle. Three postdoctoral research associates and two graduate students have been fully or partially supported by this DOE project. The PI gave 6 invited talks at national/international conferences, and 5 departmental colloquium/seminar presentations. Below is a brief summary of four topics of research achievements pertaining to this project.

(1) Flat-Band-Enabled Triplet Excitonic Insulator in a Diatomic Kagome Lattice:¹ The

excitonic insulator (EI) state is a strongly correlated many-body ground state, arising from an instability in the band structure toward exciton formation. Recently, we show that the flat valence and conduction bands of a semiconducting diatomic Kagome lattice, as exemplified in a superatomic (trianglene) graphene lattice, can possibly conspire to enable an interesting triplet EI state, based on density-functional theory calculations combined with many-body GW and Bethe-Salpeter equation. Our results indicate that massive carriers in flat bands with highly localized electron and hole wave functions significantly reduce the screening and enhance the exchange interaction, leading to an unusually large triplet exciton binding energy (~1.1 eV) exceeding the GW band gap by ~0.2 eV (Fig. 1) and a large singlet-triplet splitting of ~ 0.4



Fig. 1. DOS for triplet excitons obtained by solving Bethe-Salpeter equation of a superatomic (trianglene) graphene lattice. It clearly shows the presence of excitons with negative formation energy (EI_0) , indicative of spontaneous formation of excitons.

eV, which point to spontaneous formation of multiple triplet excitions. Our findings enrich once again the intriguing physics of flat bands and extend the scope of EI materials. Excitingly, both our proposal of the superatomic (trianglene) graphene lattice and our thereotical theoretical predictions of spontaneously formation of excitons have been supported by the latest experiments.²

(2) Effective Model for Fractional **Topological Corner Modes in Quasicrystals:**³ High-order topological insulators (HOTIs), as generalized from topological crystalline insulators. characterized with lowerare dimensional metallic boundary states protected by spatial symmetries of a crystal, whose theoretical framework based on band inversion at special k points cannot be readily extended to quasicrystals because quasicrystals contain rotational symmetries that are not compatible with crystals, and momentum is no longer a good quantum number. We have developed a lowenergy effective model underlying HOTI states in 2D quasicrystals for all possible rotational symmetries (Fig. 2). By implementing a novel



Fig. 2. Schematic illustration of the Zeeman-fieldinduced topological phase transitions in a 2D pentagonal quasicrystal. Starting from a TI phase with helical edge states, the quasicrystal is driven to a HOTI phase with five charged corner modes (CMs) by an in-plane Zeeman field. Furthermore, in proximity with an s-wave superconductor, Majorana CMs can be generated by tuning the Zeeman field and chemical potential.

Fourier transform developed recently for quasicrystals and approximating the long-wavelength behavior by their large-scale average, we construct an effective $k \cdot p$ Hamiltonian to capture the band inversion at the center of a pseudo-Brillouin zone. We show that an in-plane Zeeman field can induce mass kinks at the intersection of adjacent edges of a 2D quasicrystal TIs and generate corner modes (CMs) with fractional charge, protected by rotational symmetries. Our model predictions are confirmed by numerical tight-binding calculations. Furthermore, when the quasicrystal is proximitized by an s-wave superconductor, Majorana CMs can also be created by tuning the field strength and chemical potential. Our work affords a generic approach to studying the low-energy physics of quasicrystals, in association with topological excitations and fractional statistics.

(3) High-Temperature Fractional Quantum Hall State in Floquet-Kagome Flat Band:⁴

Fractional quantum Hall effect (FQHE) has been predicted in Chern FB by single-particle band structure combined with phenomenological theory or solution of many-body lattice Hamiltonian with fuzzy parameters. A long-standing roadblock towards realization of FB-FQHE is lacking the many-body solution of specific materials under realistic conditions. We have demonstrated a combined study of single-particle Floquet band theory with exact ED of many-body Hamiltonian. We show that a time-periodic circularly polarized laser inverts the sign of second-nearest-neighbor hopping in a Kagome lattice and enhances spin-orbit coupling in one spin channel, to produce a Floquet FB with a high flatness



Fig. 3. Left: Schematics of Floquet-Kagome lattice with a laser shining on a 2D Kagome material. Right: Calculated Floquet-Kagome band structure showing a bottom FB with large flatness ratio exhibiting high-temperature FQHE.

ratio of bandwidth over band gap (Fig. 3), as exemplified in metalorganic monolayer $Pt_3C_{36}S_{12}H_{12}$. The ED of the resultant Floquet-Kagome lattice Hamiltonian gives a one-third-filling ground state with a laser-dependent excitation gap of FQH state, up to an estimated temperature above 70 K. Our findings pave the way to explore the alluding high-temperature FB-FQHE.

(4) Structural Amorphization-Induced Topological Order:⁵ Electronic properties of crystals are inherently pertained to crystalline symmetry, so that amorphization that lowers and breaks symmetry is detrimental. One important crystalline property is electron band topology which is known to be weakened and destroyed by structural disorder. We reported a counterintuitive theoretical discovery that atomic structural disorder by amorphization can in fact induce electronic order of topology in an otherwise topologically trivial crystal (Fig. 4). The resulting nontrivial topology is characterized by a nonzero spin Bott index, developed by us in the last funding cycle for defining electronic-state topology in real space,^{6,7} associated with robust topological edge states and quantized conductance. The underlying topological phase transition (TPT) from a trivial crystal to a topological amorphous is analyzed by mapping out a phase diagram in the degree of structural disorder using an effective medium theory. The atomic disorder is revealed to induce



Fig. 4. Amorphization induced topological phase transition. (a) The initial triangular lattice. (b) Gaussian distribution of atomic displacements. (c) The lattice after amorphization. (d) Energy gap (blue) and spin Bott index (red) as functions of atomic displacement (σ).

topological order by renormalizing the spectral gap toward nontriviality near the phase boundary. As a concrete example, we further show such TPT in amorphous stanane by first-principles calculations. Our findings point to possible observation of an electronic ordering transition accompanied by a structural disorder transition.

Future Plans

We plan to expand our current studies in the following areas:

- (a) Anomalous bilayer quantum Hall effect
- (b) p-wave excitonic Bose-Einstein condensation
- (c) High-order topological point states
- (d) Ferroelectric topological superconductor
- (e) Excitonic insulator state in hydrogen-bond organic framework

(f) Continuing the efforts of experimental collaborations

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Disorder in Topological Semimetals

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Program Scope

Three dimensional (3D) topological semimetals offer exciting opportunities for controlling and exploiting exotic states of matter for the next generation of energy-relevant technologies. The topological phase and many of the unique properties these materials display are deeply connected to the underlying symmetry and disorder within the system, presenting opportunities to broadly tailor them. This project investigates the complex relationships between the properties of topological semimetals and disorder, primarily in the prototypical Dirac Cd_3As_2 system. We deliberately manipulate defects, impurities and interfaces in epitaxial layers to understand how they influence the optical and transport properties as well as the topological phase. The fundamental insights gained from the Cd_3As_2 material system are expected to set the stage for utilizing disorder within topological semimetals to design them for specific applications.

Recent Progress

Although our basic understanding of topological semimetals suggests that electron transport is less sensitive to defects than in conventional semiconductors due to topological protection against backscattering, we still do not fully understand the extent to which defects and impurities influence the Fermi level, electron mobility, and magnetoresistance. We have mainly focused on a broad range of studies on this topic. This knowledge along with methods to control defect populations will allow us to tailor these parameters in thin film topological semimetals for device applications.

Evaluation of point defects in Cd₃As₂

To study the behavior of point defects in Cd_3As_2 , we have combined defect formation energy calculations using density functional theory (DFT) with electronic structure calculations using quasi-particle self-consistent GW (QWGW) methods. We find that that this combined approach allows us to quantitatively model thermodynamic defect equilibria in light of the strong dependence of the Fermi level on the density of states and the finite size effects of the formation energies of defects in the bands [1]. We find that V_{Cd} and Cd_i principally control the electron concentration in Cd_3As_2 , while V_{As} defects are expected to occur in much lower concentrations and act as localized electron scattering centers. These findings contradict previous assumptions that V_{As} defects were responsible for electron doping as-grow Cd_3As_2 crystals [2,3] and help to guide our experimental investigation into the role of point defects on electron transport.



Figure 1. Electron transport behavior in Cd_3As_2 epilayers grown as a function of As/Cd flux ratio to manipulate point defect populations (a) Experimental magnetoresistance (MR) values compared to values calculated by the guiding center diffusion model (GCDM). (b) Disorder length scale and (c) disorder potential extracted from the GCDM.

Understanding how defects influence electron transport

In the past two years, we have made significant progress in experimentally probing the impact of point and extended defects on electron transport in Cd₃As₂. Using independent control of cadmium and arsenic fluxes during molecular beam epitaxy of Cd₃As₂ epilayers, we are able to alter the defect equilibria. Nominally, we expect greater relative Cdi and VAs defect concentrations in epilayers grown under Cd-rich conditions, while we expect greater relative V_{Cd} defect concentrations in epilayers grown under As-rich conditions. We find that growth under As-rich conditions results in a substantial increase in the magnetoresistance (MR). Using the guiding center diffusion model (GCDM), we quantitative evaluate the disorder potentials and length scales. Our analysis suggests that V_{Cd} defects are primarily responsible for influencing the MR behavior in Cd₃As₂ and point to methods for intentionally tuning MR magnitude in these materials [4].



Figure 2. Transport behavior in $(Zn_xCd_{1-x})_3As_2$ alloys. (a) Hall resistivity as a function of magnetic field, showing that doping changes from n-type to ptype with increasing Zn concentration, with a region of multiple carrier types present at intermediate concentrations. (b) Magnetoresistance vs magnetic field. The samples with intermediate Zn concentrations show a quadratic dependence typically found in compensated semimetals.

We have also been able to experimentally probe vacancy defects using positron annihilation spectroscopy. A combination of Doppler broadening variable energy positron annihilation and coincidence Doppler broadening spectroscopies, along with atomic superposition calculations, indicate that our Cd_3As_2 epilayers also have a relatively high concentration of di- or tri-vacancy defects [5]. Although the equilibrium concentrations of these defects are expected to be low, we hypothesize that they are stabilized by extended defects in our material.

Finally, we have gained additional insight into the influence of dislocations on electron mobility. Growth of Cd_3As_2 on lattice-mismatched GaAs substrates leads to high dislocation densities $\sim 10^8$ cm⁻². We have shown that growing thicker films leads to a 6x increase in electron mobility as the dislocations annihilate. These results suggest that it is still critical to control

dislocations and other extended defects that can act as small angle scattering centers in topological semimetals, and we are currently quantitatively evaluating their impact on electron scattering compared to point defects.

Influence of extrinsic doping and alloying

As-grown Cd₃As₂ bulk crystals typically have high electron concentrations (~ 10^{18} cm⁻³). Through control of the As/Cd flux ratio during growth, we are able to reduce that concentration to ~ 10^{16} cm⁻³. We have recently shown that we can dope Cd₃As₂ with Te and Se to increase the electron concentration without affecting the electron scattering behavior. This combined approach allows us to intentionally tune the electron concentration to suit the needs of materials behavior studies or technological applications [6]. As a next step, we are investigating the ability to p-type dope Cd₃As₂, which will provide full Fermi level control.

Isovalent Zn doping has been known to influence both the free carrier concentration and electronic bandstructure of Cd_3As_2 , inducing a phase transition to a p-type narrow bandgap semiconductor with Zn concentrations ~ 20 atomic percent. Zn doping therefore offers an alternative way to tune the Fermi level close to the Dirac point, but such an approach has been challenging because the amount of Zn needed to induce a p-type transition roughly coincides with the topological phase transition. Using our ability to reduce the electron concentration through the As/Cd flux ratio, we find that we can readily reduce the free carrier concentration into the 10^{15} cm⁻³ range in epilayers doped with ~6-10 atomic percent Zn, before reaching the phase transition. Surprisingly, we find at such low carrier concentrations the material acts as a compensated semimetal with co-existing electron and hole pockets. It also differs from other traditionally compensated semimetals in the fact that the total carrier concentrations here are orders of magnitude lower. We are still working to determine the origin of this behavior.

Doping with magnetic impurities, such as Mn, also offers the potential to tune the topological phase of Cd_3As_2 from a Dirac to a Weyl semimetal by breaking time reversal symmetry. Our QSGW calculations indicate that only a few atomic percent Mn is needed to realize this transition. We have now successfully incorporated Mn into Cd_3As_2 within this composition range. We currently have plans to evaluate how Mn influences the bandstructure through optical and angle resolved photoemission spectroscopy (ARPES).

The study of defects in Weyl semimetals

We have studied how disorder influences electronic doping and transport behavior in TaAs and NbAs epilayers grown on GaAs (001) substrates. All epilayers can be categorized as single crystal-like, in which the macroscopic properties resemble a single crystal, but the microscopic structure exhibits boundaries (spaced ~100-200 nm apart) across which stacking faults are not aligned. The interiors of the films are highly p-type doped (~ 10^{20} cm⁻³) compared to n-type doping in as-grown bulk crystals, but the surfaces appear to be n-type [7]. Understanding the origin of the bulk p-type and surface n-type doping will be critical to tailoring transport behavior in these epitaxial materials.

Future Plans

We plan to continue the doping and alloying studies outlined above as we examine the interplay between composition, electronic structure, carrier concentration and electron transport behavior. In particular, we will use the vacuum transfer techniques we have been developing over the past two years to study the electronic structure of our alloyed materials with ARPES. The combined DFT and QSGW computational approach we have developed will also be critical to uncovering the origins of the transport phenomena we observe in alloyed materials. We also plan to use the interface preparation approaches we have developed through this program to begin studying interface-related transport behavior [8].

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Emergent Properties of Magnons Coupled to Microwave Photons M. Benjamin Jungfleisch, Department of Physics and Astronomy, University of Delaware

Magnon, Magnon-Photon Coupling, Hybrid Magnonic Systems, Light-Matter Interaction

Research Scope

Unleashing the full potential of quantum technologies requires the development of quantum computation, memories, interconnects, detectors, and transducers. Understanding the coupling between disparate quantum systems is particularly important. The emergent properties of such hybrid systems promise to advance a wide range of quantum information applications. Due to their highly tunable dispersion and the possibility to couple with different excitations, including optical photons, phonons, and spins, magnons are ideal candidates for coherent information processing and transduction.



Fig. 1: Demonstration of microwave-to-optical upconversion using strong magnon-photon coupling in a split-ring resonator/YIG film hybrid circuit. (a) Microwave transmission as a function of the magnetic field. (b) Corresponding Brillouin light scattering intensity, representing an upconversion. Adapted from Ref [1].

This research program seeks to precisely control

light-matter interaction in hybrid magnonic systems and magnonic nanostructures, where the light part is carried either by microwave or optical photons, and the matter component is carried by magnons in engineered magnetic metamaterials. The underlying mechanisms of the interaction of magnons with photons, magnons with phonons, and magnons with magnons are determined. Controlling the collective properties of magnons is a transformative advance; its impact extends beyond spintronics to the wider research arenas of quantum science.

Magnons efficiently couple with electromagnetic waves at microwave frequency through highquality resonators, forming magnon-photon polaritons [R1]. We recently succeeded in optically detecting these magnonic hybrid excitations by Brillouin light scattering (BLS) [R2] in a system comprising a split-ring resonator loaded with epitaxial yttrium iron garnet thin films [1], see Fig. 1. Our findings demonstrate a coherent conversion between microwave and optical frequencies by magnon-induced BLS, which could serve as a crucial link between superconducting qubits operating at microwave frequencies and long-distance communication at optical frequencies.

By coupling the generalized Landau-Lifshitz-Gilbert equation with RLC equation, we revealed the coupling between magnon and photon modes under damping-like and field-like torques [2], see Fig. 2. Our modeling shows that the magnitude of the level repulsion and, hence, the magnon-photon coupling strength can efficiently be controlled by varying the magnitude and the direction of the dc current density. Our results suggest that an on-demand manipulation of the magnon-photon coupling strength can be achieved in yttrium iron garnet/Pt hybrid structures.

Furthermore, we studied the magnon dispersion in magnetic hybrid systems and revealed the existence of nonlinear magnon-magnon scattering processes and their coherence in arrays of nanostructures [3-10].

Recent Progress

<u>Observation of thermally activated coherent magnon-magnon coupling in a magnonic hybrid</u> <u>system:</u> We recently observed strong magnon-magnon coupling by thermal spin excitations in yttrium iron garnet/permalloy (YIG/NiFe) bv microfocused Brillouin light scattering. The thermally activated magnons in the bilayer lead to a hybrid excitation between the uniform mode in the conductive NiFe layer and the first perpendicular standing magnon modes in the insulating YIG laver. The coupling is mediated by strong interfacial exchange coupling. Our theoretical model reveals that a band of thermally excited higher-order magnon modes in NiFe hybridizes with the YIG mode. Demonstrating coherent coupling of magnon modes of incoherently - thermal - magnons is important for the rapidly developing field of magnon hybrid systems. Based on these coherently coupled magnonmagnon studies, we have recently started exploring



tripartite coupling between the magnon modes in YIG, microwave photon mode in a 3D microwave cavity, and the uniform magnon mode in NiFe.

<u>Coupling micro-cavity microwave photons to magnons in magnetic microstructures:</u> The detection of ferromagnetic resonance (FMR) signal and magnon-photon coupling in finite elements of nano-to micron-sized ferromagnetic samples using conventional cavities is challenging due to the small ferromagnetic volume. To address this challenge, we developed R-type micro-resonators (Fig. 3), which have much smaller effective volumes than 3D cavities and allow for better coupling efficiency with magnetic dipoles [R1].

Caustic spin wave beams in an extended thin film excited by a nano-constriction: The ability to



Fig. 3: (a) Schematic illustration of an R-type micro-resonator. The inset displays an optical microscope image of the fabricated R-type resonator, with a ring diameter of 200 μ m and an array of NiFe stripes inside the ring. (b) Magnitude of the RF field distribution, obtained through HFSS simulation of the resonator with the same dimensions, demonstrating an almost uniform RF field distribution inside the ring. (c) Preliminary field modulated FMR measurement results from the sample shown in (a).

control the directionality of magnons is important for magnonic logic and computing applications and could be a powerful tool to modify magnon-photon coupling in an on-chip device. We recently realized caustic-like spin-wave emission from a nano-constricted microwave waveguide in an extended 200 nm thick YIG film, Fig. 4. Caustic-like spin waves exhibit an anisotropic nature of the spin-wave dispersion, which occurs when the direction of the spin wave-group velocity and spin-wave wavevector do not coincide. Using spatially resolved micro-focused Brillouin light spectroscopy in both the backward volume and the Damon-Eshbach geometry, we reveal the propagation of two directional spin-wave beams directly emitted from the nano-constriction. These measurements lie the foundation for coupling directional magnons with microwave photons. Instrument development: In order to improve the signal-tonoise ratio of FMR and microwave spectroscopy measurements, we developed a field-modulated **FMR** spectroscopy system that is now in daily operation. We started upgrading this system with inplane rotation, polar angle, and temperature-dependent

capabilities. Furthermore, we are in the process of setting up a low-temperature BLS system for the optical investigation of magnon-photon coupled hybrid systems when a smaller number of magnons is populated (approaching $k_BT \ll \hbar \omega_{FMR}$).



Fig. 4: Spatially resolved BLS map of spin-wave caustic emission in a 200 nm thick extended yttrium iron garnet film from a nano-constricted microwave antenna. Externally applied field $H_{ext} = 185 mT$, excitation frequency f = 7.5 GHz. Corresponding iso-frequency curves with caustic wavevector k_c and spin-wave group velocity v_G are depicted next to the 2D BLS maps. (a) Magnetic field is applied perpendicular to RF magnetic field. (b) Magnetic field is applied parallel to RF magnetic field.

Future Plans

We will continue our efforts to understand the mechanisms of magnon interactions with other quasi-excitations and the precise control of their collective properties. In particular, we will focus on:

- 1. Based on our previous results, we will determine the spatial distribution of the magnonic hybrid excitation, extract critical length scales, and study their temporal characteristics.
- 2. Informed by our recent magnon-magnon coupling studies, we will continue investigating the magnon-magnon coupled system's emergent properties when strongly coupled to a planar microwave antenna. In particular, we aim to understand the temporal dynamics of the triple resonant excitation using time-resolved BLS.
- 3. A major research focus will be on low-temperature characterizations of magnon coupling physics. For this purpose, we will complete setting up cryogenic measurement capabilities at UD. Additional measurements will be conducted using the dilution refrigerator at Argonne National Laboratory. We plan to utilize the unique properties of magnons, such as non-reciprocity [see preliminary room temperature results, shown in Fig. 4(b)] and quantization, to generate new types of hybrid systems based on magnetic micro- and nanostructures and superconducting resonators.
- 4. We plan to electrical readout magnon-photon coupling using spin pumping and inverse spin Hall effect in a planar geometry. These results will lay the foundation for experimentally demonstrating control of magnon-photon coupling using spin torque (see theoretical prediction [1], Fig. 2).

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Multiparticle Interactions in Plasmonic Platforms for Quantum Simulation

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Multiparticle systems, quantum statistics, quantum interference, quantum plasmonics, quantum simulation.

Research Scope

One of the main goals of quantum physics is to exploit nonclassical interactions in nanoscale systems to implement operations that cannot be performed on classical devices¹. Remarkably, this possibility depends on the preparation of robust and controllable quantum systems comprising multiple interacting particles¹⁻⁵. These complex quantum systems can host many forms of interference and scattering processes that are essential to simulate specific physical effects that are intractable on classical systems^{1,5}. These complex quantum devices are known as quantum simulators⁵. Recently, there has been an enormous interest in demonstrating quantum simulation on diverse platforms that include trapped atoms, quantum dots, superconducting qubits, nitrogenvacancy centers in diamond, and photonic quantum systems^{2,4}. However, due to the remarkable properties of photons to exhibit quantum properties at room temperature, large quantum photonic systems constitute a promising platform for the development of quantum simulators¹.

This research program aims to develop a novel family of nanoscale platforms in which tunable plasmonic near fields enable deterministic manipulation of scattering and interference effects of multiphoton systems²⁻⁴. Furthermore, these interactions will be used to perform quantum simulation of light transport in plasmonic networks. Specifically, the presence of controllable near fields in our multiparticle platform will enable the simulation of light transport under different conditions of noise and dynamic disorder⁵. These capabilities will enable the simulation of hyper-transport of light. It is worth mentioning that the simulation of effects involving noise and dynamic disorder remains challenging in existing quantum simulators. This due to the fragility of the quantum coherence properties of multiparticle systems against noise and disorder¹.

Recent Progress

The demonstration of a functional plasmonic platform for multiparticle quantum simulation requires tunable multiphoton sources¹, robust control of multiphoton states^{2,4}, and efficient detection schemes for the characterization of multiparticle systems³. As discussed below, over the last two years, we developed these enabling capabilities to demonstrate quantum simulation of bosonic and fermionic interactions. In addition, we have conducted initial experimental simulations of quantum transport⁵. Below we discussed recent progress made along these directions.

Multiphoton systems: Engineering and characterization

The demonstration of a robust platform for quantum simulation depends, to an important extent, on scalable multiphoton systems with tunable properties of entanglement, photon coherence, and quantum statistical fluctuations¹⁻⁴. As reported in Figure 1**a**, we have developed highly indistinguishable sources of entangled multiphoton systems with up to twelve indistinguishable particles. The indistinguishability of the multiphoton source was certified

through the highest multiphoton Hong-Ou-Mandel visibility ever reported. In a publication, we reported multiphoton interference with visibilities of 99.36(5) %. Moreover, in a recent paper, we demonstrated the possibility of producing systems multiphoton with sub-thermal. thermal. and super-thermal photon statistics through the spatial modulation of coherent light using digital micromirror devices. We show some experimental results in Figure 1b. As discussed below, each of these multiparticle systems host different multiparticle interactions that can be used for quantum simulation 1,5 . This kind of systems can be characterized through the implementation of photonnumber-resolving detection³. As shown in Figure 1c, we developed measurementefficient photon-numberresolving (PNR) detectors and cameras that enables performing imaging beyond



Figure 1. Engineering and characterization of multiphoton systems. We developed a bright source of entangled multiphoton systems with up to twelve particles. The experimental setup together with the tomography of the photon-number-resolving (PNR) detectors are shown in **a**. In addition, as shown in **b**, we demonstrated generation of sub-thermal, thermal, and super-thermal multiphoton systems using computer-generated holography. These systems are characterized by our measurement-efficient detectors and cameras for PNR detection³. The results reported in **c**, indicate the potential of these techniques to perform superresolving imaging of nanostructures³.

the diffraction limit³. This is relevant to image plasmonic nanostructures and networks^{2,4}.

Quantum control of multiphoton systems in plasmonic platforms

The multiphoton sources and detection schemes discussed in Figure 1 enabled us to perform the first kind of multiparticle experiments in plasmonic platforms^{2,4}. As reported in Figure 2**a**, we demonstrated that the multiparticle dynamics that take place in plasmonic nanostructures can be deterministically controlled through the strength of the optical near fields confined in their vicinity⁴. This work was selected as a Feature Article in Nature Communications and highlighted in Nature Physics News & Views⁴. The new physics uncovered in our article lies at the hearth of our scheme for quantum simulation. In this work, we applied the quantum theory of coherence to the scattering effect depicted in Figure 2**a** to demonstrate that electromagnetic near fields in
plasmonic nanostructures can be used to modify the quantum statistical properties of multiparticle systems. The physical realization is depicted in Figure 2b.

These ideas enabled us to demonstrate the attenuation of the quantum fluctuations of multiphoton systems through plasmonic near fields². Despite the enormous potential of plasmonic

interferometers for sensing, this class of sensors is ultimately limited by the quantum statistical fluctuations of surface plasmons^{2,4}. As demonstrated in Figure 2c, we showed that the conditional detection of plasmonic fields, via plasmon subtraction, provides a new degree of freedom to control quantum fluctuations of plasmonic fields. This mechanism enables improvement of the signal-tonoise ratio of interferometers relying on plasmonic signals that are comparable to their associated field fluctuations².

Quantum simulation of bosonic and fermionic interactions in plasmonic nanostructures

Even though surface plasmons are formed from bosons and fermions, it has been



Figure 2. Control of the quantum statistics and fluctuations of multiphoton systems in plasmonic platforms^{2,4}. The idea behind the control of multiparticle scattering trough electromagnetic near fields is shown in **a**. This possibility was implemented through the plasmonic nanostructure shown in the right panel of **a**. The results in **b** report the deterministic modification of quantum coherence of multiphoton systems as a function of the strength of the plasmonic field⁴. As in indicated in **c**, this multiparticle dynamics enabled us to attenuate the quantum fluctuations of a multiparticle system in a plasmonic interferometer².

observed that this kind of near-field waves exhibits bosonic properties in the limit of many electrons^{2,4}. Interestingly, plasmonic near fields have resulted essential for diverse purposes ranging from the exploration of novel light-matter interactions to the development of novel sensing platforms^{1,2-4}. As shown in Figure 3**a** and **b**, we recently demonstrated that the quantum dynamics that underlie the scattering among photons and plasmons can lead to the formation of either bosonic or fermionic correlations. The quantum correlations reported in Figure 3**b** demonstrate the coalescence and anti-coalescence of plasmonic multiparticle near fields. In our experiment, we isolate specific multiparticle dynamics through the implementation of PNR detection³. These

results uncover universal multiparticle properties of electromagnetic near fields with important implications for diverse fields ranging from condensed matter to quantum information.

Finally, we performed quantum initial transport simulation with the goal of near-field identifying couplings that will ease the design of plasmonic nanostructures for the remaining milestones of our research program. More specifically, we employed electrical oscillators for the simulation of singleexcitation quantum transport phenomena⁵. This platform was used simulate to Anderson localization. This tunable platform enabled us to map the strength of static disorder to couplings



Figure 3. Quantum simulation of bosonic and fermionic interactions in plasmonic nanostructures. The setup in **a** was used to simulate bosonic and fermionic scattering in plasmonic nanostructures. The data in **b** shows this possibility for a five-particle system. The results in **c** show our quantum simulation of Anderson localization using electrical oscillators.

between sites. In Figure 3c, we show a comparison between the quantum model used to describe Anderson localization and the experimental simulation implemented with our platform⁵.

Future Plans

These capabilities described above¹⁻⁵ will be used to *a*) demonstrate control of classical-toquantum transitions in plasmonic quantum networks, and *b*) to explore deterministic schemes to simulate exotic forms of light transport attributed to dynamic disorder. These capabilities have important implications for information processing and for the physics that define the performance of technologies for light harvesting⁵.

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Session II

Enabling Reversible Hydrogen Storage and Transfer with Graphene-Based Carbon-Boron-Nitrogen Materials T. Autrey, M. Sushko, L. Liu, N. Washton, B. Ginovska, O. Gutierrez, Z. Dohnalek, P. Rice, G. Lee, B. Schwartz Pacific Northwest National Laboratory

Key terms: Long duration energy storage, hydrogen activation, two-dimensional materials Research Scope

Two-dimensional graphene-like materials composed of carbon, nitrogen, and boron (CNBs) have great potential as storage media for hydrogen. These CNB materials are: (i) lightweight, allowing for use in mobile applications where a high ratio of hydrogen to material weight is critical; (ii) durable, allowing for long-term storage applications where stability is required; and (iii) scalable, allowing for both high storage capacity, e.g., gigawatt hours, and chemical storage for decarbonizing industrial sectors, e.g., hundreds of metric tons of hydrogen. However, the practical use of graphene-based materials is hampered by the kinetic limitations of diffusion and recombination on surfaces. We are using a combination of experimental and computational techniques to gain insight into how boron and nitrogen atoms in graphene-like structures lowers the barriers for hydrogen activation and reversible hydrogen storage on CNBs as well as the subsequent transfer of hydrogen from CNBs to liquid organic hydrogen carriers (LOHC).

Recent Progress

The peer-reviewed literature is settling on a consensus that the binding energy of physi-



Scheme 1. Dopant-induced structural and electronic inhomogeneities in quasi-two-dmensional C-N-B materials facilitate hydrogen binding, diffusion and transfer to and from liquid organic hydrogen carriers.

sorped hydrogen to N-doped¹ (or B-doped²) carbon is not significantly different than binding energy to graphene. There are reports that suggest hydrogen chemi-sorbs, reversibly, to N-doped carbons at moderate temperatures enabling activation of both molecular hydrogen and the C-H and N-H bonds liquid organic hydrogen carriers.³ Our studies are focused on understanding how the initially physi-sorbed hydrogen is activated to chemi-sorbed hydrogen, and subsequently transported and transferred on 2D materials between the gas and liquid phase by investigating both supported and free standing N-doped 2D carbon materials.

The free-standing materials are synthesized using pyrolysis method.⁴ Anticipating that defects sites are the most likely sites for N-doping, we control the concentration by controlling the concentration of defects in the precursor graphene oxide. The structure of the synthesized N-doped graphite is characterized using high-resolution transmission electron microscopy (HRTEM), Xray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The results indicate that the pyrolysis at 350 and 550 °C produces N-doped graphite with N content of $5.1\pm0.1\%$. Pyrolysis at higher temperature (800 °C) causes partial release of N and reduces the overall N content to 3.2%. The XPS analysis of the N bonding in N-doped graphite revealed that about 70% N is pyridinic (Figure 1). The results strongly suggest preferential doping at point defect sites or the boundary. Associated density functional theory (DFT) simulations identify the energetics of N-doping at defects and terraces of graphite to predict the structure of N-doped materials and its evolution at elevated temperatures. The preliminary data indicate a clear energetic preference of N-doping at defect sites, which produces pyridinic N at point defects (one missing C) and graphitic N at one of the most stable 5-8-5 defects or terraces (Figure 1).

In parallel, we are using quantum chemical calculations to elucidate how the underlying electronic structure of N-doped carbon materials influence the hydrogen binding free energy (HBFE). For this purpose, we have identified four well-defined carbon allotropes



Figure 1. Structure of N-doped graphite. XPS spectra show pyridinic and graphitic-N (top). The energy-dispersive. X-ray spectroscopy (EDS) analysis (inset) shows even distribution of carbon (green) and nitrogen (orange) within the material. The experimental data correlate with theoretically predicted sites for the most energetically favorable N-doping (bottom).

(Figure 2) to build bridges between molecular and heterogeneous systems and to provide an ideal framework for understanding the functional role that the carbon lattice has on the HBFE.



Figure 2. Ball-and-stick representation of the carbon allotropes used for probing how the underlying local electronic structure can influence the preferential nitrogen doping site and the binding of hydrogen.

Our approach is to first identify the relative stability of the N-doped graphitic compounds, then develop descriptors to compare structure-function relationships between the HBFE's of adsorbed hydrogen. For D_{5d} - C_{120} structure there are 14 unique positions to add a single N atom, with formation energies ranging over 0.75 eV. The most stable N-doped structure locates the N near the end caps in the five membered rings (6 symetric sites represented) highlighted in blue. Adding a hydrogen atom directly to the defect N results in a very weak N-H bond, HFBE ca. 0.75 eV. From this lowest energy structure, the HBFE were calculated for the 61 unique hydrogen adsorption sites spaning a range of ~1.7 eV.

To analyze these sites further, we derive a general deformation parameter (κ) for identifying unique sites for hydrogen adsorption based on the ratio of bond angles (φ^{bond}) and dihedral angles ($\phi^{dihedral}$):



Figure 3. Hydrogen binding free energy (HBFE) for 61 unique sites on D_{5d} - C_{120} as a function of the deformation parameter. For comparison, the value for a spherical C_{60} molecule is indicated by the blue dotted line, while planar graphene is indicated by the red dotted line. The colored balls indicate unique regions on the D_{5d} - C_{120} molecule based on the curvature parameter.

$$\kappa = \frac{\left|\left\langle \phi^{dihedral}(rad)\right\rangle - \pi\right|}{\left|\left\langle \varphi^{bond}(rad)\right\rangle - \pi\right|}$$

Lower κ value indicates a higher degree of deformation/curvature. Here, we measure how the bonding within the first and second coordination sphere of an adsorption site deviates from planarity. From **Figure 3**, we identify several regions based on the deformation parameter for D_{5d}-C₁₂₀ and find a correlation between the degree of curvature and HDFE, with

sites at the capped end of the nanotube having a higher affinity for hydrogen adsorption. The hydrogens with the lower deformation parameter, i.e., $\kappa = 1.75$ +/-0.05, show a HFBE distributed within the optimal range for reversible addition of hydrogen, ca. 0.08-0.10 eV. Notably, the hydrogens at positions with the larger

deformation parameter, i.e., $\kappa = 2.20$ +/- 0.05, are less stable. These initial results are promising in showing that the binding energies of hydrogen are in the range that can be expected to undergo reversible addition. Our prepared N-doped graphene materials, described below, are expected to have defects more closely aligned with defects consistent with the larger deformation parameters. The carbons further from the defect do not appear to stabilize the addition of hydrogen but the carbons closer to the N functionality are within the region expected to show reversible addition of hydrogen. We will test these predictions by using pulsed isotope scrambling experiments in future work.

Future Plans:

Free standing 2D materials. Guided by our modeling studies we are preparing, and characterizing, a series of layered N-doped graphene materials with modified ratios of graphitic, pyrrolic, and pyridinic N-functionalities. Our DFT results suggest that the HBFEs of a hydrogen atom to N-doped carbon allotrope D_{5d} - C_{120} , graphene model, spans a range where we expect to observe the reversible addition of hydrogen to carbons near a graphitic N-defect, providing a source of weak chemi-sorption for the reversible addition of hydrogen. Figure 4 illustrates a representation of the expected interactions for reversible addition of both molecular H₂ and H transfer to and from the CH and NH bonds of a N-heterocyclic LOHC molecule. Isotope



Figure 4. Schematic of layered graphene materials with H₂ activation in presence or absence of LOHC molecules.

scrambling experiments will provide insight into the kinetics of hydrogen adsorption where the Ndoped layered materials will be transiently exposed to inert gases, H_2 and D_2 .⁵ The time dependence of HD formation as a function of temperature provides quantitative information on the ability of the 2D N-doped materials to store and activate H_2 .

Supported 2D materials. The detailed analysis of the dynamics of hydrogen adsorption and diffusion at N-doped carbon surfaces requires spatially resolved analysis of the electronic structure. Both periodic and cluster simulations will be performed to get insights into the strain effects on hydrogen adsorption, dissociation, and mobility. We are focusing on the controlled synthesis of proximal configurations for our studies of H₂ activation on dopant-anchored single metals and for H stability and diffusion studies on various types of sites and carbon networks. Such studies will allow us to develop unique experimental signatures of different species and allow us to pursue more complex precursor molecules that possess the desired configurations of multiple dopants (e.g., melamine, borazine, BN-cyclohexane⁶). On selected metal substrates that can dissolve carbon in the bulk (e.g., Ni(111)), we will utilize post-annealing to allow the growth of graphene layer underneath the functionalized graphene. This will allow us to decouple the functionalized 2D layers from direct contact with the metal. These studies will yield information about hydrogen stability, its spatial distribution on the surface, diffusion mechanisms, and recombinative desorption kinetics.

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Complex chalcogenides under pressure Janice L. Musfeldt, University of Tennessee

Self-identify keywords to describe your project: van der Waals solids, chalcogenides, pressure-driven phase transitions, phase diagrams, vibrational spectroscopies

Research Scope

Our research program focuses on the spectroscopic properties of complex chalcogenides and how external stimuli such as pressure and chemical substitution control the development of new states of matter and functionality. Building on prior advances, we combine synchrotron-based infrared and Raman scattering spectroscopy with diamond anvil cell techniques to reveal charge-structure-function relationships in intercalated chalcogenides, analyze metal-site substitution and the role of local structure on symmetry breaking in magnetic systems, uncover energy transfer processes and phase diagrams in superconducting chalcogenides, and explore the generality of these phenomena and their underlying mechanisms in new settings - such as in chiral materials. What brings these efforts together is our interest in light-matter interactions under extreme conditions and the spectroscopic techniques with which we investigate the new states of matter that emerge from the interplay between charge, orbits, structure, and magnetism. Findings from this comprehensive experimental program will advance theoretical development and energy-related applications.

Recent Progress

Complex chalcogenides are exceptionally responsive to external stimuli. Under compression, systems like CrSiTe₃, FePS₃, MnPS₃, and CrGeTe₃ host layer sliding, insulator-metal transitions, magnetic dimensionality crossovers, piezochromism, the possibility of orbital-selective Mott and polar metal states, and superconductivity. The 33 K ferromagnet CrSiTe3 has earned widespread recognition for remarkable properties in both single crystal and monolayer form. The discovery of pressure-induced superconductivity above 7.5 GPa and below 4.2 K is one of these exciting developments [1]. Establishing the local lattice distortions and the precise relationship between the structural and insulator-metal transitions is crucial to unraveling how superconductivity develops and distinguishing between conventional vs. unconventional mechanisms in this class of materials. At the same time, CrSiTe₃ is a layered van der Waals material that has attracted extraordinary attention for the demonstration of single-layer ferromagnetism and current-driven control of the spin state. Whether superconductivity arises in the ultrathin limit is currently unexplored, although the fact that the Curie temperature $T_{\rm C}$ rises with decreasing layer number as well as under strain and pressure suggests that the superconducting transition temperature might do so as well. Further developing the phase diagram and resolving the connection between the structural and insulator-metal transitions as well as the intersection of competing phases is a significant step toward evaluating such a relationship.



In order to explore these themes in a complex chalcogenide, we combined synchrotron based infrared spectroscopy and diamond anvil cell techniques to measure the far infrared response of CrSiTe₃ under extreme pressure-temperature conditions. Because closing an indirect gap screens the phonons much less effectively than closing a direct gap, we can follow the evolution of the phonons into the metallic state. The ${}^{2}E_{u}$ symmetry Si-Te stretching mode at 368 cm⁻¹ - noteworthy for engaging in spin-phonon coupling across the magnetic ordering transition - is particularly informative in this regard. This vibrational mode hardens strongly on approach to the pressuredriven structural transition, broadens and develops weak doublet character in the mixed-phase region, and rides on top of a gradually increasing electronic background as the indirect gap begins to close. In the end, the insulator metal transition is swift and sharp. What differentiates our work from previous results is the finding that the first-order structural phase transition in CrSiTe₃ is triggered before (but in close proximity to) the insulator-metal transition. The latter is set in motion almost immediately afterwards. With decreasing temperature, the two-phase region associated with the structural transition broadens, and the insulator-metal transition shifts to slightly higher pressure, indicative of a positive entropy change. Our findings run counter to previous results [1] and completely revise the entire character of the temperature - pressure (T - P) phase diagram for this compound. These trends lead to a critical nexus of activity opening possibility that the juxtaposition of events both hides a quantum critical point and lays the foundation for superconductivity.

Future Plans

We initiated several exciting projects designed to reveal the properties of complex chalcogenides under extreme conditions. These include (i) uncovering pressure-driven structural distortions and metallicity in CrSBr, (ii) unraveling how compression impacts the exciton-polaritons in WS₂ nanotubes as a function of size, (iii) exploring band gap closure and color changes in CdPS₃ and CuInP₂S₆ under pressure, and (iv) developing structure-property relations in the Fe_{1/3}TaS₂, Fe_{1/4}TaS₂, Cr_{1/3}TaS₂, and Cr_{1/3}NbS₂ family of intercalated chalcogenides. Three new PhD students (Luther Langston, Brian Taylor, and Sambridhi Shah) have been identified to lead these projects. They will be able to move ahead once the spring semester is finished. I also hired a postdoctoral research associate Yanhong Gu to explore whether strain will be an effective tool to tune the spectroscopic properties of these materials.

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Investigating Excitonic Properties through Photon Correlation in Quantum Optical Materials

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Keywords: quantum dot, nanocrystal, quantum emitter, perovskite, photon correlation

Research Scope

Exploring Perovskite Nanocrystals as Quantum Emitters

The spectroscopy of single nanocrystals (NCs) at cryogenic temperatures provides important insights into their fundamental optical properties. Understanding their underlying optical physics is crucial for the potential application of NCs as single-photon sources of spectrally coherent emission. Diffraction-based single-emitter spectroscopy, the conventional method used for single-emitter line shape investigations, is limited by the payoff between high spectral and temporal resolution and thus cannot generally discern optical dephasing mechanisms occurring on sub-millisecond timescales. Over the past decade, our group has developed a technique called Photon-Correlated Fourier Spectroscopy (PCFS), which achieves both high spectral and high temporal resolution for a single emitter, rendering it a uniquely suited technique for the investigations of spectral diffusion and single emitter decoherence. This year, we utilized PCFS, as well as other established correlation techniques such as Hong-Ou-Mandel quantum interference, to identify and study new materials for the generation of quantum light.

Colloidal perovskite quantum dots (PQDs) have recently been identified as promising candidates for quantum emitters. Cesium lead halide perovskite quantum dots (CsPbX₃, X = Cl, Br, I) combine the advantages of chemical synthesis in large batches and precise control over the size and shape with the extensive compositional tunabilities and near-unity photoluminescence quantum yields. Our lab recently identified CsPbBr₃ PQDs as a potential source of indistinguishable single-photons¹.

Recent Progress

a) Elastic phonon scattering dominates dephasing in weakly confined cesium lead bromide nanocrystals at cryogenic temperatures.

As the development of perovskites as quantum emitters continues, understanding the photo-physics and the behavior of dephasing in PQD excitons becomes more important. Optical dephasing processes at cryogenic temperatures are critical to the quality of a quantum emitter, making a mechanistic understanding of coherence losses of fundamental interest. We utilized PCFS, which can measure emission linewidths with high precision via spectral correlations, to probe the temperature-



Figure 1. PCFS interferograms and the corresponding spectral correlations (inset) for a ~ 20 nm perovskite quantum dot at various temperatures. As the temperature is increased, the coherence of the quantum dot rapidly decreases, due to phonon-mediated pure dephasing (inset).

dependent dephasing of the zero-phonon line (ZPL). Using PCFS, we obtain a lower bound to the optical coherence times of single PQDs as a function of temperature (Fig. 1). Through these measurements we demonstrate the dominant nature of phonon-induced pure dephasing at these temperatures, which provides insight into the primary mechanisms of dephasing and line shape broadening in PQDs.

b) Hong-Ou-Mandel (HOM) Quantum Interference in Perovskite Nanocrystals

Two-photon Hong-Ou-Mandel (HOM) interference is a hallmark experiment to showcase the potential of PQDs as quantum emitters. By creating a delayed interference stage, we can overlap two photons in time perfectly. If these photons are emitted from a single-photon source, the interference is indicative of a quantum mechanical interaction between the photon wavefunctions. This process is the primary driver behind many quantum computation schemes, most notably linear optical quantum computing.

This year, we demonstrated HOM interference in CsPbBr₃ nanocrystals, a first for any colloidal material. This work signals a significant milestone in the characterization of perovskite nanocrystals as quantum emitters. We conducted studies on weakly-confined 20 nm PQDs, curating the emission suitable for studies on photon indistinguishability, including isolating individual exciton states via polarization filtering and spectrally filtering multiexciton emission to attain excellent single photon purity. We used an asymmetric Michelson interferometer to collide pairs of single photons at a beam splitter, and the resulting interference from photon wavefunction overlap is seen in the reduction of the center peak of the HOM interferogram (Fig. 2). This interference, commonly referred to as HOM visibility, is measured to be around 0.3 - 0.5 in these larger nanocrystals, without the use of any engineered optical structure, exceeding previous estimates obtained through PCFS measurements. This hallmark experiment provides a measure of photon indistinguishability and firmly establishes colloidal perovskite nanocrystals as a new class of potential quantum emitters for various quantum optical applications.



Figure 2. Left panel: Lifetime histogram of a ~20 nm perovskite nanocrystal, showing a fast, mono-exponential lifetime from the exciton. Right panel: HOM interferograms for overlapping (colored) and non-overlapping (grey) single photon pairs, showing a standard quintet structure, with the center peak corresponding to colliding photons. The dip in coincidence counts of the center peak for overlapping photon pairs (colored) relative to non-overlapping photon pairs (grey) arises from HOM interference, its magnitude being the HOM visibility, which is a measure of the degree of photon coalescence or indistinguishability.

c) Exploring the Excitonic Properties of Anisotropic Perovskite Nanocrystals

While research on PQDs has largely concentrated on the three-dimensional cuboid-shaped nanocrystals and their properties, PQDs of anisotropic dimensionalities have recently gathered significant interest. The adjustment of the morphology of PQDs gives access to two-dimensional nanoplatelets (NPLs) and one-dimensional nanorods (NRs), which exhibit striking differences in their optical properties as a consequence of this morphological change, such as blue-shifted absorption and emission features as a result of quantum confinement effects, accelerated photoluminescence lifetimes, increased exciton binding energies, changes in fine structure energies, and reduced dielectric screening.

i) Controlled Assembly of CsPbBr₃ Nanoplatelets

We investigated 2 mono-layer (2 ML) thick CsPbBr₃ NPLs as a model system. We demonstrated the controlled assembly of these nanostructures into face-down or edge-up

orientations, and reported the anisotropy observed in the polarization and decay rate of their emission. The evaporation rate of the dispersion solvent determines the orientation of the NPLs in the solid-state. Face-down and edge-up configurations arise from hexane and toluene solvents, respectively. The ability to control NPL orientation in this fashion indicates that self-assembly of lead halide perovskite NPLs is kinetically driven. Fast evaporation of the solvent results in the kinetically trapped facedown orientation. Slow evaporation of the solvent leads to the thermodynamically favored edge-up orientation. Variable temperature PL measurements show that these materials display a surprising blueshift in the emission wavelength with decreasing temperature, as well as dark



Figure 3. a) Absorption (Abs) and PL spectra obtained for NPL films. Included is an image of the deep blue thin film. Inset are the PL lifetimes recorded for the face-down (blue trace) and edge-up (purple trace) films, showing a faster lifetime for the edge-up configuration. b,c) Plot of the PL intensities obtained for face-down (blue trace) and edge-up (purple trace) films as a function of the angle of the polarization analyzer, the angular dependence shown in (c). Solid lines are sinusoidal fits to the data points. The extracted polarization factors are 0.04 and 0.29, respectively.

exciton emission at low temperatures: trends which differ from the behavior of less confined nanocrystal structures. We explain these findings based on the exciton fine structure and the structural evolution of the NPLs, the latter of which includes a rare negative thermal expansion (NTE) effect.

ii) Engineering Enhanced Stability in Perovskite Nanorods

One-dimensional (1D) colloidal lead halide perovskites NRs have potential as quantum emitters. Their study, however, has been hampered by their previous instability, leaving a gap in our understanding of structure–property relationships in colloidal LHPs with anisotropic shapes. We have studied stable, highly-confined 1D CsPbBr₃ nanorods (NRs) and demonstrated their

structural details and photoluminescence (PL) properties at both the ensemble and single particle levels (Fig. 4)².



Figure 4. Characterization of CsPbBr3 short rods at the ensemble-averaged single particle level. (a) Schematic demonstration of the measurement at the sample-averaged single particle level. (b) Room-temperature solution $g^{(2)}$ measurements show that the ratio of biexciton to exciton events is 5%, indicating a fast Auger recombination rate at room temperature. (c) PL lifetime measurements and fits to a radiative lifetime of 3.9 ns. (d) sPCFS measurements shows similar spectral line width between the ensemble and the sample-averaged single NR, indicating that the line width broadening originates at the single particle level

Our pioneering technique, solution-PCFS (sPCFS), allows us to probe simultaneously the ensemble and single particle line shapes through photon correlations. Our results reveal that the ensemble and single-particle linewidths are near-identical, indicating that the broad PL spectrum from NRs does not originate from ensemble-based heterogeneous broadening, but rather from mechanisms that effect the single particle line shape (Fig. 4d).

Future Plans

We will continue investigating dephasing and HOM interference in a size series of PQDs, altering the surface morphology to tune phonon coupling³. We will also investigate the potential for polarization entanglement. We will continue to study the effect of anisotropic properties on the biexciton lifetime and biexciton quantum yields at both room- and low-temperature. We will investigate the origins of the room temperature broad NR PL spectrum.

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Nanoscale free-electron lasing

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Keywords: (Stimulated) Smith-Purcell radiation, free-electron lasing, electron-photon interaction, nanoscale light-matter interaction.

Research scope High-energy, free-electron-laser facilities based on large-scale electron accelerators and undulators provide access to high-brightness, tunable light from the microwave to the x-ray regime. It has been shown that low-energy, high-charge-density, focused electron beams produced in scanning or transmission electron microscopes can induce a coherent, super-radiant buildup of terahertz radiation upon interaction with micron-scale gratings [1]. This radiation is akin to that generated in a free-electron laser. However, the physical mechanisms underlying this lasing process are not fully understood, and it is not known precisely how the process scales to the infrared and visible spectral regions where there is increased frequency dependence of the optical properties of materials.

In this research, we will use $\sim 1 - 10$ keV, high-density, free-electron bunches to investigate coherent, super-radiant, near-infrared light emission from nanostructured periodic surfaces with periods ranging from tens to hundreds of nanometers. We will study this nanoscale free-electron lasing process in the stimulated regime, with particular attention given to *the impact of the nanostructured grating geometries and materials* as well as the *spatiotemporal electron-beam properties* on the nanoscale free-electron lasing process.

Recent progress In the first year of this new program, we have made significant progress in the development of patterned grating structures and the surrounding infrastructure and modeling needed to systematically investigate superradiance and free-electron lasing at the nanoscale. A major challenge of this project is the large amount of custom apparatus that is needed and that is unavailable commercially, and thus be constructed by hand (see Fig. 1 which highlights our infrastructure development to date). Below we summarize our infrastructure



Figure 3: Experimental Testbed. Completed custom components are noted. These have been integrated into our 1-10 keV scanning electron microscope. Further discussion provided in the text.

developments over the first 1 year of this program, with an emphasis on (1) the electron

interaction zone, (2) the laser system and electron modulator, (3) the electron spectrometer, and (4) the beam alignment and referencing. Various aspects of this work have been presented at the WE-Heraeus-Seminar on Quantum Electron Optics in Israel, where it won Best Poster and was upgraded to an oral presentation. Aspects of the apparatus will also be presented at EIPBN 2023.

Nanostructured Fiber Tips The core experiment revolves around a nanoscale grating pattern that is fabricated directly on top of the tip of a fiber-optical cable. The nano-patterned fiber is used to simplify light collection. Since the depth of focus of the beam is on the order of 10 μ m, the nanostructure protrudes to allow close impact of the beam. These fibers were fabricated via a customized process of hydrofluoric acid vapor etching, polishing a flat 10- μ m plateau onto the tip, gold evaporation, and ion beam milling of nanostructures on top. In Fig. 2a we show a micrograph of a patterned fiber structure. The fiber is covered with a thin (~50-nm) gold layer that prevents the build-up of electric charge on the otherwise electrically insulating fiber and acts to favor the radiation of photons into the fiber rather than into free-space. We calculate up to 25-fold improvements in the photon collection efficiency at targeted wavelengths compared to conventional free-space approaches.



4: Module Progress - (a) A nanofabricated fiber, with various pitch gold gratings shown on top; 100-nm-period gratings are visible. (b) Photon counts vs. delay from photon detection to electron detection event, demonstrating ultrafast triggering of our electron source, as evidenced by varied delay times when propagating down the column. (c) Phosphor image of the dispersion of our electron spectrometer for various beam energies. The 10-V steps in beam voltage were easily detected, and sub-V changes in the beam energy should be resolvable.

Laser Triggering and Electron Modulators for Controlled Beam Bunching Our experimental configuration enables us to study spontaneous emission of Smith-Purcell radiation into the optical fiber. In a more involved configuration, we will propagate the electron across a modulated electric

field before passing aloof to the fiber pattern. With this approach, as the electron bunch (or wave function in the case of a single electron wavepacket) exits the modulation field, it obtains a spatial probability distribution with local maxima that coincides with the period of the nanosized patterned structure. The modulating electric field is generated by illuminating a metallic aperture grid (the '*modulator*') with a pulsed laser. The addition of a modulator to the experimental configuration enables us to study stimulated and super-radiant Smith-Purcell radiation into the fiber. So far we have integrated the modulator grid (shown in Fig. 1) as well as demonstrated ultrafast electron emission required for such a process (see Fig. 2b). Our next step is to check that we generate modulated sidebands using the electron spectrometer, described below.

Low-Energy Electron Spectroscopy with Sub-eV Resolution We also have designed, constructed, and tested an electron spectrometer to allow us to verify the generation of electron bunching, as well as to characterize the electrons after superradiant emission. The spectrometer is integrated into our SEM as shown in Fig. 1. Early results from the spectrometer are shown in Fig. 2c. Our results indicate we can measure electrons with sub-eV energy resolution, and nanosecond temporal resolution. This time and energy resolution will allow us to directly observe single-photon modulation once the phosphor is replaced by a scanned slit.

SE image of scan across edge detector Oscilloscope time trace of edge detector voltage



Figure 5: Electron Edge Synchronization - Micrograph of the electron beam going over the edge, with the fast synchronization scan output shown. By repeatedly scanning over the edge and then aloofly exciting the fiber, we can accurately calibrate the spatial position of the beam despite beam vibrations inherent in our system.

Edge-Detection for Nanometer-Scale Beam Alignment The intensity of the generated radiation decreases exponentially as a function of the separation distance between the pattern and the passing electron. This separation, referred to as the impact parameter, must be calibrated and controlled in measurement with nanometer-scale accuracy for proper data interpretation, in order to ensure superradiant light enhancement is not due to a varying impact parameter. Furthermore, beam impact with the sample can lead to incoherent background radiation in the form of cathodoluminescence which must be either avoided or accounted for properly during the experiment or in post-analysis. To this end, we have developed a form of active scan synchronization, in which a cleaved semiconducting edge is used to detect the presence of a constantly scanned electron beam. By repeatedly scanning the beam over the edge of the sample faster than vibrations and instabilities of the system, we can use the edge detector signal to calibrate all of our output photon and electron signals to when we know the beam exited the edge. Sample data of the edge and the reference signal are shown in Fig. 3. The setup is shown in the inset of Fig. 1, showing the edge detector and fiber placed on nanostages for alignment.

Modeling Efforts We have made significant progress on a fully numerical model of stimulated Smith-Purcell radiation as well as on a novel, analytical approach to self-stimulated, superradiant Smith-Purcell. Firstly, we developed a frequency-domain numerical model to analyze light emission driven by free-space electrons in an arbitrary three-dimensional material and geometric environment. This generalized Smith-Purcell simulator was benchmarked via basic Cherenkov radiation simulations via the Frank-Tamm equation. Furthermore, this solver was adapted to handle arbitrary electron phase space distributions; the solver can take in arbitrary temporal and energetic distributions of electrons. This solver is currently being used to optimize preliminary grating designs for our stimulated Smith-Purcell experiments. The solver is also being used to develop initial expectations for the dependence of the emission on beam parameters. Beyond this fully numerical solver, we have also made significant strides in developing an analytical approach to understanding self-stimulated, superradiant Smith-Purcell. This analysis adapts core assumptions of free-electron laser theory to low-energy electron beams. The analytical approach takes the form of a coupled set of first-order equations similar in structure to the pendulum and wave equations from free-electron laser theory. This analytical model will guide our efforts to achieve superradiant Smith-Purcell and will orient our experimental investigations into the ultrafast dynamics of this process.

Future plans Now that the bulk of the experimental apparatus is in place, we will begin measurement work toward the scientific goals of this program. Our future experiments will include (1) generating and characterizing attosecond electron bunches, (2) demonstrating energy modulation via the inverse-Smith-Purcell effect from our fibers, (3) demonstrating standard Smith-Purcell radiation into our fibers, (4) demonstrating enhanced light generation due to bunched charges, and lastly (5) using electron spectroscopy and multiple modulation stages to understand electron dynamics during this process. In parallel with this work, we will also seek to further improve our modeling and understanding of seeded and self-amplified superradiant processes.

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Nanoscale Quantum Sensing and Imaging of Topological Magnets Chunhui (Rita) Du, University of California, San Diego

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Self-identify keywords to describe your project: Topological materials, quantum sensing, scanning single-spin magnetometry, hybrid quantum devices.

Research Scope

The major research focus of this program is to utilize nitrogen-vacancy (NV) centers [1], optically active spin defects in diamond, to realize nanoscale quantum sensing and imaging of topological magnets, probing the fundamental physics underlying the interplay between band topology, electron correlations, and magnetism in emergent quantum states of matter. Specifically, we will visualize the exotic noncollinear spin textures of (anti)ferromagnetic Weyl semimetals [2] and investigate magnetic phase transitions in topologically protected condensed matter systems. We are also interested in using scanning NV microscope to perform concurrent imaging of local magnetic structures and electric current flow patterns in intrinsic magnetic topological insulators, uncovering the underlying mechanism behind the recently observed "high-temperature" quantum anomalous Hall effect [3]. Our "stretch" goal is to develop hybrid quantum systems consisting of quantum magnets and NV centers to establish controllable quantum entanglement between distant spin qubits via energy dissipationless chiral edge states.

The proposed research will make important contributions to the burgeoning field of quantum materials and promote the role of topological materials in the development of next-generation, transformative quantum information sciences and technologies. By developing the cutting-edge quantum sensing techniques and demonstrating their operations under broad experimental conditions, we propose to provide a versatile NV-based quantum microscopy platform, which could be extended naturally to a large family of untapped material systems and benefit the material science community in the long run by expediting progress towards future quantum technologies.

Recent Progress

After starting this early career program, the Du research group has been intensively working on developing state-of-the-art cryogenic scanning NV microscope for the proposed research study. The measurement system consists of a home-built confocal and a custom-designed atomic force microscope operating in a cryostat. The variable temperature insert is placed inside the bore of a three-dimensional superconducting vector magnet. The microscope head is positioned at the bottom of the insert. A window on top of the cryostat provides an optical access for NV measurements. A diamond cantilever is glued to a quartz tuning fork for force-feedback atomic force microscopy operations. The NV-to-sample distance typically lies in the range from 20 nm to 100 nm. A sample holder with pre-designed coplanar waveguides is fixed onto a stack of piezo-based positioners and scanners to perform engagement with the diamond cantilever and two-

dimensional (2D) scanning measurements. The spatial resolution of the scanning NV microscope can reach tens of nanometers with single-spin sensitivity capable of resolving nanomagnetic patterns of various condensed matter systems from 1.8 to 300 K.

Currently, the Du research team is using the cryogenic scanning NV system to study local magnetic properties of (anti)ferromagnetic Weyl semimetal Mn₃Sn [2]. Figure 1 presents nanoscale magnetic imaging of a 50-nm-thick polycrystalline Mn₃Sn thin film. It is evident that Mn₃Sn shows vanishingly small magnetization in the low-temperature spin glass phase, while robust magnetic features emerge in the high-temperature regime with the characteristic inverse triangular spin state. Our results bring the possibility of direct visualization of local spin orders of non-collinear



Figure 1 (a)-(d) Our scanning NV images of local magnetic stray field emanating from a 50-nm-thick Mn_3Sn thin film at 100 K, 200 K, 250 K, and 300 K. Scale bar is 500 nm for all images.

antiferromagnets. Taking advantage of the unprecedented spatial resolution of a scanning NV microscope, we are also working on developing hybrid quantum systems consisting of nanoscale magnetic domains and spin qubits to realize electrical control and measurements of local NV spin properties [4]. We have used the scanning NV magnetometry to image spin-orbit-torque (SOT)-driven domain wall dynamics in Co-Ni-based magnetic multilayer heterostructures as shown in Figs. 2(a)-2(c). By applying different electrical write currents to systematically control the SOT-induced domain wall motions, the local field environment of a proximate NV center can be precisely engineered, enabling electrical switching of NV spin properties between two (multiple) different states. Electrical measurement of NV properties is achieved through the variation of anomalous Hall voltages, which is intimately tied to nanoscale domain-wall-motions in the magnetic channel of the magnetic device. Our work demonstrates the two-fold advantages of NV centers in quantum sensing and quantum information science studies. The observed electrically

tunable coupling between NV centers and propagating domain walls magnetic further highlights the appreciable opportunity for promoting the scalability, interconnection, quantum control of entanglement, and other tailored functionalities of NV-based hybrid quantum systems.



Figure 2. (a) Nanoscale stray field imaging of a magnetic domain wall formed in a Co-Ni multilayer device. (b)-(c) Application of a negative (-24 mA) and a positive (28 mA) electrical write current pulse reversibly drives domain wall forward propagation (b) and backward retraction (c) motions. Scale bar is 200 nm for all images.

Future Plans

We plan to investigate temperature and field

dependent evolutions of chiral magnetic domains in Mn₃Sn, providing a microscopic assessment of magnetic phase transitions in topologically protected quantum magnets. We also suggest probing local variations of chiral spin textures in response to the external stimuli such as external

magnetic field, spin-orbit torque, and Joule heating, probing the underlying mechanism of unconventional magnetization switching strategy in topological non-collinear antiferromagnets.

In parallel, we plan to use NV centers to image magnetic and electric-current patterns in emergent quantum anomalous Hall insulators $MnBi_2Te_4$ (Bi_2Te_3)_n (MBT) [3][5]. By studying the quantum transport behaviors in different magnetic phases and correlate this information to proposed scanning NV measurements, we propose to provide a new experimental platform to probe the underlying mechanism of quantum anomalous Hall effect in the unconventional high-temperature regime, shedding light on the fundamental correlations between microscopic spin textures and quantized electron flows in intrinsic topological magnets.

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Mid-Infrared Colloidal Quantum Dots LEDs. Philippe Guyot-Sionnest, James Franck Institute, The University of Chicago.

Research Scope

This project explores colloidal quantum dots as mid-infrared electroluminescent devices. The objectives that will be pursued in parallel are (i) a determination of the main non-radiative mechanisms affecting the mid-IR luminescence for interband and intraband colloidal quantum dots, (ii) a solution-based synthesis of core/shells and of a material matrix that maximizes the photoluminescence (iii) the invention of mid-IR LEDs based on such materials (iv) the exploration of the performance limits and comparison with state-of-the-art solid state and thermal sources.



The research is motivated by the need for midinfrared sources for molecular spectroscopy and sensing, affording high modulation rates, low average power consumption, and also frequency tunable and rather monochromatic. These needs are relevant to DOE programs associated with the monitoring of environmental. mining and The existing industrial gaseous emissions. technology relies primarily on thermal sources, which are not so readily compatible with battery or solar energy power. The solid-state dominant technology uses epitaxial materials based on quantum well and cascade emission. The performances achieved with these advanced materials decays rapidly with increasing

wavelength as shown in Fig. 1.[1] Moreover, these epitaxial material performances seem to be within reach of the simpler solution processed CQD mid-IR LEDs. Additionally, CQD LEDs promise relatively unlimited production scalability, extreme cost reduction and fabrication in extended pixelated format.

This project proposes a novel use of CQDs with novel modalities using either interband and intraband chromophores. The II-VI materials first targeted have toxicity issues because of Hg or Cd. The small amounts needed in the active layers should be within the RoHS (restriction on hazardous substances) requirements, but the extension to less toxic material such as III-V is explored. This project supports a graduate student full time over three years to cover the material synthesis/ characterization and the LED device fabrication. The research is synergetic with a decade of our prior work on infrared quantum dots and photodetector, and could lead to a demo sensor with a high frequency CQDs LEDs and detectors in one single unit.

Recent Progress

Since the beginning of the grant, our yet unpublished results have demonstrated the first instance of cascade emission with CQDs, the first instance of electrically driven intraband emission, a record electron-photon quantum efficiency of 5% and power conversion efficiency of 0.1% for emission at 5 microns, which are comparable to quantum well epitaxial devices, and 50 x improved compared to our previous Mid-IR LED based on HgTe CQDs.[2] The figure 2 shows a schematic device structure and the mid-IR emission as a function of drive current.

Figure 2. (a) Schematic of the CQD mid-IR LED device. (b) mid-IR emission with increasing current.



Future Plans

Prior results with mid-IR CQDs in solution led to a record 2% emission efficiency at 5 microns and 300K, but we do not yet know if this is limited by the material interfaces, rather than by multiphonon processes. We therefore explore the photoluminescence efficiency limits of core/shell CQDs in inorganic matrix in the mid-infrared. The materials used in our recent LEDs had a PL conversion efficiency of about 0.1% and any increase in emission efficiency will improve the overall power efficiency, possibly surpassing the epitaxial quantum well structures. We will also explore intraband CQDs of existing commercial core/shell materials, such as the InP/ZnS currently applied for TV displays. Such materials might be more acceptable for commercial applications.

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Session III

On the Nature of Rejuvenation and Memory in Spin Glasses

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Keywords: rejuvenation, memory, spin-glasses, glasses, correlations

Research Scope

We focus on the dynamical response of random systems far from equilibrium. Historically glassy materials, polymers, and gels fall into this category, and now there are social science examples that exhibit similar properties. We use spin glasses in our research because their dynamics are far from equilibrium, and because we can directly measure their properties via their magnetic signature, a distinct advantage over other systems. We test the relevance of the basic physical laws that have been derived under equilibrium conditions in non-equilibrium situations. Remarkably, we find that many equilibrium properties are present under non-equilibrium conditions, thus displaying the generality of response functions that were thought unconnected. An example is temperature chaos which had been an equilibrium concept. We have found that equilibrium scaling applies to a non-equilibrium state as well. Our future work (see below) will continue this exploration.

An example of the reach of our research is our microscopic explanation for rejuvenation and memory. It is a common phenomenon in glassy materials, having been reported most recently for structural glasses.¹ Our observation of temperature chaos in spin glasses has provided a quantitative basis for rejuvenation.² Through the "lens" of time and temperature dependent correlation lengths, we have derived a quantitative expression for memory.

We use a variety of measurement facilities to probe spin glass dynamics. These include a commercial SQUID magnetometer at The University of Texas at Austin, a sensitive home-built SQUID magnetometer at the Indiana University of Pennsylvania, an electrical resistance noise system, a commercial dc/ac magnetometer, and a home-built ac susceptometer with perpendicular capability at the University of Minnesota. An important additional strength is our relationship with the numerical simulations and theory of the Janus II Collaboration, based in Spain and Italy. We interact very closely with them, and have published joint papers (see Publications below). Their insights derived from their numerical simulations for memory served as guidance for our experimental extraction (and understanding) of this phenomenon.

One example of this relationship was the derivation of a scaling law for the response of spin glasses near the condensation temperature T_g .⁴ The use of the spin glass correlation length obviated the need for an accurate knowledge of T_g , as required for all previous scaling relationships. We have explored the non-linear properties of spin glasses, using these scaling laws, and developed a microscopic description of the correlated region.

Recent Progress

At first sight, rejuvenation and memory seem contradictory concepts. Rejuvenation is the observation that when a system is aged at a temperature T_1 for a time t_{w1} , and then cooled to a (sufficiently) lower temperature T_2 ,³ the system reverts to the same state it would have been had the system been directly cooled to T_2 . The state at temperature T_2 is independent of its having approached equilibrium at T_1 . We have shown that this is caused by temperature chaos in the case of spin glasses.² The conundrum arises when the system is warmed back to T_1 and it exhibits its aged behavior, hence memory. How is it possible to return from a state created by chaos to its original aged state?

The experimental expression for rejuvenation and memory is pictured below for the imaginary part of the susceptibility, χ'' , for a spin glass. The χ'' data are for a single crystal of 7.92 at.% Mn in Cu as measured by Ms. Jennifer Freedberg (School of Physics and Astronomy, The University of Minnesota, Minneapolis, Minnesota 55455, USA).



The dashed lines is the "reference" curve, with the spin glass continuously cooled to a low temperature (here, 5 K) below the transition temperature ($T_g = 41.6$ K) and then heated above the transition temperature. The spin glass is then cooled to $T_1 = 22.5$ K and held at T_1 for a time t_{w1} (here, 1 hour). As seen in the figure, χ'' is reduced when aged at T_1 . After t_{w1} the spin glass is then cooled to a lower temperature. As seen in the figure, χ'' returns to its reference curve value after a sufficient temperature drop. This is termed "rejuvenation." The spin glass is then cooled to a temperature T_2 , held for a time t_{w2} (the effect of waiting at T_2 is not shown in the data), and then heated back to above T_g . Remarkably, χ'' partially traces out its values that aging for t_{w1} created at T_1 . This is termed "memory." But how can memory happen if the spin glass went through a chaotic transition to achieve rejuvenation?

The solution of this conundrum was resolved by the Janus II Collaboration. When the spin glass is cooled to T_1 and aged for a time t_{w1} , a correlation length is grown from nucleation (at t = 0 when the temperature reaches T_1) to a value $\xi(t_{w1},T_1)$. When the spin glass is rapidly cooled to T_2 , the spins in this correlated state are "imprinted" on the system. Because the temperature

difference, $T_1 - T_2$, is sufficient for temperature chaos, a new correlation length grows from nucleation at T_2 as a consequence of aging for t_{w2} : $\xi(t_{w2},T_2)$. But this correlated state has nothing to do with the initial spin correlations created at T_1 after t_{w1} . Hence, as $\xi(t_{w2},T_2)$ grows, it "destroys" the correlations of $\xi(t_{w1},T_1)$. If $\xi(t_{w2},T_2)$ is sufficiently small (the correlation length growth slows considerably as the temperature is lowered), then memory results. If one waits until $\xi(t_{w2},T_2) \approx \xi(t_{w1},T_1)$, memory is destroyed. A quantitative expression for memory derived from this hypothesis is then,

$$\mathcal{M} = 1 - \left[\frac{\xi(t_{w2}, T_2)}{\xi(t_{w1}, T_1)}\right]^{[D - (\theta/2)]}$$

where D = 3 is the spatial dimension, and θ is the replicon exponent, roughly equal to 0.34. The ratio on the right is just the ratio of the volume of the regions subtended by $\xi(t_{w2},T_2)$ and $\xi(t_{w1},T_1)$, respectively. The question is, is this true? Experiments of Jennifer Freedberg find,

which have the correct trend with memory increasing as t_{w1} increases, and memory decreasing as t_{w2} increases; a more quantitative analysis is in progress



We have measured the 1/f electrical noise in thin CuMn thin films.⁵ The probability distributions for the free energy barriers at T = 0 as a function of thickness were extracted. The magnitude of the barrier heights was found to be considerably larger than those extracted from conventional dynamical measurements on thin film and in bulk samples. Our analysis suggests that this difference derives from the different range dependences of the RKKY interaction between the two measurements. The 1/f electrical noise range is limited by the electron mean free path, while single crystals experience the full oscillatory range of the RKKY interaction.

Future Plans

The quantitative expression for memory requires knowledge of the correlation lengths at temperature T_1 with waiting time t_{w1} , and at T_2 with t_{w2} , namely $\xi(t_{w1},T_1)$ and $\xi(t_{w2},T_2)$ in the expression for *M* above. We have used the growth law to estimate these quantities, but there are unknown constants that obviate a direct comparison. Instead, we propose to measure $\xi(t_{w1},T_1)$ and $\xi(t_{w2},T_2)$ directly using the effect of a magnetic field on the spin glass response function. While this is (now) standard procedure, it nevertheless requires some sophistication with respect to the extraction of the signal from the noise. We shall measure these quantities at the same temperatures and waiting times as those exhibited in the above figures. A side benefit will be the establishment of the values for the constants in the growth laws for $\xi(t_w,T)$.

Using a sensitive home-built SQUID, we shall use the scaling law² to fit the non-linear behavior for temperatures just below T_g . This will extend our understanding of spin glass dynamics controlled by the $T = T_g$ fixed point. The correlation length is set by the critical fluctuations near T_g , the so-called "Josephson length"⁴, while previous experiments have only probed the growth law correlation length controlled by the T = 0 fixed point. Our preliminary experiments have shown a rapid reduction in the effective response time, t_w^{eff} , as $T \rightarrow T_g$ from below. That is, $t_w^{eff} \approx t_w$ in the limit that $H \rightarrow 0$, but for $t_w = 10,000$ sec, we are finding $t_w^{eff} \approx 100$ sec. This implies that the free energy barriers are tending toward zero as $T \rightarrow T_g$ from below. We shall follow this line of inquiry to establish the nature of spin glass dynamics in the immediate vicinity of T_g .

Previous measurements of electrical 1/f noise on CuMn thin films have established the probability distribution of the free energy barriers at T = 0 K. They were found to be larger than those extracted from spin glass dynamics using the conventional method for their extraction from measurements of t_w^{eff} . This was thought to be a consequence of the differing length scales in the two approaches: the electron mean-free path for 1/f noise measurements vs the full RKKY length in single crystals for the extraction of t_w^{eff} . New measurements on AgMn thin films are underway. The comparison between the two systems will be used to separate the effect of scattering on the RKKY coupling in metallic spin glasses.

The use of a Heisenberg-like spin in CuMn and AgMn metallic alloys has been bedeviled by the similarity of behavior to Ising-like spin glasses. This is thought to be a consequence of Dzaloshinsky-Moriya anisotropy that results in a freezing of the longitudinal component of spin at the condensation temperature T_g. However, it has been predicted in mean field theory that the conventional ac susceptometers that measure spin glass response in the direction of the magnetic field, *i.e.* in the longitudinal direction. We shall search for transverse freezing in single crystals of CuMn to test the predictions of mean field theory.

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Optical, Electrical and Magnetic Studies of Hybrid Organic-Inorganic Perovskite Semiconductors

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Keywords: Hybrid organic-inorganic perovskites, magneto-optics, transient quantum beatings, field induced circular photoluminescence, Landau levels

Research scope

We have studied magneto-optical and spin responses of photocarriers and excitons in hybrid organic inorganic perovskite semiconductors (HOIPs). During the last two years we have investigated: (i) The photocarriers spin response in various 2D and 3D HOIPs using ps transient quantum beatings in the time-dependent circular reflectivity; (ii) The magneto-optic response of these materials using the high magnetic field national laboratory (MagLab) in Tallahassee Florida, that included magneto-excitons and Landau levels of the continuum bands.

Recent Progress





Figure 1. Photoinduced quantum beatings (QB) in MAPbI₃ single crystal at various magnetic field strengths measured at 4K with light incident along [100] and applied magnetic field along [001]. a-c Magnetic field (*B*) dependence of the circularly polarized reflectivity (c-PPR(t)) response measured at 758.5 nm pump/probe beams at various field strengths as denoted, and theirs corresponding FFT spectra, d-f. g The corresponding QB frequencies for the fast (red) and slow (blue) beatings vs. *B* up to 700 mT and the Landé *g*-factors obtained from the two slopes, as indicated [2].

MAPbI₃: Utilizing the spin degree of freedom of photoexcitations in hybrid organic inorganic perovskites (HOIPs) for quantum information science applications has been recently proposed and explored [1]. However, it is still unclear whether the stable photoexcitations in these compounds correspond to excitons, free/trapped electron-hole pairs, or charged exciton complexes such as trions. We have investigated quantum beating (QB) oscillations in the picosecond time-resolved circularly polarized photoinduced reflection (c-PPR(t)) of single crystal methyl-ammonium tri-iodine perovskite (MAPbI₃) measured at cryogenic temperatures [2]. We observed two quantum beating oscillations (fast and slow) whose frequencies increase linearly with the magnetic field, *B* with slopes that depend on the crystal orientation with respect to the applied magnetic field (Fig.

1). We assign the quantum beatings to positive and negative trions whose Landé *g*-factors are determined by those of the electron and hole, respectively or by the carriers left behind after trion recombination. We obtained $g_{[001]}^e = 2.52$ and $g_{[1\overline{1}0]}^e = 2.63$ for electrons, whereas $|g_{[001]}^h| = 0.28$ and $|g_{[1\overline{1}0]}^h| = 0.57$ for holes. The measured *g*-values are in excellent agreement with an 8-band k.p calculation for orthorhombic MAPbI₃ [2]. Using the technique of resonant spin amplification of the quantum beatings we measured a relatively long spin coherence time of ~11 (6) nanoseconds for electrons (holes) at 4K. This work was published in *Nature Communication* [2].



Figure 2. Temperature and magnetic field dependencies of the photocarriers' spin relaxation rates in CsPbBr₃ measured along <001> crystal orientation at B = 10 mT. (a) Spin dephasing rate of electrons and holes as a function of *B* measured at 4K. (b) Spin dephasing rate of electrons as a function of temperature up to 60K, which is fitted using $\Gamma_0 + \Gamma_{\omega} \frac{1}{e^{K_B T} - 1}$ (red curve); due to Elliot-Yafet mechanism dominated by a LO phonon.

CsPbBr3: We have studied the magneto-optical properties of photoexcitations in CsPbBr3 single crystals using the technique of picosecond time-resolved quantum beatings (QBs) in the circularly polarized photoinduced reflection, as well as steady state magneto-circular dichroism (MCD) in CsPbBr₃ film [3]. In the Voigt configuration at magnetic field strength B>0, we observed fast and slow QB oscillations that we attribute to the Larmor precession frequency of electrons and holes, respectively. From the linear frequency dependence on B, we extracted the carrier anisotropic Landé g factors for applied **B** along [010] and [001]; for electrons $|g_e|[001]| = 1.95 \pm 0.04$ and $|g_e|[001]| = 1.95 \pm 0.04$ $[010] = 1.82 \pm 0.04$, whereas for holes $|g_h[001]| = 0.69 \pm 0.02$ and $|g_h[010]| = 0.76 \pm 0.02$. These values are in excellent agreement with a k·p model calculation applied to CsPbBr₃. Surprisingly, we found that at B = 0 there is still electron QB oscillation of ~500 MHz that we interpreted as due to the Overhauser field from the nuclei [3]. This field originates from the spin-aligned nuclei caused by the Knight field related to the spin oriented photocarriers that produce dynamic nuclear spin polarization [4]. From the measured MCD spectrum vs B, we obtained the g-factor of the bright excitons $g_{ex} = g_e + g_h = 2.18$ showing that the g-value of holes in CsPbBr₃ is positive. We also measured the temperature and magnetic field dependencies of the electron and hole spin dephasing times (Fig. 2) which support the Elliot-Yafet spin-relaxation mechanism based on LO phonon. This work was recently published in *Phys. Rev. B* [3].

(ii) <u>Dark exciton in 2D hybrid halide perovskite films revealed by magneto-</u> photoluminescence at high magnetic field

We have studied the exciton fine structure (EFS) in 2D-phenethylammonium lead iodide (2D-PEPI) films using magnetic field induced circular and linear polarization of the photoluminescence (PL) in both Faraday and Voigt configurations at fields up to 25 Tesla. The measurements were performed at MagLab in Tallahassee Florida. We identified three exciton bands in the PL spectrum associated with bound excitons, dark exciton and bright excitons, respectively. Under high magnetic field in Faraday/Voigt configuration, large field-induced



Figure 3. (A and B) The field induced circularly polarized PL (FICPO) spectra of 2D-PEPI measured at 4K in the Faraday configuration at various B_z . The bottom plot within each panel shows the PL deconvolution using three Voigt functions as denoted. (A) Left circular polarization (σ +), and (B) right circular polarization (σ -). (C) The summation of the magneto-photoluminescence (MPL) response of EX_L, EX_{A1} (DEX or dark exciton) and EX_{A2} (BEX or bright exciton), respectively at various B_z . The lines through the data points for EX_{A1} and EX_{A2} are fits using Lorentzian functions. (D) The degree of field induced circular polarization, P_c (namely FICPO) of the three PL bands vs. B_z . The lines are fits from which we could extract the effective g-value.

circular or linear polarizations have been observed in the PL band related to the dark exciton, which is magnetically activated. Furthermore, we found that the dark exciton has an anomalous field induced circular polarization that cannot be explained by the classical Boltzmann distribution of spin-polarized species. Our findings are well explained by an effective mass model that includes exchange terms unique to the monoclinic symmetry as a perturbation of the EFS in the approximate tetragonal symmetry. This work has been recently submitted to publication.

(iii) Anomalous Landau levels in 2D hybrid organic inorganic perovskites with strong Rashba spin orbit coupling

The two-dimensional (2D) layered HOIPs self-assemble into multiple quantum well structures having strong spin-orbit coupling (SOC), which in the presence of inversion symmetry breaking may lead to giant Rashba splitting [5]. We used magnetic circular dichroism (MCD) spectroscopy for studying the excitons and charge carriers in a prototype 2D-HOIP, namely $C_6H_5C_2H_4NH_3)_2PbI_4$ (2D-PEPI) at magnetic field, *B* up to 25 T at MagLab in Florida. The MCD spectra contain sharp oscillations above the band edge that are caused by optical transitions from Landau levels (LL) in the valence band to LL in the conduction band. The presence of the strong Rashba SOC in the monoclinic crystal structure of 2D-PEPI causes giant LL energy spacing and mixed MCD polarity. We also found that an external in-plane electric field causes substantive increase in the Rashba SOC which increases the LL energy spacing.

Future Plans

During the 6th support year of our program we have worked on several projects that involve circular dichroism, magneto-circular dichroism and field induced circularly polarized PL of 2D

and 3D HOIPs. We have preliminary results that show MCD of Landau Levels in 2D PEPI. Next we plan to study the exciton fine structure and LL in PEPI films and crystals having 2 and 3 layers of the inorganic component in the building blocks, using similar techniques. We also plan to use these techniques for studying the excitons and continuum bands in *chiral* 2D HOIP. **References**

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Charge, ions, and chirality in 2D metal halide perovskite quantum wells

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i) Program Scope

Metal halide perovskite (MHP) multiple quantum wells which consist of multilayers of alternate organic and inorganic layers exhibit large exciton binding energies due to the dielectric confinement between the inorganic and organic layers. These naturally formed multiple quantum wells have strong spin-orbit coupling (SOC) due to the presence of heavy elements in their crystal structures. Although the fundamental properties of 2D MHPs are far from being entirely understood, it is widely accepted that their band edge absorption coefficient results from strong exciton interactions. However, studies demonstrating how different exciton interactions and doping effects influence electronic traps and disorder on the band edge absorption coefficient of 2D MHPs have not been demonstrated. Understanding these interactions in MHPs will allow us to access low energy optical transitions for the fabrication of solution processable short-to-midwavelength IR photodetectors $(1 - 8 \mu m)$. Moreover, upon doping, it is possible to move the Fermi energy into the conduction band (CB) to favorably promote the transport of charges in a working device. Herein, we study the development of 2D MHPs having strong SOC, high carrier mobility, and tunable quantum well structures. Our studies shed light on the design and modulation of fundamental physical phenomena by carefully elucidating the role of dopants (n-type and p-type), exciton heterogeneity, orientation, structure, and bias stress effects on the performance of MHPs as potential IR photodetectors.

ii) Recent progress

Franz-Keldysh and Stark Effects in Two-Dimensional Metal Halide Perovskites

When the 2D limit (n = 1) is realized in MHPs, unique quantum and dielectric confinement effects sum together to increase the exciton binding energy (E_B). This enhancement of E_B translates to greater spectroscopic separation of the exciton, which we have investigated using electroabsorption (EA) spectroscopy to answer long-standing questions regarding the effect of chemical substitutions on E_B as well as the nature of lattice-exciton interactions. EA simulations and measurements allow for a deepened understanding of the redshift of exciton energy, according to the quadratic Stark effect, and the continuum wave function leaking, according to the Franz-Keldysh effect.

Findings: The spectroscopic isolation of the 2D MHP's exciton not only allows for accurate determination of the exciton's energy level, but also its transition dipole moment μ_{ge} and polarizability α_{ge} which are given by the EA line shape. As shown in **Figure 1A**, the EA spectrum for a 2D phenethylammonium lead iodide (PEA₂PbI₄) thin film acquired at 30 K (red) follows the absorption spectrum's first-derivative (solid black), corresponding to a large polarizability that is expected for a 2D Wannier exciton. Surprisingly, however, the EA line shape transitions primarily to a second-derivative (dotted black) near room temperature, as shown in **Figure 1B**. Such drastic temperature dependence in the EA line shape has never previously been observed for solid materials and represents a significant puzzle. As depicted in **Figures 1C-D**, the first-to-second derivative line shape transition is gradual with temperature $-\mu_{ge}$ increases by a factor of ~3, moving from 30 K \rightarrow 300 K. We believe this anomalous trend is caused by a disorder-induced dipole moment. In MHPs, the thermal motion of the atomic coordinates significantly perturbs the band-edge electron states, creating a so-called "dynamically-disordered" energy landscape. Asymmetry in a charged particle's energy landscape naturally shifts

its charge density, resulting in a substantial dipole moment that gives rise to the observed second



Figure 1. (A) The EA spectrum for PEA₂PbI₄ in the exciton range (red) closely matches the first derivative of the absorption (solid black) at 30 K. In contrast, (B) the EA spectrum acquired at 295 K closely matches the second derivative of the absorption (dotted black). (C) Temperaturedependent EA spectrum from 30-310 K. At each temperature, the EA spectrum is fit to a linear combination of first and second derivative absorption spectrum to obtain the exciton's transition dipole moment μ ge and polarizability α ge. (D) μge and αge as a function of temperature. The near 10-fold increase in μ_{ge} from 30 to 310 K infer the presence of a dynamic disorder induced dipole moment.

derivative line shape at room temperature. These findings demonstrate the magnitude of the MHP lattice's perturbation to band-edge electrons prior to the lattice response. The inducing of a dipole moment has been an overlooked component of the chargelattice interactions in MHPs, which are criticalthrough polaronic and Rashba effects-in protecting charge carriers from recombination.

b. Low Exciton Binding Energies and Localized Exciton–Polaron States in 2D Sn-based MHPs

Among the most popular atomic substitutions within the prototypical methylammonium lead iodide (MAPbI₃) structure is tin replacing lead (Sn \rightarrow Pb) resulting in MASnI₃. The effect of the Sn \rightarrow Pb substitution on the exciton–polaron states (binding energy, polarizability, etc.) or charge-lattice interactions are still open for debate and have large implication on the observed optoelectronic properties upon alloving or moving completely to Sn MHPs.

Findings: The Sn and Pb 2D MHPs have different EA line shapes in the exciton region—we observe a predominantly first derivative line shape for PEA₂PbI₄ and BA₂PbI₄, i.e., the applied field redshifts the exciton peak, whereas for PEA₂SnI₄ and BA₂SnI₄ the line shape is far more second-derivative-like, i.e., the applied field broadens the exciton peak. The exciton's EA response is presented in **Figure 2A** for PEA₂PbI₄ and **Figure 2B** for PEA₂SnI₄. The

derivative fits corroborate that the PEA₂SnI₄ EA spectrum is far more second-derivative-like. We determine a first derivative (second derivative) percentage of 92% (8%) for PEA₂PbI₄ in comparison to 33% (67%) for PEA₂SnI₄. The first derivative response (redshift) observed in the Pb-based MHPs is expected for a Wannier exciton while the second derivative (broadening) observed in the Sn-based MHPs is far more anomalous. The difference in line shape originates from a real difference in the exciton dipole moment (μ_{ge}) and polarizability (α_{ge}) between the Pb and Sn 2D MHPs. For tightly bound excitons, it can be shown via a Taylor expansion of the EA signal that the μ_{ge} and α_{ge} determine the derivative-like EA line shapes. In accordance with the line shape difference, we measure much larger μ_{ge} (≈ 75 vs 10 D) and much smaller α_{ge} ($\approx 7 \times 10^3$ vs 50 $\times 10^3$ Å³) for the Sn-based 2D MHPs. The excitons within the Sn-based MHP films are more affected by disorder because they reside in a shallower potential well (smaller $E_{\rm B}$) and therefore the charge density shifts more substantially in the presence of disorder. It is the sum of these two effects, low $E_{\rm B}$ and high disorder, that produces the observed seven-fold increase in $\mu_{\rm ge}$ when moving from Pb \rightarrow Sn. The reduced exciton polarizability in the tin-based 2D MHPs indicates that the excitons have smaller radii $\alpha \propto (er)^2$. This finding places excitons in Sn-based 2D MHPs on the border between Frenkel and Wannier classifications, as depicted in Figure 2C, since the length of the radius is roughly equivalent to one [SnI₆]⁻⁴ octahedral subunit, in contrast to roughly three $[PbI_6]^{-4}$ octahedral subunits in the case of lead. The electron localization was correlated to the elongation of specific tin-halide bonds and the formation of a tightly-bound small polaron. The



Figure 2. The exciton's EA response (blue) at low temperature fit to first and second derivatives of the absorption (dashed black) for A) PEA₂PbI4 and B) PEA₂SnI₄. The downward pointing arrows marks the exciton's absorption peak. C) Cartoon representation of the 1s exciton state. The excitons in tin-based 2D MHPs have smaller binding energies, larger dipole moments, smaller polarizabilities, and smaller radii than their lead counterparts.

trend was robust and observed for a wide range of ABX₃ compositions. Thus, we believe a similar effect is present here in the 2D case, namely, the dynamic disorder of the polar lattice localizes exciton states in tin-based 2D MHPs via Anderson localization resulting in smaller exciton radii. Considering that within the Fröhlich formalization the exciton-phonon coupling strength is proportional to the exciton radius, the factor of ≈ 3 decrease in the exciton radius moving from Pb to Sn also explains the significantly reduced exciton-phonon coupling in the Sn-based MHPs. Electron and hole localization typically results in the trapping of charge carriers which is detrimental to optoelectronic device performance. However, for MHPs there is substantial evidence that localization and polaron formation increases carrier lifetime by decreasing electron-hole wavefunction overlap. Indeed, by performing time resolved PL on single crystals we measure the exciton lifetime to be $\approx 3 \times 1000$ longer for PEA₂SnI₄ than PEA₂PbI₄.

c. Strong Rashba-Dresselhaus Effect in Nonchiral 2D Ruddlesden-Popper Perovskites

Chiral 2D MHPs have garnered attention from the spintronic research community because they potentially possess large Rashba-Dresselhaus effect that enables them as promising materials for spin-logic devices, such as spin transistors. Optically, the spintronic properties of chiral 2D MHPs are usually studied by two

complementary methods: circular dichroism (CD) and circularly polarized luminescence (CPL). The CD process originates from thermally equilibrated electronic ground states within the structure, while the CPL process originates from the vibrationally relaxed electronic excited states. Chirality transfer from organic chiral molecules to lead halides is theorized as the origin of the strong Rashba-Dresselhaus effect causing large circular dichroism (CD) and circularly polarized luminescence (CPL) in MHPs. Although it is widely accepted and used to explain the CD and CPL signatures in others chiral organic-inorganic system, e.g., chiral molecules-quantum dots, such as thiol capping ligands L- and D-cysteines-cadmium selenide quantum dots, and chiral moleculescolloidal perovskite nanoplatelets such as R- or S-phenylethylammonium-methylammonium lead bromide perovskite nanoplatelets, "chirality transfer" is a new and vague concept. Moreover, CD and CPL responses can be observed in several nonchiral materials. Therefore, whether "chirality transfer" is the only reason for the large CD and CPL in MHPs has not been clearly answered. In our work, nonchiral 2D MHPs exhibit extrinsic chiral behavior when interacting with light. The circularly polarized dependent absorption is caused by the combined effect of strong Rashba-Dresselhaus splitting in-plane symmetry breaking, and the effect of the exciton momentum on its fine structure.



Findings: we systematically studied the Rashba-Dresselhaus effects in nonchiral 2D**RPPs** $(BA)_2MA_{n-1}Pb_nI_{3n+1}$ with n =1. 2. 3 3D and CH₃NH₃PbI₃ (MAPbI₃) ($n = \infty$) by using CD and CPL spectroscopies. Remarkably, we observe a giant CD \approx 100 mdeg at room temperature and a CPL response of \approx 4.8% at 10 K and \approx 2.8% at 293 K from the 2D RPP n =1 thin film in the absence of an applied magnetic field. However, the measured CD and CPL signals are an order of magnitude smaller in the 2D RPP n = 2 thin film and are not detectable for the quantum well perovskite thin films n = 3, and $n = \infty$ (Figure 3). Our observation indicates that there is a nontrivial mechanism other than "chirality transfer" that causes the giant CD and CPL responses in these 2D MHPs. We hypothesize that the strong CD and CPL signatures observed are associated with the strong Rashba-Dresselhaus splitting in the 2D RPPs. Owing to strong lattice distortions at the organic/inorganic interface, the quantum well with more interfaces leads to more distortions, thus larger Rashba-Dresselhaus splitting. This hypothesis is confirmed by density functional theory (DFT) calculations where the interlayer distortions of the superlattices leads to the major Rashba-Dresselhaus splitting. To quantify to magnitude of the Rashba-Dresselhaus effect, we conduct magnetic circular measurement and estimate the Rashba-Dresselhaus effective magnetic field in 2D RPP n = 1 to be ≈ 600 mT which is significant for an organic metal halide material not having an organic chiral molecule attached to the metal halide moiety. iii) Future plans

Tailoring the symmetry and spin of 2D MHPs with strain: One of the greatest contributors of strain in MHP thin films is substrate clamping, which is caused by the mismatch in the coefficients for thermal expansion (CTE) between the HP and substrate and high annealing temperatures used in HP thin film fabrication. Most MHPs possess a large and positive CTE, so high annealing temperatures cause them to crystallize into an expanded unit cell. As the film is cooled to room temperature, the MHP is only able to contract in-plane so much as the CTE of the substrate allows, inducing a biaxial in-plane strain. Thus, maximizing the CTE mismatch and annealing temperature will maximize this strain. Combining preferential orientation and substrate clamping could allow for similar effects as that of epitaxial strain to be achieved without the need for expensive epitaxial substrates and deposition. We hypothesize that strain-induced polar phases of 2D MHPs may be accessed through combined strain and orientation engineering (CSOE). Accessing the polar phase of these materials will induce unambiguous net polarization and Rashba-Dresselhaus effects. We will further characterize the resulting strain, symmetry, and spin properties achieved via CSOE to better understand fundamental spin and symmetry relationships in MHPs.

v) Publications supported by this award

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Complex magnetism and emergent phenomena in correlated electron oxide materials

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Program Scope:

The overall goal of our DOE funded project is to employ a unique approach that combines DC and AC magnetic susceptibility measurements, neutron diffraction, synchrotron X-ray diffraction with relatively unconventional RF transverse susceptibility (TS), magnetocaloric effect (MCE), magnetoresistance (MR), anomalous Hall effect (AHE), anomalous Nernst effect (ANE) and spin Seebeck effect (SSE) to yield new insights into the ground state magnetism in a wide variety of complex oxides and emerging magnetic systems. In particular, we have demonstrated the important impacts of phase coexistence, reduced dimensionality, magnetic proximity, and anisotropy on the exotic magnetic and spin transport properties in ferrimagnetic rare-earth iron garnets (YIG, GdIG, TmIG), exchange-coupled bi-phase iron oxide nanoparticles (Fe₃O₄/a-Fe₂O₃), Heusler type spin gapless semiconductors, bi-phase iron oxide thin films (Fe₃O₄/a-Fe₂O₃), spintronic heterostructures consisting of two dimensional material (graphene (Gr), hexagonal Boron nitride (hBN), magnetic transition metal dichalcogenides (TMDs e.g., V-WS₂, V-WSe₂), and ferrimagnets (Fe₃O₄, NiFe₂O₄, CoFe₂O₄).

Recent Progress:

<u>1. Scaling of the thermally induced sign inversion of longitudinal spin Seebeck effect in a compensated ferrimagnet: Role of magnetic anisotropy</u>

Thermally induced spin currents based on the spin Seebeck effect (SSE), which was discovered by Uchida et al. (*Nature* 2008, 455, 77; *Nature Materials* 2010, 9, 894), laid the foundation for a new generation of spin-caloritronic devices. Analogous to the well-known charge Seebeck effect in which an electric potential arises as a result of an applied temperature gradient across a metallic/semiconducting material, the application of a magnetic field and a temperature gradient in a ferromagnetic material (FM) generates a pure spin current. This spin current can then be converted into a technologically useful voltage via the inverse spin Hall effect (ISHE) in a nonmagnetic metal (NM) with strong spin-orbit coupling (e.g., Pt) in an NM/FM stacked system. Unlike the conventional charge Seebeck effect, the SSE has been observed in a wide range of magnetic materials ranging from metal (e.g., FeNi) to semiconductor (e.g., GaMnAs) and insulator (e.g., Y₃Fe₅O₁₂ or YIG). Owing to its insulating and low-damping nature, YIG has been extensively exploited as the benchmark material to create a pure spin current. The majority of research in spin-caloritronics is centered around boosting the spin current across the Pt/YIG interface by either: (i) reducing the conductivity mismatch between the metallic NM layer and the insulating FM layer and/or (ii) enhancing the so-called spin mixing conductance, as seen in latest studies by us (*Materials Horizons* 2020, 7, 1413) and others (*Advanced Functional Materials* 2020, *30*, 2003192). However, the origins of the observed SSEs remain unclear, as contributions from bulk and surface magnetization to the spin-charge current conversion efficiency were not disentangled, and the important role played by magnetic anisotropy of the FM layer on the SSE was not investigated. The lack of such understanding imposes a challenging task in the design of highly energy-efficient SSE-based nanodevices. To address this, it is essential to examine whether there exists a universal behavior for the temperature evolution of SSE in a NM/FM system.



Figure 1: (a) Schematic illustration of sublattice magnetizations in GdIG, (b) XRD spectrum of GGG/GdIG(50nm), (c) Temperature dependence of saturation magnetization of GGG/GdIG(50nm)/Pt, (d) schematic illustration of the experimental configuration of our LSSE measurements, (e) magnetic field dependence of LSSE voltage for GGG/GdIG(275nm)/Pt(5nm) at different temperatures, (f) 2D H-T phase diagrams of the LSSE voltage for the GGG/GdIG(272nm)/Pt(5 nm), (g) $\frac{V_{LSSE}(T,\mu_0H_{sat})}{|V_{LSSE}^{Max}|}$ vs. θ curves for the G(S)GG/GdIG(t)/Pt heterostructures with t =272, 221, 145, 89, 50, and 31 nm, respectively. Here θ is the rescaled temperature.

In this context, we have selected a *compensated* ferrimagnetic insulator Gd₃Fe₅O₁₂ (GdIG) as a model system to probe the temperature evolution of LSSE in the vicinity of its compensation temperature (T_{comp}) while varying thickness of GdIG (Fig. 1(a)-(c)). In particular, a systematic investigation of SSE in a GGG/GdIG(t)/Pt(5nm) film series exhibiting an in-plane magnetic easy axis with T_{comp} that decreases from 270 to 220 K when decreasing GdIG film thickness from 272 to 31 nm, respectively, has been conducted. For all films investigated, we have found that the LSSE signal flips its sign below T_{comp} (Fig. 1(d)-(f)). Using a newly proposed rescaling method, we have demonstrated for the first time that the thermospin voltage for the GGG/GdIG(t)/Pt heterostructures with different thicknesses and hence, different T_{comp} fall onto a single "master curve" in the vicinity of their respective T_{comp} , which highlights the universal behavior would provide us with a unique opportunity to fabricate novel spincaloritronic devices wherein the thermo-spin voltage can be switched by appropriately tailoring the operational temperature. Our

findings also underscore a strong correlation between the LSSE signal and the magnetic anisotropy in compensated ferrimagnets and opens a new door to exploit highly efficient anisotropic and switchable spincaloritronic devices. These results have been published in *Advanced Functional Matererials* 32, 2109170 (2022) and *IEEE Transactions on Magnetics* 58, 1500505 (2022).

<u>2. Emergence of asymmetric skew-scattering dominated anomalous Nernst effect in spin gapless</u> <u>semiconductors $Co_{1+x}Fe_{1-x}CrGa$ </u>

Over the past decade, fundamental studies on the magneto-thermoelectric effects have been of great interest for the condensed matter and materials community for efficient energy harvesting and other thermal management applications. The Anomalous Nernst effect (ANE) is of particular interest for its larger heat to charge current conversion efficiency as compared to other sister phenomena like the planar Nernst effect (PNE), the spin Nernst effect (SNE), and the spin Seebeck effect (SSE). Recently, spin gapless semiconductors (SGSs) have been explored for tunable thermal spintronics applications, owing to their intriguing electronic structure. While they exhibit a finite band gap for one spin channel, the conduction and valence band edges touch for the other spin channel. Because of such unique feature of their band structure, their transport properties are extremely susceptible to external stimuli, e.g., temperature and magnetic field, as well as chemical doping. Heusler alloys-based SGS materials appear to have more advantages over the diluted magnetic semiconductors-based SGSs because of their high Curie temperature (T_C) and large spin polarization. Although, ANE has been investigated in full Heusler compounds e.g., the well-known topological Heusler alloy Co₂MnGa, Co₂TiSn, Co₂MnSi, Ni₂MnGa, etc., ANE in SGS based materials has not been explored so far. In this context, we have reported the first experimental observation of ANE in newly discovered high-T_C (~650 K) quaternary Heusler alloys-based SGSs Co_{1+x}Fe_{1-x}CrGa (Fig. 2(a)-(c)). We found that the electron-electron elastic scattering and the weak localization effect play dominant roles in electrical transport for all the samples at low temperatures and the contributions from these scatterings increase considerably with x for x < 0.4. (in Co_{1+x}Fe_{1-x}CrGa) but has a drastic increase for x = 0.5 when the system transforms from the SGS state to the completely halfmetallic state. On the other hand, the magnon-drag effect was found to dominate the longitudinal thermoelectric transport in all the samples. We found that the ANE coefficient at room temperature increases significantly from $\approx 0.018 \ \Box V$. K⁻¹ for x = 0 to $\approx 0.063 \ \Box V$. K⁻¹ for x =0.5 (Fig. 2(d)-(f)), which is higher than that for Permalloy ($Ni_{81}Fe_{19}$) and compressively strained SrRuO₃ films. Our findings underscore a strong correlation among transverse thermoelectric coefficient (S_{xv}), longitudinal Seebeck coefficient (S_{xx}) and the longitudinal resistivity (ρ_{xx}) and indicate that the observed ANE in these samples originates from the asymmetric skew-scattering of charge carriers (Fig. 2(g)-(h)). Our systematic studies also emphasize that there are several possibilities to enhance the conversion efficiency of heat into Nernst thermopower by tuning the chemical composition of SGSs. These results have been published in *Physical Review B* 106, 134416 (2022).



Figure 2: (a) Schematic illustration of ANE measurement on $\operatorname{Co}_{1+x}\operatorname{Fe}_{1-x}\operatorname{Cr}Ga$ samples. Magnetic field dependence of the Nernst voltage, $V_{xy}(H)$ hysteresis loops for (b) x = 0.0 and (c) x = 0.5 in $\operatorname{Co}_{1+x}\operatorname{Fe}_{1-x}\operatorname{Cr}Ga$ at selected temperatures for $\Delta T = +10$ K. (d) Comparison of the magnetic field dependence of the transverse Seebeck coefficient, $S_{xy}(H) = \frac{V_{xy}(H)}{\Delta T} \times \left(\frac{L_z}{L_y}\right)$ for all $\operatorname{Co}_{1+x}\operatorname{Fe}_{1-x}\operatorname{Cr}Ga$ samples at T = 300 K for $\Delta T = +10$ K. (e) Comparison of the x-dependence of the background-corrected anomalous Nernst coefficient, $S_{ANE}(\mu_0 H_{sat}) = \frac{V_{ANE}(\mu_0 H_{sat})}{\Delta T} \times \left(\frac{L_z}{L_y}\right)$ at T = 300, 200, and 150 K. (f) Normalized anomalous Nernst voltage, $S_{ANE} \times \Delta T$ as a function of $\Box T$ showing linear $\Box T$ -dependence. Temperature dependence of the anomalous Nernst coefficient $S_{ANE}(T)$ for (g) x = 0.0 and (h) x = 0.2.

3. Influence of 2D interlayer on interfacial magnetism and spin transport in magnetic insulator/semiconductor based spinterfaces

Magnetic insulators (MI) have been studied extensively recently due to their potential ability to generate coherent and incoherent magnon excitations without heat dissipation effects due to conduction electrons, which is important for high efficiency spintronic and spincaloritronic applications (*Physics Reports 885, 1–27, 2020*). Commonly studied magnetic insulators include garnets, ferrites etc., (*ACS Applied Materials & Interfaces 13, 37500, 2021*). Recently, it has been shown that insertion of an intermediate layer in these MI based spintronic heterostructures improve the so-called "spinterface", through which spin excitations propagate (*Advanced Functional Materials 30, 2003192, 2020*). Two-dimensional (2D) interlayers have been studied as a means for improving the spinterface (*ACS Applied Materials & Interfaces 13, 45097, 2021*) The local magnetic properties at the MI/2D interface determine the nature of the transport and spin transport of the overall heterostructure. Though the induced magnetic properties in the 2D layers have been studied, the corresponding effect of the 2D material on the interfacial properties of the MI remains unresolved.



Figure 3: (a) Schematic illustration of a heterostructure composed of a ferrimagnetic insulator (FMI), nickel ferrite (NFO), and Gr or hBN. (b) M(H) loops for NFO/Gr and NFO/hBN heterostructures. (c) transverse susceptibility measurements on these heterostructures. Temperature dependence of effective magnetic anisotropy fields for these heterostructures for (d) in plane and (e) out of plane configurations. (f) ZFC and FC M(T) for Pt/BPIO and Pt/WS₂/BPIO heterostructures. (g) 2D surface plot of the Hall resistivity (ρ_{xy}) difference between Pt/BPIO and Pt/WS₂/BPIO.

To address these important issues, we have fabricated heterostructures of NFO/Gr and NFO/hBN (Fig. 3(a)). Utilizing a control sample of NFO to assess NFO/Gr and NFO/hBN, the changes in both their bulk and surface properties are analyzed. Surface sensitive measurements include X-Ray diffraction, Raman spectroscopy, and thickness-dependent X-Ray photoelectron spectroscopy (XPS). XPS measurements indicate an oxygen-rich surface, suggesting a layer of adsorbed oxygen at the interface between NFO and Gr/hBN. Temperature dependent magnetization versus field measurements suggest an increase in the saturation magnetization due to the inclusion of Gr and hBN, by as much as 40% (for NFO/Gr) (Fig. 3(b)). To independently confirm these results, tunnel diode oscillator based transverse susceptibility measurements over the same temperature range were performed for both in-plane and out-of-plane configurations (Fig. 3(c)). It is observed that the inclusion of Gr reduces the effective anisotropy field by as much as 50%, whereas hBN has a more subtle effect, generally decreasing (Fig. 3(d)-(e)). To further explore these unique results, spin-polarized density functional theory calculations were performed. These results show that the surface termination at the interface between NFO and Gr/hBN has a significant impact on the nature of the interfacial magnetism. Different surface terminations are analyzed, and interestingly for the oxygen terminated interface, a large increase in the magnetic moment per unit cell is confirmed by DFT, in agreement with both XPS and magnetometry measurements. In the oxygen terminated system, interfacial charge transfer and bonding induces changes in the super-exchange interactions deeper into the unit cell. These results elucidate on previously unexplored aspects of the interfacial magnetism in FMI/2D heterostructures. Furthermore, by understanding the surface sensitive properties in these systems, novel physical phenomena may be leveraged to extend possible applications. A part of the experimental findings has been published in AIP Advances (AIP Advances 12, 035132 (2022)).

The comprehensive experimental and theoretical results are being written for publication in *ACS Applied Materials and Interfaces*.

Furthermore, the magnetic proximity effect (MPE) has recently been explored to manipulate interfacial properties of 2D van der Waals material/ferromagnet heterostructures for use in spintronics and valleytronics. However, a full understanding of the MPE and its temperature and magnetic field evolution in these systems is lacking. In this study, the MPE has been probed in Pt/WS₂/BPIO (biphase iron oxide, Fe₃O₄ and a-Fe₂O₃) heterostructures through a comprehensive investigation of their magnetic and transport properties using magnetometry, four-probe resistivity, and anomalous Hall effect (AHE) measurements. We find that the presence of monolayer WS₂ flakes reduces the magnetization of BPIO and hence the total magnetization of Pt/WS₂/BPIO at $T_V \ge 120$ K - the Verwey transition temperature of Fe₃O₄ (T_V). However, an enhanced magnetization is achieved at $T < T_V$ (Fig. 3(f)). In the latter case, a comparative analysis of the transport properties of Pt/WS₂/BPIO and Pt/BPIO from anomalous Hall effect (AHE) measurements reveals ferromagnetic coupling at the WS₂/BPIO interface (Fig. 3(g)). Our study forms the foundation for understanding MPE-mediated interfacial properties and paves a new pathway for designing 2D van der Waals material/magnet heterostructures for applications in spintronics, opto-spincaloritronics, and valleytronics. We have submitted a manuscript on these important findings to Nanomaterials.

Future plans:

Noncollinear spin textures (MnSi, MnP), spin-caloritronic heterostructures Fe₃O₄/TMD/Pt, CoFe₂O₄/TMD/Pt, NiFe₂O₄/TMD/Pt, and YIG/TMD/Pt, YIG/graphene, YIG/h-BN, gate controlled LSSE, gapless semiconductors, etc. will be explored (where TMD monolayers are V-doped WSe₂, MoS₂, and MoSe₂). Our research efforts over the next few years will be targeted towards elucidating these emergent aspects of correlated magnetic systems that could have important impacts on quantum spintronics, valleytronics, and quantum information.

Publications:

List of papers acknowledging DoE grant support during the 2-year period (2021-2022): (Students and postdocs' names are italicized, PI and co-PI names are in bold)

1. *A. Chanda*, *C.-M. Hung*, A.T. Duong, S. Cho, H. Srikanth, and M.H. Phan, Magnetism and spin-dependent transport phenomena across Verwey and Morin transitions in iron oxide/Pt bilayers, *Journal of Magnism and Magnetic Materials* 568, 170370 (2023).

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Physical Mechanisms and Electric-Bias Control of Phase Transitions in Quasi-2D Charge-Density-Wave Quantum Materials

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Self-identify keywords: charge density waves; quantum materials; two-dimensional materials; strongly-correlated phenomena; collective currents

Research Scope

This DOE project (08/15/2020 to 08/14/2023) aims at understanding the physical mechanisms and developing methods for electric-bias control of phase transitions in quasi-two-dimensional (2D) charge-density-wave (CDW) quantum materials. The investigation mostly focuses on thin films of transition metal dichalcogenides (TMD), which reveal phase transitions at room temperature (RT) and above. The specific objectives of the project include (i) the development of innovative approaches for investigation and controlling CDW phases with external stimuli; (ii) understanding the physical mechanisms behind the phase transitions in quasi-2D van der Waals materials; (iii) investigating the "hidden phases" at temperatures below the transition to commensurate CDW phase; and (iv) separating the electric field CDW switching from Joule heating induced switching. The physics of CDW phases in quasi-2D materials of the TMD group is substantially different from and much less understood than their bulk counterparts with the quasi-1D crystal structure. In addition to the above RT phase transitions, 1T-TaS₂ reveals such intriguing properties as multiple step-like resistance changes and hysteresis and surprising radiation hardness. Reports on the de-pinning and sliding of CDWs in 2D material systems are scarce. The role of the electric field and local heating in inducing the transitions in 2D CDW is not clear. The use of innovative characterization techniques such as low-frequency noise spectroscopy, Brillouin and Raman light scattering spectroscopy, nanoscale thermometry, and ultra-fast current pulses are utilized to investigate and understand these phenomena. The physics insights gained on 2D van der Waals quantum materials' properties will enable transformative changes in materials for electronics, potentially leading to new - DOE mission-relevant technologies for operation in high-radiation environments as well as in medical diagnostics. The CDW switching above RT can potentially be used in low-energy information processing. The strongly-correlated quantum 2D CDW materials are also relevant to developing quantum communication and computing technologies.

Recent Progress

In the reported period, we achieved the electrical gating of the CDW phases and currents in h-BN capped three-terminal 1T-TaS₂ heterostructure devices [1]. This is an important development because the gating of the CDW quantum phases, particularly near RT, contributes to the fundamental understanding of CDWs in 2D materials, and can enhance the functionality of the CDW devices. Electrical gating is important for answering a fundamental science question: "Can one achieve an electrical switching of CDW phase *via* the pure field effect, without any local Joule heating involved?" The main difficulty of electrical gating of the CDW phases and currents in 2D van der Waals materials was associated with the fact that different CDW phases in 2D materials still have a rather high concentration of charge carriers. Below 550 K, 1T-TaS₂ is in the metallic-like incommensurate CDW (IC-CDW) phase. The nearly commensurate phase (NC-CDW) appears below 350 K and persists approximately until 180 K. Below this temperature, 1T-TaS₂ enters the commensurate CDW (C-CDW) phase. The high concentration of charge carriers, *N*, results in a small relative change of the carrier concentration, $\Box N/N$, due to the large *N* and strong screening of the gate potential. Reducing the thickness of 1T-TaS₂ thin film for a stronger gating effect is not necessarily a viable approach because at small thicknesses (below ~ 9 nm) the CDW phases can be locked and some phase transitions disappear. We have successfully demonstrated that the application of a gate bias in the h-BN/1T-TaS₂ device structure can shift the source-drain current-voltage hysteresis associated with the transition between the nearly commensurate and incommensurate CDW quantum condensate phases.



Figure 1: Switching the CDW phases with the electrical gate. (a) Illustration of the IC-CDW and NC-CDW phases. (b) Current as a function of the source-drain voltage at two fixed gate biases, measured at T = 210 K. In this device the transition from IC-CDW to NC-CDW phase, depicted with the red and blue dots, occurs at the voltage close to V_d = 1.83 V. (c) Current as the function of the gate bias at the fixed sourcedrain voltage $V_d = 1.83$ V. The current change of $\Delta I \sim 3$ mA, induced by the gate, corresponds to the 1T-TaS₂ channel switching between IC-CDW and NC-CDW phases. (d) Current switching by the gate within the same NC-CDW phase for small, the fixed bias of $V_d = 0.13$ V.

The evolution of the hysteresis and the presence of abrupt spikes in the current while sweeping the gate voltage indicated that the effect was electrical rather than self-heating. We attributed the gating to an electric-field effect on the commensurate CDW domains in the atomic planes near the gate dielectric. The transition between the nearly commensurate and incommensurate CDW quantum phases can be induced by both the source-drain current and the electrostatic gate (see Figure 1). Since the CDW phases are persistent in 1T-TaS₂ at RT, one can envision memory applications of such devices when scaled down to the dimensions of individual commensurate domains and few-atomic plane thicknesses.

During the reported period, we also succeeded in the demonstration of the CDW quantum phases in the solution-processed 1T-TaS₂ thin films and printed CDW device structures [2]. This shows that the CDW phases are robust and can be present in materials with high defect density. The inks were prepared by liquid-phase exfoliation of CVT-grown 1T-TaS₂ crystals to produce fillers with nm-scale thickness and \Box m-scale lateral dimensions. Exfoliated 1T-TaS₂ fillers were dispersed in a mixture of isopropyl alcohol and ethylene glycol to allow fine-tuning of their thermo-physical properties for inkjet printing. The temperature-dependent electrical and current fluctuation measurements of printed thin films demonstrated that the CDW properties of 1T-TaS₂ are preserved after processing (see Figure 2). The functionality of the thin-film devices was defined by the nearly-commensurate to commensurate CDW phase transitions in the individual exfoliated 1T-TaS₂ fillers rather than by electron-hopping transport between them. The lowfrequency noise spectroscopy was used for monitoring CDW phase transitions (see Figure 2).



Figure 2: Temperature-dependent lowfrequency electronic noise characteristics of the printed devices. (a) Low-frequency noise spectra of voltage fluctuations, S_v , as a function of frequency measured at different temperatures. as a function of frequency at different temperatures. The device has been cooled down to 80 K. (b) Normalized current noise spectral density at different temperatures. (c-d) S_v and normalized current noise spectral density as a function of temperature at the constant frequency of f = 10 Hz. The device voltage was kept constant at 0.1 V.

Future Plans

We plan to complete the investigation of the process of the

CDW depinning and sliding in 2D materials as a function of temperature. In this project, we established that the depinning in 1T-TaS₂ does not result in a substantial current increase [3]. The CDW depinning in 1T-TaS₂ can be understood more like the CDW domain depinning, *i.e.*, the C-CDW domains in the NC-CDW phase become softer, looser, start rotating and changing in size at the depinning conditions [1, 3]. The latter contributes to the resistive fluctuations, observed in the derivative current-voltage characteristics and low-frequency noise, and allows for electrical gating of the CDW domains [1]. The reported depinning studies with electrical means in 1T-TaS₂ have been limited to RT [3]. In order to understand the physics of CDW transport in 2D materials it is important to study the depinning threshold field as a function of temperature. The questions we will ask are: Does the threshold field in quasi-2D 1T-TaS₂ increase with decreasing temperature? Is the dependence monotonic or there is a minimum? Is there an abrupt change in the threshold field as the material enters the commensurate CDW phase? The answers to these questions may have a profound effect on understanding the physics of CDW phase? The answers to study use a profound effect on understanding the physics of CDW phase? The answers to these questions may have a profound effect on understanding the physics of CDW phase? The answers to these questions may have a profound effect on understanding the physics of CDW phenomena in quasi-2D van der Waals materials and, at the same time, determine possible device applications of such quantum materials [4-5].

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The synthesis 2D Janus vdW crystals and novel quantum phenomena arising from mirrorsymmetry breaking Sefaattin Tongay, Arizona State University

Keywords: 2D materials, Janus, excitonics, synthesis, heterostructures

Research Scope

Named after the two-faced Roman god, Janus monolayers are the newest addition to the twodimensional (2D) quantum materials. These two-faced materials contain different atoms on each face of the unit cell, hence breaking their mirror symmetry¹ (Fig.1a-c). Coupled with the broken mirror symmetry, a two-faced atomic arrangement warrants a large charge exchange within a unit cell and induces a colossal self-driven *vertical dipole* (Fig.1b). It is well known that broken symmetry can change the physical behavior of 2D solids. To date, broken inversion symmetry has already led to the discovery of many novel quantum properties in classical 2D materials. Now the question arises, what new quantum phenomena could be realized when mirror symmetry, the last degree of freedom, is broken in these 2D Janus layers? Theoretical studies



Fig. 1 Why 2D Janus vdW crystals and vdW lattices? a. Named after Roman god Janus 2D Janus layers are new-class of 2D quantum materials **b.** exhibit broken mirror symmetry and colossal vertical dipole field. c. Depiction of 2D Janus layers with different atomic arrangement on their top and the bottom sides. Their unique properties allow [Top left] stabilization of new exciton complex, [Bottom left] new 2D polar magnets and skyrmions, [Top left] new dipole architecture enabled behavior, and [Bottom right] Anderson-Blaunt metals.

have shown that this vertical dipole together with the broken mirror symmetry leads to new skyrmionic magnetic phases and potential high T_c ferromagnetic order in 2D magnets, giant Rashba splitting, and induces exotic excitonic phases and novel polarization field driven valleytronic physics. This is just the tip-of-the-iceberg and many exciting quantum effects are waiting to be discovered in 2D Janus monolayers. Due to limitations in sample preparation and quality, experimental studies remained rather limited.

As such, the overall objective of this research program is to discover and establish the electronic, excitonic, and magnetic quantum phenomena that arise from the strong vertical dipole and broken mirror-symmetry in 2D Janus monolayers as well as their superlattices with designer polarization architectures. More specifically, this DOE project will (Obj 1) Further in-depth understanding of excitons, establish discrete quantum emitters and defects library of Janus excitonic layers, (Obj 2) and explore exotic exciton complexes (biexcitons, quadron, etc.) created



Figure 2 The synthesis starts with CVD growth of **a**. classical TMDs and **b**. each X atom is replaced by Y chalcogen atoms to form **c**. MXY 2D Janus layers **d**. the actual image of the small and **e**. large scale chamber **f-e**. Real-time PL and Raman spectroscopy datasets collected using unit shown in Fig.2(d) and **h**. extracted our strain, optical quality, defect concentration as well as **i**. chemical composition datasets.

by designer dipole architectures in Janus superlattices (Obj 3) Investigate the fundamental properties of 2D Anderson and Blount polar metals and interface 2D polar metals to unleash new quantum phenomena and create new magnetic phases and skyrmions in 2D Janus magnets owing to colossal vertical dipole present and much-enhanced DM interaction strength. Recent Progress

1. In-situ monitoring growth for 2D Janus, their heterostructures, and Moire lattices With this DOE funding, our team has discovered a completely new Janus layer growth technique named Selective Epitaxial Atomic Replacement process (SEAR) which has enabled our team to convert CVD grown monolayers to Janus counterparts with different chalcogen atomic faces. These results introduced a holistic 2D Janus synthesis technique that allows real-time monitoring of the growth process as the classical 2D layers was converted to 2D Janus layers (Fig.2a). Our prototype chamber integrates in-situ spectroscopy, offering fundamental insights into the structural evolution and growth kinetics, that allow us to evaluate and optimize the quality of Janus monolayers (Fig.2b). With the integrated in-situ optical spectroscopy, we were able to monitor and optimize the SEAR growth (Fig.2c) to achieve quantum-quality Janus materials, with extremely narrow exciton linewidths and fewer defects, by converting them from their parent classical layers.

These studies and established in-situ SEAR process resulted in 2022 Advanced Materials coverage image (Fig.3a) and the results enabled the first access to lateral and vertical heterostructures of 2D Janus layers, Janus nanoscrolls (Fig.3b-d), and their moire lattices (Fig.3f). Current excitonic and electronic studies are targeted to understand novel excitonic



Figure 3 [Preliminary results] a. 2022 *Advanced Materials* cover image depicting our in-situ Janus growth system. The system allows **b-c.** vertical and lateral Janus bilayers **d.** Janus vertical superlattices and nanoscrolls. **e.** Automated 2D transfer station allows our team to create designer Janus stacks and **f.** Moire lattices.

phenomena arising from symmetry breaking and polarization architecture engineering as well as establishing the fundamental excitonic properties of 2D Janus moire lattices, 2D Janus nanoscrolls, and 2D heterojunctions.

2. Further understanding of exciton complexes in Janus monolayers

With our established SEAR process, we were able to achieve high-quality 2D Janus layers as evidenced by low-temperature PL measurements in Fig.4. This is currently enabling us to establish valleytronics and excitonic lifetimes of excitonic grade Janus monolayers (SMoSe and SWSe). In our recent work (Fig.4a-b), established and re-assigned neutral (X_0), charged ($X^{+/-}$), and (if present) bound (X_B) emission lines at 4K (Fig4c-d), and assigned their initial g-factors (Fig.4e-f). Building on this work, we will carry out ultra-fast spectroscopy measurements at low temperatures under different magnetic fields and electrical bias probe the lifetimes of different excitonic species as well as thermalization pathways. An *immediate step* will be directly



Figure 4 [Preliminary results] Excitonic properties of 2D Janus layers a-b. Illustration and optical image of the device. Janus 1L-WSSe encapsulated in ML-hBN (blue) and electrically contacted by FLG (black) for magnetic field and electrical field dependent low temperature PL and PR measurements. c. PL from the encapsulated 1L-SWSe (red) compared to the PL from unencapsulated 1L-SWSe (blue) **d.** Reflectance contrast (RC) from the encapsulated 1LWSSe compared to the PL spectrum at the same location. **e.** RC derivative at the voltages at different voltages for identifying exciton complexes and **f.** magnetic field to determine g-factors.

measuring the vertical dipole moment of excitons in 1L-SWSe by applying an out-of-plane electric field in a capacitor-like device structure (Fig.4a-b). The predicted permanent electric dipole moment of 0.24 D for the Janus X₀, means that the resulting Stark shift of 5 meV at 1 V/nm would be resolved with our ~6 meV linewidths². More studies will target identifying the transitions that give rise to the as-yet unidentified PL peaks and extending excitonic physics more towards the positively doped regime. Similar to our earlier work, we will excite 2D Janus layers using circularly polarized light in resonance conditions to understand valley-contrasting physics (valleytronics) under a certain bias when X₀ excitons are clearly observable. 3. Establishing the defects library of 2D Janus layers

Our long-term goal is to establish the discreet emitters in 2D Janus TMDs and understand the differences their properties compared to 2D classical layers. Thus, it will be critical to establish the defects library and excitonic signatures in 1L-Janus. For this purpose, we are currently using *a one-of-a-kind capability to access excitons with unparalleled 4nm resolution* using low-energy electron energy loss spectroscopy (nano-EELS UltraSTEMTM 100 see Fig.5a) to produce EELS spectra to identify neutral and bound excitons, SOC strength, and crystallographic properties of point defects as shown for 1L-SWSe in Fig.5b. These samples prepared by polymer assisted method (Fig.5b inset) and examined under STEM to determine the crystallographic properties of intentionally or unintentionally introduced point defects, establish their bound exciton defect



Figure 5 a. STEM and nano-EELS setup enables us to b. measure excitons (labelled A and B), bound excitons (green dashed circle), spin orbit coupling (SOC) and collect atomic resolution images (top image) c. Identified point defects in 1L-SWSe layers with d. V_{S+Se} , $V_{S/Se}$, and adatoms defects (STEM line intensity image) e. Microscale defects observed in AFM scans and f. illustration of strain surface-anisotropy induced buckling.

signatures from nano-EELS (see Fig.5b) and create their statistical occurrence ensemble (Fig.5cd for 1L-SWSe). In parallel, we are carrying out these measurements on SMoSe, SWSe, and SNbSe and running low-temperature PL measurements to further correlate structural defects (STEM) to bound exciton emission characteristics from EELS and low-T PL³. In parallel to these studies, current efforts are focusing on how microscale defects (Fig.5e-f) influence the global properties of 1L-Janus layers.

2D Anderson and Blount metals and superconductors in 2D Janus layers Over 50 years ago, Anderson and Blount proposed that highly polar (ferroelectric-like) metals⁴



can be present despite the expected screening of the Coulomb interactions that often drive polarity. Within this project, our team was able to synthesize the world's first truly 2D Anderson and Blount metals SNbSe (Fig.6) and these initial experimental studies have shown that 2D SNbSe Janus layers can be experimentally realized by stripping the top layer Se of 2H-phase NbSe₂ and replacing with the S atoms using our in-situ growth process⁵. The studies have shown that 2H-NbSe₂ undergoes a phase transition and becomes 1T-SeNbS (Fig.7a-d). Here, the next immediate step will be to better understand the nature of this phase transition and exploring the physical properties of 2D Janus Anderson Blaunt metals.

Future Plans

Our future studies will concentrate on understanding the excitonic physics in 2D Janus Moire lattices, 2D higher order structures including 2D Janus nanoscrolls, establishing the defects library of 2D Janus layers to

stabilize discreet emitters in these materials. Comparison between Janus and classical 2D layers will enable us to establish the governing physics arising from symmetry breaking and colossal polarization field within Janus layers. Additional measurements will target stabilizing exotic excitonic complexes stabilized by polarization architecture engineering. Additional measurements will stabilize new 2D Janus materials, establish the material physics of 2D Anserson-Blaunt metals, and take innovative directions in skyrmionics within 2D Janus magnetic material systems.

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Electron Transfer in Heterostructures based on Two-Dimensional Materials Hui Zhao, University of Kansas, Lawrence, Kansas

Keywords: two-dimensional material, van der Waals heterostructure, charge transfer, semiconductor, photocarrier dynamics

Research Scope

Two-dimensional (2D) materials provide a new route to fabricating van der Waals multilayer heterostructures, which can potentially transform material discovery. One key issue in this approach is to understand and control interlayer electron transfer, which is the fundamental process to integrate the individual layers for harnessing emergent properties for various electronic and optoelectronic applications. Riding on the recent progress on interlayer charge transfer in heterobilayers, this program aims to provide experimental results for developing fundamental understanding on electron transfer, including charge and energy transfer, in van der Waals multilayer structures. The research goal is achieved through three thrusts. In Thrust 1, the material library to fabricate van der Waals heterostructures with novel electron transfer properties is expanded. Thrust 2 focuses on understanding electron transfer through thin barriers in van der Waals multilayers. In Thrust 3, the effect of electric field on electron transfer is studied.

Recent Progress

In Thrust 1, we studied electron transfer in 2D materials with different crystalline structures. Previous studies of electron transfer have mostly focused on the heterostructures formed by materials of similar lattice structure, such as heterobilayers formed by two hexagonal transition metal dichalcogenide (TMD) monolayers (1Ls). Time-resolved measurements, such as transient absorption, photoemission, THz, and nonlinear spectroscopy, have revealed that charge transfer

in such heterostructures with type-II band alignments occurs on a time scale shorter than 100 fs, regardless of the interlayer twist angle, lattice temperature, and dielectric environment. To expand the material library and probe the impacts of lattice structure on charge transfer, we performed steady-state spectroscopic and time-resolved pump-probe measurements on electron transfer dynamics in heterobilayers formed by a hexagonal TMD 1Ls and a nonhexagonal 1L, such as Bi₂O₂Se (tetragonal), PtSe₂ (trigonal omega), MoTe₂ (orthorhombic),



Fig. 1: (a) Band alignment of the heterostructure formed by F_8ZnPc , MoS₂, and graphene. (b) Schematics of in-plane carrier distributions in strong binding regime, where the immobile holes in F_8ZnPc prevent free motion of electrons in graphene. (c) Significant in-plane diffusion of electrons in graphene in weak binding regime with thicker MoS₂ middle layer.

and $TIGaS_2$ (monoclinic). Efficient charge transfer, with transfer times on the order of 100 fs, has been achieved in such incommensurate heterobilayers. [1]

In our next step, we studied electron transfer in organic-inorganic hybrid heterostructures, which are fabricated by depositing a thin layer of organic semiconductor on a 1L TMD. We have observed efficient charge transfer in heterostructures of F_8ZnPc/ReS_2 , PTCDA/MoS₂, PTCDI/MoS₂, and F_8ZnPc/WS_2 . [2] Here we focus on our latest experiment to demonstrate the versatility of such hybrid heterostructures on controlling photocarrier properties for optoelectronic applications. We studied hybrid trilayers that are composed of graphene, few-layer TMD, and F_8ZnPc . [3] As shown in Fig. 1(a), the electrons photoexcited in F_8ZnPc can transfer to graphene due to the laddered conduction band alignment, while the holes are confined in F_8ZnPc by the MoS₂ barrier. The interlayer exciton formation, shown in (b), prevents free inplane movement of the electrons in graphene, due to the low carrier mobility in F_8ZnPc . By increasing the MoS₂ thickness, as shown in (c), we can reduce the Coulomb attraction and free the electrons in graphene. Figure 2 shows the results of transient absorption measurements of 4 samples with 1L, 2L, 3L, and 4L MoS₂ as the middle layers, respectively. The spatiotemporally resolved differential reflectance (a-d) reveals the dynamics of the electrons in the graphene layer.



By fitting the spatial profiles at various probe delays by Gaussian functions (e-h), we deduce the

Fig. 2: (a)-(d) Spatiotemporally resolved differential reflectance measured from $F_8ZnPc/MoS_2/graphene$ heterostructure samples with different MoS_2 thickness as labeled. (e)-(h) Selected spatial profiles of differential reflectance with probe delays of 5.5 (black), 20.4 (red), 35.3 (blue), 50.2 (pink), and 65.0 ps (green). Solid curves are Gaussian fits. (i)-(l) Change of the variance of the spatial distributions as a function of probe delay. Lines are linear fits that results in the electron diffusion coefficients as labeled in each panel.

variance of the spatial profiles as a function of probe delay (i-l) for each sample. Linear fits (red lines) show that the diffusion coefficient of the electrons in graphene increases with the thickness of the middle layer (that is, their distance from the holes). With 4L MoS₂, the diffusion coefficient of 36 cm²/s is similar to carrier diffusion coefficient in CVD graphene, indicating quasi-free movement of the electrons.

In Thrust 2, we studied resonant hole tunneling between two $MoSe_2$ 1Ls separated by a 1L-WS₂ barrier. We obtained a tunneling time constant of 20 ps, which is consistent with theory. We also studied electron tunneling from $MoTe_2$ to MoS_2 through an energy barrier of 1L WSe₂ was also studied for comparison.

Thrust 3 focused on control of charge transfer in van der Waals heterostructures by electric field.

In our first approach, we used an optically induced electric field by using a three-pulse control-pump-probe technique, where a control pulse produces an electric field due to charge transfer it initiates. We found, by using MoS₂/MoSe₂ heterostructures as an example, that the control pulse can effectively tune both the charge transfer time and the lifetime of the interlayer excitons. [4] Here we focus on the second approach achieved by using Janus TMDs. A Janus TMD 1L is composed of a transition metal atomic layer sandwiched by two different chalcogen atomic layers, such as S-Mo-Se or S-W-Se. The asymmetric layer structure results in a builtin electric field pointing from the Se to the S layers. Our goal is to utilize this field to regulate charge transfer. By combining Janus (WSSe) and regular TMD 1Ls (WS₂ or WSe₂), we fabricated three heterostructure samples with different atomiclayer sequences: S-W-Se/S-W-S



Fig. 3: Top row: Crystal model of the three heterostructure (HT) samples studied. The magenta arrow indicates the built-in electric field (Janus field) in Janus WSSe. Bottom row: The band alignment of the three samples (solid black lines). The dotted lines represent the conduction band minima and valence band maxima of WS_2 and WSe_2 , as labeled. The magenta lines illustrate the change of the carrier potential energy across the Janus layer due to the Janus field. The blue arrow of the present electrons and holes indicates the flow direction of interlayer charge injection enabled by the type-II band offset. Our transient absorption measurements show that the Janus field only governs the charge flow within the Janus layer but cannot restrict interlayer charge injection due to insufficient strength. The green check mark indicates that the charge transfer is allowed and not blocked by the Janus field. The red cross mark indicates that the Janus field will block the charge injection flow.

(HT1), Se-W-S/S-W-S (HT2), and Se-W-Se/Se-W-S (HT3), as shown in Fig. 3 (top). Transient absorption measurements of the three samples consistently reveal the following conclusions: [5] First, the band-offset-allowed charge transfer from Janus to regular layers is directional: The Janus field allows the transfer with the charge current direction along the field while blocks that with opposite current direction. Second, the charge transfer from regular to Janus layers is unaffected by the Janus field and are similar to regular TMD heterostructures. These conclusions are schematically summarized by the green check and red cross signs in Fig. 3 (bottom). The ultrafast and directional charge transfer between Janus and regular TMD layers introduces the Janus structures as an important building block for 2D heterostructures with efficient and directional charge transfer properties.

Future Plans

In the final 5 months of this project, we will study factors affecting carrier tunneling in van der Waals multilayer heterostructures, with emphasis on the effect of the electric field. We will further study on-demand charge transfer pathways in sophisticated van der Waals heterostructures, with the goals of utilizing the built-in electric field in Janus 1Ls to control interlayer excitons and achieve free charge generation in graphene and other 2D materials. Beyond that, we would like to continue this research direction. The studies on the interlayer vertical transfer of the electrons provided a solid foundation to study and control their in-plane transport properties. Since we have demonstrated the feasibility of constructing multilayer heterostructures with sophisticated band alignment and novel electron transfer properties. A natural next step is to utilize this capability of fine tuning the photocarrier properties in such heterostructures. We will focus on a specific goal of controlling in-plane carrier transport properties in targeted 2D semiconductors by combining them with other materials. The expanded material library allows us to combine 2D materials with different and complimentary transport properties to harness their emergent in-plane transport properties.

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Hexcitons and Oxcitons in WSe₂ monolayers Hanan Dery and Dinh Van Tuan University of Rochester

Keywords: excitons, trions, transition-metal dichalcogenides, many-body interactions **Research Scope**

Hydrogen-like bound states of photoexcited electron-hole pairs in semiconductors -- that is, excitons -- have been a focus of considerable study for more than half a century. In undoped direct-gap semiconductors, neutral excitons comprise the photogenerated electron and hole in the conduction and valence bands (CB and VB), respectively, and typically manifest as discrete optical resonances below the free-particle band-gap energy. More interesting states arise when electron-hole (e-h) pairs are photoexcited into doped semiconductors containing a Fermi-sea of mobile carriers.

In the archetypal monolayer semiconductor WSe₂, the distinct ordering of spin-polarized valleys (low-energy pockets) in the CB allows for studies of not only simple neutral excitons and charged excitons (i.e., trions), but also more complex many-body states that are predicted at higher electron densities [1]. We discuss magneto-optical measurements of electron-rich WSe₂ monolayers, as shown in Figure 1, and interpret the spectral lines that emerge at high electron doping as optical transitions of 6-body exciton states ("hexcitons", see Figure 2) and 8-body exciton states ("oxcitons", see Figure 3) [2]. These many-body states emerge when a photoexcited electron-hole pair interacts simultaneously with multiple Fermi seas, each having distinguishable spin and valley quantum numbers.



Figure 1: (a) Helicity resolved optical transitions in ML-WSe₂. Light excitation with right-handed (left-handed) helicity corresponds to optical transitions at the K (-K) valley. Resident electrons occupy the bottommost valleys, whereas photoexcited electrons belong in the top valleys. (b) Optical reflectance spectra at 4K as a function of gate voltage and photon energy. (c) and (d) Helicity resolved magneto-optical reflectance spectra when the out-of-plane magnetic field is 20T, shown in the spectral and voltage windows that are marked by the dotted box in (b).



Figure 2: (a) Calculated inter-particle distances in the hexciton as a function of the Fermi energy ($E_F \sim$ 5 meV amounts to $n = 10^{12} \text{ cm}^{-2}$). The Hexciton corresponds to the resonance X-⁴ in Figure 1. Results are shown for average distances between the CB electron and VB hole (r_{he}), between the two CB electrons of the core trion (r_{ee}), between the VB hole and the outer top-valley electron (r_{ht}) or CB holes (r_{he}), and between the CB holes (r_{ee}). Inset: Calculated binding energy of the satellite electron to the hexciton. (b) and (c) Schemes of the hexciton in *k*-space and real-space, respectively. The trion at the core of the hexciton binds to two CB holes and a satellite electron.



Figure 3: (a) Magneto-optical absorption spectra as a function of magnetic field and photon energy in a second device. The voltage level is at the threshold of filling the top CB valley of K. The shaded boxes show the regimes at which the top valley at K is filled. (b) Spin- and valley-resolved LL diagrams in the CBs within a single-electron picture. The solid black line denotes the chemical potential of the Fermi sea. (c) The oxciton state, formed when the trion at its core binds to three Fermi holes in the CB and two satellite electrons. The hexciton-to-oxciton transition takes place when the top CB valley at K has one filled Landau level, marked by the shaded regions in (a).

I will discuss composite excitonic states in cases that the exciton binding energy of the semiconductor exceeds the Fermi energy. As shown in Figures 2 and 3, the composite state is made of one or more electron-hole pairs, where the hole of at least one pair is from the VB. Other electron-hole pairs are made of CB holes (missing electron in the Fermi-sea) and electrons with distinct spin-valley configuration. The possible number of pairs in a composite excitonic state is determined by the spin-valley space at the edge of the CB (or VB by reversing the discussion to *p*-type doping).

Recent Progress

Most recently, we have studied the energy band structure of excitons in periodic potentials produced by the short-range interaction between the exciton and electrons of Wigner lattices [3]. Treating the exciton as a point-like dipole that interacts with the periodic potential, we have solved a simple one-body problem that provides valuable information on excitons in many-body problem settings. Figure 4 shows results of this calculation for the case of trigonal Wigner lattice. Using this approach, we have emulated the response of optically active exciton and trion states to a change in electron density (through the change in the lattice constant), as shown in Figure 5. We gain important insights on the relation between the electron order in a Wigner crystal and the energy blueshift of the bright exciton. We have discussed the consequences of this relation in the context of optical absorption experiments in monolayer semiconductors.



Figure 4: (a) Illustration of the short-range potential profile experienced by an exciton in a triangular electron lattice. The unit cell and basis vectors $a_{1,2}$ are highlighted, where the distance between two neighboring sites is $r_s = |a_{1,2}|$. An electron-hole pair propagating in this lattice can form bound or unbound states with the lattice (X⁻ or X⁰), corresponding to trion or exciton energy bands, respectively. (b) The first (white) and second (green) Brillouin zones of the triangular lattice, along with the reciprocal-lattice basis vectors $G_{1,2} = 2\pi(1/\sqrt{3}, \pm 1)/r_s$ and high-symmetry points Γ , M, and K. (c) and (d) Exciton band structures along axes between high-symmetry points, shown for lattice constants $r_s = 15.2$ and 6.8 nm, or equivalently, electron densities $n = 5 \times 10^{11}$ and $2.5 \times 10^{12} \text{ cm}^{-2}$, respectively. The energy bands in (d) are labeled with their Γ -point irreducible representations [3]. (e) Square amplitude colormaps of the Γ -point wave functions in the unit cell, where (f) shows these results along the axis marked by the dashed white line in (e).

Future Plans

In the near future, we plan on studying the energy shifts of trions and excitons in cases of electrostatically-doped monolayer semiconductors whose electrons (or holes) are randomly placed. The goal is to see how the energies of excitons and trions shift when the electron-order is increased, starting from complete random positioning of the electrons, continuing with quasi-random arrangements, and ending with trigonal Wigner lattice. One can then use temperature or far-infrared spectroscopy as experimental knobs to look for the elusive Wigner crystal [3]. Ramifications of this study can be used to emulate various lattices in which excitons propagate in the same manner that electrons propagate in atomic crystals or light in photonic crystals. Beyond Wigner crystals, such lattices can emerge in Moire heterostructures or atom-decorated monolayer semiconductors. In the latter case, advanced fabrication techniques can engineer artificial lattices with various symmetries through controlled placement of atoms or molecules in or adjacent to 2D semiconductors. Such fabricated lattices can be used as far-infrared light detectors, as a means to enhance the functionality of polariton cavities, or as a platform to further investigate excitonic band structures.



Figure 5: (a) Γ -point energies of the trion (X–), bright exciton (X0), and excited exciton state with E1 symmetry as a function of electron density n (bottom x-axis) or Fermi energy EF = h2n/4 π me (top x-axis, where me = 0.4m0). The dashed line denotes the energy gap (E $\Gamma\Delta$) of the nearly-free exciton model. (b) Energy band structure of the nearly-free exciton model when n = 2.5 × 1012 cm–2. (c) Γ -point energies of the trion and exciton in three lattice structures: triangular (green), square (orange), and honeycomb (magenta). The dashed lines are the respective energy gaps of the nearly-free exciton model.

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Understanding and designing phosphide solar absorbers with high carrier lifetime G. Hautier, J. Liu (Dartmouth), K. Kovnir (Iowa State), D. Fenning (UCSan Diego), Sage Bauers, A. Zakutayev (NREL), I. Dabo (Penn State)

Self-identify keywords to describe your project: photovoltaics, photocatalysis, defects, first principles, phosphides

Research Scope

Solar energy will be an important component of a carbon-free energy system. Solar energy can be harnessed in many ways for instance using photovoltaic devices (i.e., transforming light into electricity) or photoelectrochemical devices (i.e., transforming light into fuel, for instance hydrogen gas). Both approaches rely on materials capable of absorbing light and forming electron-hole pairs that are either collected by electrical contacts or used to split water into hydrogen and oxygen for instance. These solar absorber materials need to have specific properties to be efficient: a right band gap to absorb the solar spectra, good transport properties (i.e., carrier mobility) to easily move the electrons and holes and, most importantly, low carrier recombination rates. Recombination of electrons and holes is obviously detrimental as it leads to losses and has been identified as the main factor affecting the quality of a solar absorber. Recombination rates are controlled by the Shockley-Read-Hall (SRH) mechanism which facilitates the recombination of carriers through defects. The recently emerging hybrid organicinorganic perovskite solar absorbers have shown very low SRH rates which has been related to the lack of problematic defects, leading to the concept of "defect-tolerance". These perovskite materials have however shown stability issues in photovoltaic devices and are water-soluble, which makes them inadequate for photoelectrochemistry. There is a major need for inorganicbased, long-lasting and stable solar absorbers that would offer the type of defect-tolerance and long carrier lifetime seen in hybrid organic-inorganic perovskites.

The goal of this project is to discover new phosphide materials with exceptional carrier lifetime using a combination of first principles computations and experiments. Phosphides offer a quite unexplored yet very promising space for solar absorbers as the band gap of many phosphides range between 1 and 2 eV, perfectly aligned with the solar spectrum. First principles computations within the Density Functional Theory (DFT) framework can be used to assess the SRH recombination rate for each defect (e.g., vacancies, anti-sites, ...) in a material. We will harness this predictive power to computationally screen in a high-throughput manner for phosphides with favorable defects that will favor long lifetime. The computationally identified materials will be synthesized and characterized extensively. A tight integration between theory and experiment is central to the project and will advance our understanding of the fundamental factors leading to defect tolerance. The experimental work will involve the synthesis of phosphide powder and thin films and their lifetime measurement through photoluminescence experiments. Photoelectrochemistry will also be used to not only test the potential for generating solar fuels from light but also to provide a powerful way of characterizing the materials without having to build devices. The question of water stability of these phosphides will be also addressed.

Recent Progress

The project just started and the team is currently working (powder synthesis and photoluminescence) on a ternary phosphide identified through high-throughput computations. The computational efforts have also focused on known binary phosphides such as Zn_3P_2 as benchmark to our approach and the high-throughput infrastructure to screen for other phosphides is being set in place.

Future Plans
Our identified ternary phosphide will be further studied as thin films but also in water through photoelectrochemistry. We will start the larger scale high-throughput computational screening.

Data-Driven and Computationally Assisted Design of Near-Infrared Emissive Metal-Organic Complexes with Earth-Abundant Cu(I) and In(III) Metal Centers. Svetlana Kilina, North Dakota State University (Principal Investigator); Dmitri Kilin, North Dakota State University (Co-Principal Investigator); Bakhtiyor Rasulev, North Dakota State University (Co-Principal Investigator); Wenfang Sun, University of Alabama (Co-Principal Investigator)

Keywords: photoexcited nonadiabatic dynamics, charge transfer optical transitions, photoluminescence quantum yield, infrared emitters, transition metal complexes.

Research Scope

Our research is focused on identifying the criteria for rational design of abundant metal

complexes (AMCs) by modifying the ligand types, the substituents on the ligands, and the metal centers to increase (i) the absorption energy shift to near infrared (NIR) regions, (ii) the emission quantum yields, and (iii) the radiative decay rates, while lowering the nonradiative decay rates. For this, we develop the methodology that combines experimental data and quantum chemistry calculations with machine learning and chem-informatics to elucidate structural factors responsible for NIR emission and guide the design of novel NIR-active complexes with earthabundant Cu and In metals.



Recent Progress

We have performed calculations based on density functional

(DFT) and linear response time dependent DFT (TDDFT) of hypothetical Cu(I) complexes coordinated by dipyrrin and diimine analogues. Totally, up to 340 Cu(I) complexes have been calculated with various modifications of their ligands holding different π -conjugated length and substituting groups varying in electron-withdrawing (EW) and donating (ED) abilities. These calculations were instrumental in the predictions of the following structure-property relationships: (1) The considered Cu(I) complexes with diamine-based ligands exhibit the most redshifted absorption at the range of 500-570 nm, with the lowest singlet transition holding a strong metal-to ligand (MLCT) charge transfer character and being nearly optically inactive. The triplet emission of these complexes is predicted at the range of 700-1000 nm, but likely not very efficient due to mixing with optically inactive singlet states. Increasing the conjugation length and using strong ED groups (-NH₂) at substituents result in the largest redshift of the first absorption band and the triplet emission. (2) All considered Cu(I) dipyrrin-based complexes demonstrate a stronger redshift in absorption energies at the range of 730-1500 nm. However, the complexes with the first absorption peak above 780 nm have optically inactive lowest-energy transitions with strong MLCT and intra-ligand charge transfer (ILCT) character, suggesting not a high fluorescence of these complexes. Our calculations evidence that π -extended dipyrrins coordinated with Cu(I) result in redshifted absorption at 700-750 nm with optically active lowest transitions having mixed π - π * and MLCT/ILCT character. Thus, these complexes are promising as intensive emitters at the NIR range. (3) Trained on our DFT/TDDFT data for Cu(I) complexes, an interpretative machine learning-based QSAR model has been developed using the approach previously developed by our team for Ir(III) complexes.¹ The created OSAR model can reliably predict the energy of the lowest absorption band of the Cu(I) complexes with thousands variations in the ligands based on dipyrrin and diimine analogues.

We also have modified and adapted the DFT-based non-adiabatic dynamics coupled to the Redfield theory (NAMD/Redfield) for simulating photoexcited dynamics and photoluminescence quantum yields (PLQY) in molecular complexes.^{2,3} In particular, these calculations were performed for In(III) and Cu(I) metal centers coordinated with dipyrrin-based (M-a-DIPY) ligands. For both metal centers, two modification schemes were considered for M-a-DIPY ligands³: (i) substituting aryl with EW and ED groups and (ii) saturated or unsaturated annulation of the dipyrrin ligand increasing its structural rigidity.

We found the following features in photoexcited dynamics of studied complexes: (1) For In(III) complexes with neutral or ED groups, the lowest-energy optically active states exhibit primarily π - π * character with a small admixture of ILCT character, while EW groups substantially increase the ILCT character of optical transitions.^{3,4} (2) Also the EW groups in In(III) complexes redshift luminescence to 820 nm, compared to 700-730 nm singlet emission of complexes with ED groups.³ (3) In(III) complexes with primarily π - π * character of their lowest transitions show significantly enhanced PLQY (up to 80%) for unsaturated annulation, compared to the nonannulated and saturated annulation complexes (Fig.1). However, for complexes with primarily ILCT character (with EW groups), the PLQY decreases down to 10% for both annulation schemes due to the interplay between decreased radiative and increased non-radiative recombination rates.³ (4) For the In(III) complex without annulation and with neutral substituents, the calculated PLQY of 62% is comparable to the experimental value⁵ of 67%, which justifies the used methodology. (5) The Cu(I) complexes with M-a-DIPY ligands show the same trends in their photoexcited dynamics with respect to the ligand modifications as related In(III)-M-a-DIPY complexes. However, the highest PLQY of 3% at 1300 nm wavelength is observed for Cu(I)- M-a-DIPY complexes elucidating that they are not efficient emitters. Overall, our calculations show that improvement of PLQY goes beyond a simple concept of structural rigidity (annulation) that is expected to suppress torsional vibrational modes governing non-radiative rates. In contrast, the charge transfer character of excitonic states is a key parameter for engineering the photo-physical properties of dipyrrin-based complexes through chemical functionalization schemes for enhanced performance in NIR optoelectronic applications.

Future Plans

- (1) Our experimental team is synthesizing Cu(I) complexes coordinated by dipyrrin and diimine derivatives choosing the ligand modification according to our data-driven/computational predictions on their best photophysical behavior. Then the complexes will be characterized by means of optical spectroscopy to verify accuracy of our computational predictions.
- (2) We will further modify our NAMD/Redfield method by incorporating a spin-polarized approach and spin-orbit couplings (SOC) to generate radiative/nonradiative rates between the states with different spin multiplicities, lifetimes of the triplet and singlet excited states, and related phosphorescence quantum yields. This method will be applied to Cu(I) coordinated with π -extended dipyrrins and dimines showing the optically bright lowest-energy singlet transitions at 700-750 nm, as has been predicted by our TDDDFT calculations. Application of spin-polarized NAMD/Redfield techniques to these complexes will get fundamental insights on the dissipation pathways, including singlet-to-triplet intersystem crossing.
- (3) We will generate a virtual library of thousands of hypothetical NIR-emitting Cu(I) complexes using our derived QSAR model for candidate screening and rational design using ML/cheminformatics methods. These efforts on calculations will be helpful in providing navigations of synthetic effort in designing Cu(I) complexes with improved NIR emission. References

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Optically controlled quantum phase transitions at van der Waals interfaces Lian Li, West Virginia University

Keywords: van der Waals heterostructures, quantum phase transition, optical control, machine

learning

Research Scope

This project aims to control emerging quantum phases in van der Waals (VdW) materials through an innovative design of epitaxial heterostructures, the implementation of novel optical excitations, and atomic-scale lattice tracing using cutting-edge synchrotron tools. The project will be carried out in close collaboration with two scientists at the Advanced Photon Source (APS) of Argonne National Laboratory. The joint efforts of material scientists, data scientists, and national laboratory partners will allow us to 1) elucidate light-induced quantum phase transitions at FeSe/oxide interfaces and 2) develop interface-enhanced optical control of quantum phases in other transition metal dichalcogenide (TMD)/oxide heterostructures.

Recent Progress

• Mechanism for the UV light enhanced superconductivity in single-layer FeSe/SrTiO₃ We reported earlier that the superconducting transition temperature (T_C) in single-layer FeSe epitaxially grown on SrTiO₃(001) (STO) can be manipulated optically by exposure to a cw UV light with photon energy above the optical bandgap of STO [1]. In addition to raising the T_C by 25%, switching between the superconducting and normal state can be persistently driven using a tailored sequence of UV light pulses and voltage pulses applied to the back of the STO substrate. We have attributed this effect to the strong photocarrier-phonon coupling in the STO and the resultant metastable lattice distortion at the FeSe/STO interface.

To quantitively measure the structural distortions at the interface, we have carried out in-situ CTR/COBRA (crystal truncation rod/coherent Bragg rod analysis) measurements at APS. Working closely with the beamline scientists, we built a multi-wavelength LED illumination setup inside the cryostat at the X-ray beamline. This allowed us to optically excite the samples during CTR X-ray surface diffraction measurements of UV light-enhanced superconductivity in single-layer FeSe/STO from room temperature to 10-15 K.

Pronounced and persistent CTR signal changes are observed in all samples after the in-situ excitation by UV light pulses at the base temperature of 10K, confirming our earlier theory of a light-induced metastable interfacial structural distortion [1]. As shown in Figs. 1a&b, the UV illumination triggers structural perturbations mainly at the interface between the 2^{nd} TiO₂ layer and the bottom Se layer of the Se-Fe-Se trilayer. The lattice distortion at the top of the double-TiO₂ layer is subtle, showing a downward displacement of the Ti ions. The most substantial disturbance is the bottom Se layer, resulting in a significant lattice displacement upward by 0.41 Å along the vertical direction (Fig. 1b), a 28% reduction from the nominal anion height (h_a) of 1.46 Å between the Fe and Se for bulk FeSe [2]. As a result, a metastable structure is formed after the UV light exposure, where the h_a changes from 1.46 Å for the up Fe-Se layer to 1.05 Å for the bottom Fe-Se layer (Fig. 1c). Note that the anion height recovers the nominal value for temperatures > 80 K. The formation of this metastable structure directly explains our discovery of UV light-enhanced T_C in single-layer FeSe/STO [1]. Such enhancement is consistent with the

trend in iron-based superconductors, where the T_C is strongly correlated with the anion height [3]. A manuscript is under preparation to report these findings.

• Atomic-scale electronic inhomogeneity of single-layer iron chalcogenides alloys revealed by machine learning of STM/S data

Chemical pressure can effectively tune the properties of quantum materials, particularly at the single-layer limit. For example, for a single-layer FeSe/STO, we have recently shown that the h_a , thus T_c , can be controlled by chemical pressure applied with the isovalent substitution of S or Te for Se [3]. Here, the local chemical composition is a critical parameter that can be obtained by visually inspecting atomic resolution STM images. However, chemical disorders and electronic



Figure 1 (a) COBRA electron-density map showing vertical atomic rumpling in the Fe and Se layers. (b) The atomic positions determined from the COBRA electron-density maps before and after the UV exposure at the temperature specified. (c) Ball-and-stick model of the UV light-induced metastable single-layer FeSe/STO.

inhomogeneities make such determinations challenging beyond the diluted limit. For example, shown in Fig. 2(a) is an STM image of a single-layer FeSeTe film, where several types of vacancy defects (circled) are evident. In addition, darker and brighter regions are also prevalent on the surface due to interfacial inhomogeneity (e.g., oxygen vacancies in the STO substrate). These make determining alloy composition challenging, if not impossible, through the conventional visualization method.

To this end, we apply machine learning to discern Te and Se atoms on the surface. First, defect locations are identified by analyzing the spatial-dependent dI/dV tunneling spectra using the K-means method, which produces the map shown in the inset of Fig. 2(b), where the blue regions

are identified as defects with Vshaped spectra, and red areas are the FeSe film exhibiting U-shaped spectra. Excluding the detect regions (Fig. 2(c)), the remaining dI/dV spectra are further analyzed using the singular value decomposition, where the Te dopants are associated with the feature at -280 meV, while the Se atoms are associated with the peak at -230 meV. For the image shown in Fig. 2(a), the analysis yields a defect population of $\sim 16\%$ and Se and Te composition of 46% and 38%, respectively. This method has been applied to analyze the alloy composition of various Te- and Ssubstituted FeSe films. In addition to providing an efficient and reliable determination of local elemental composition, the analysis further reveals correlations of nanoscale chemical inhomogeneity to superconductivity in single-layer iron chalcogenide films. Two manuscripts have been submitted to report these findings.

• A new dry-patterning fabrication



Figure 2 (a) STM image of a single-layer FeSeTe/STO. (b) dI/dV spectra taken at defect (V-shaped, blue) and defect-free locations (U-shaped, red). The inset: a dI/dV map showing the defect spatial distribution (blue regions). (c) dI/dV map at -260 meV taken in the same area as in (a). (d) Tunneling spectra of the Se-rich vs Terich regions. In the Se-rich region, the peak at -230 meV, and in the Te-rich region, the peak shifted to ~-280 meV.

method for transport studies of quantum materials

Accurate, repeatable patterning of quantum materials is desirable for magneto transport measurements. However, the most common method, photolithography, can degrade or even damage chemically sensitive quantum materials during fabrication. In this part of the research, we developed a new dry-patterning method for device fabrication with lateral etching resolution down to ~30 μ m. In this approach, a tabletop computer numerical control (CNC) router machine is utilized to gently etch patterns into thin films, leaving behind the desired devices on the substrate. This approach is demonstrated in Fig. 3, where Hall bars (HBs) were made with conductive channel widths of 30-120 μ m in a superconducting single-layer FeSe grown on STO substrate and capped with 20 layers thick FeTe. Transport measurements show the same zero resistance Tc of 9.5 K from Van der Pauw (vdP) geometry and Hall bar structures. However, the onset temperature T* is the largest at 23 K for the vdP geometry and decreases with the width of the Hall bar to 12 K for the 60 \Box m devices. These results suggest that interfacial inhomogeneity plays a critical role in the superconducting properties of single-layer FeSe/STO films. Our

method provides a new time-saving, cost-effective, and chemical-free strategy for fabricating devices from quantum materials. A manuscript is in preparation to report these findings. **Future Plans**



Figure 3 (a) Hall bars are designed, and a CNC router machine controls a drill bit to (b) etch the outlined path on the surface of the sample. Resulting shapes (c, inset) can be reliably recreated for repeatable measurements.

1. Transport measurements on Fe(SeTeS)/STO heterostructures with different capping layers, comparing their ground state electrical properties and STM/ARPES band structure data to shed light on the unconventional superconducting pairing mechanism.

2. Investigating light-controlled quantum phases in other TMDs/STO vdW heterostructures.

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4. J. Benigno, Q. Zou, C. Cen, and L. Li, *Development of a new dry-patterning fabrication method for transport studies of quantum materials* (in preparation).

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Quantum Transduction with Abundant Elements for Cleaner Energy PI: Michael E. Flatté (U. Iowa); Co-PIs Denis R. Candido (U. Iowa), Durga Paudyal (Ames National Laboratory)

Keywords: quantum transduction, noise, critical elements

Research Scope

Quantum remains a major goal for next-generation quantum technologies. Here we propose to theoretically investigate the fundamental properties of erbium and ytterbium doped cerium orthovanadate and cerium orthophosphate and assess their potential impact on quantum transduction fidelity. This effort is a collaboration between Flatté (PI) and Candido (Co-PI) of the University of Iowa and Paudyal (national laboratory collaborator) of Ames Laboratory. The effort proposed here will build on the theoretical advances at Ames Laboratory, e.g., "localized density functional theory" [1] to obtain high-quality calculations of the 4f electronic states of rare-earth (RE) materials and contribute to the broader dissemination and improvement of these techniques. The team will perform ab initio calculations of the electronic structure of erbiumdoped cerium orthovanadate, including the properties of magnetic excitations, the optical transitions, and the formation of various impurities and defects. We will use electronic structure and atomistic models, with improved descriptions of on-site electron, spin-orbit, crystal field, quadrupolar, hyperfine, and Zeeman interactions, to predict host-RE ion configurations in CeVO4 and CePO4 to achieve desired properties (isolated or entangled spins, energy levels, long quantum lifetimes). Then the team will analyze these material parameters for their relevance to quantum transduction using this material, including the effects of charge and spin fluctuation noise in the host. Further explorations of other rare-earth dopants for quantum information science will be explored as time permits in subsequent years, along with ytterbium doping of the host material for long coherence time "clock transitions" and quantum memories. A major challenge for RE-doped materials for quantum transduction is the linewidth of the optical transitions and the dependence of that linewidth on the concentration of these RE ions and the presence of surrounding defects. At their most dilute conditions the RE linewidth will be determined by the surrounding environment, including vacancies, other unintentional dopants, any surfaces, any unrelaxed strain or crystal damage. As the concentration increases the states of the ion will overlap with neighbors (mediated by d and p states with which the f electrons hybridize) and the linewidth will reach a limit determined by the concentration. So a major challenge is to determine how dense the RE ions can be doped before the linewidth increases beyond that determined by the purity and perfection of the host crystal. As the quality of the host improves the maximum concentration before linewidth broadening will decrease, so evaluating these features will not only determine the current practical limits of RE-ion coupling but will inform an evaluation of the maximum transduction efficiency that can be achieved for dense doping of RE ions in a nonmagnetic host.

Ab-initio approaches face considerable challenges when used to evaluate the coupling between dilute ions due to the length scales involved. Typical practical unit cells only accommodate doping levels that are in excess of 1%, which may be too high for the narrow lines of RE ions. As a result a hybrid multiscale approach is desirable in which the single-ion properties are accurately calculated and then used to construct effective propagators for electronic interaction between spatially-separated ions. The ingredients of such a theory (e.g. Refs. 2 and 3 for transition-metal dopants in semiconductors) include a high-quality electronic structure

description of the host states, with elements obtained from experimental measurements of the material properties (or *ab-initio* calculations if the experimental quantities are not known), along with a good description of the single-ion hybridization with the host electronic structure, and then an efficient method of calculating the properties of pairs, random distributions, or other collections of RE dopants.

An important goal of this project is to include, develop and incorporate simulations of other sources of noise, including hyperfine interactions from nuclear spin, phonons, defects, impurities and contamination. Accordingly, to make progress on the understanding of the noise in crystal containing rare-earth ions, we will adapt and advance the previously developed noise theory and calculations for spin centers. This will require translating the noise theory for single spin centers to dopants, in addition to also expand the theory to an ensemble of dopants, which contribute to an average noise. We hypothesize that the presence of a surface is less important for rare-earthdoped materials than it is for scanning sensor applications, but that the surface will remain important to a measurable degree. As these materials are expected to be incorporated into integrated photonic devices the evanescent optical waves are likely to extend a couple hundred nanometers below the surface. Flatte and Candido previously found that fluctuations in regions a micron away from a spin center can be significant [4], and thus we hypothesize surface defects may contribute to noise that is significant for quantum transduction and memories. This project will establish a fundamental understanding of rare-earth hosts with abundant elements (with cerium replacing rare elements) for quantum information science (QIS), and identify whether the current advances in RE-solids for QIS can be translated to specific hosts consisting entirely of abundant elements. This will provide clear targets for clean-energy rareearth quantum information materials. In addition to the advances for cerium-based hosts this project will advance the theoretical understanding of RE-solids in general and assist in translating novel RE materials physics to real-world QIS applications for quantum transduction and memories.

Recent Progress

<u>Ab initio electronic structure of host cerium</u> <u>orthovanadates and orthophosphates.</u> The *ab initio* study of defect formation and 4f states in RE materials has relied broadly on electronic structure techniques that assume 4f electrons in the core level. Although they describe chemical bonding relatively accurately, they have bypassed the proper treatment of the 4f quantum states that are



Fig. 1: Crystal structure (a) and density of states (b) of $CePO_4$.

crucial for magneto-quantum technologies, especially for the formation of coherent magnon states. Density functional theory (DFT) incorrectly positions 4f states at the Fermi level, especially those states which should clearly be the unoccupied states, giving an erroneous notion of 4f electrons taking part in the chemical bonding. Our calculations in rare earth orthovanadates and orthophosphates now show that the incorporation of electron correlation parameter in DFT does correct the occupied and unoccupied 4f states (see Fig. 1 for CePO₄). Further, the hybrid functional, which incorporates a portion of exact exchange from Hartree–Fock theory with the rest of the exchange–correlation energy from DFT, provides more accurate corrections to the occupied and unoccupied states and help produce more accurate band gaps and the positionings of 4f states.

Development of exchange interaction calculation method for dilute dopant-dopant interactions. We have developed a method, which calculates exchange interactions employing total energies of different possible magnetic spin configurations and implemented it. As a test case prior to applying to the RE-doped materials that are the topic of this project we have applied the technique to functionalized and doped Cr_2C Mxenes (Fig. 2). The dopant-dopant interactions are key to assess the fidelity and efficiency of the transduction when using hosts with high density of RE ions. This interaction will quantify the hybridization between distinct RE ions, which is one of the factors dictating the RE linewidth. With the theory developed here, we will be able to obtain the maximum densities for RE ions, thus setting practical limits for dense doping of RE ions in a nonmagnetic host.



Fig. 2: Exchange interactions $(J_1, J_2, and J_3)$ of the bare and functionalized Cr₂C MXenes. The black, red, and green lines represent the trend of J_1, J_2 , and J_3 .

Development of exchange-magnon Hamiltonians and frequency dispersion. We hypothesized that use of magnon modes can enhance the quantum transduction from microwave to optical. Accordingly, we first have developed a general theory characterizing magnon excitations. Again, as a test case prior to applying to RE-doped materials, we have applied this theory to the bare and functionalized Cr_2C Mxenes, using the exchange interactions obtained above (see J_1 , J_2 and J_3 in Fig. 2). For the ferromagnetic case, the following Hamiltonian for the magnons was obtained.

$$\mathcal{H} = S \sum_{\mathbf{k}} \begin{bmatrix} a_{\mathbf{k}}^{\dagger} & b_{\mathbf{k}}^{\dagger} \end{bmatrix} \begin{bmatrix} J_2 \left(1 - \gamma_{-\mathbf{k}}^{(2)} - \gamma_{\mathbf{k}}^{(2)} \right) & -\mathcal{Z}_1 J_1 \gamma_{\mathbf{k}}^{(1)} \\ -\mathcal{Z}_1 J_1 \gamma_{-\mathbf{k}}^{(1)} & J_2 \left(1 - \gamma_{-\mathbf{k}}^{(2)} - \gamma_{\mathbf{k}}^{(2)} \right) \end{bmatrix} \begin{bmatrix} a_{\mathbf{k}} \\ b_{\mathbf{k}} \end{bmatrix}$$
 where Z₁ (Z₂) are the number

of nearest (next-nearest) neighbors, $\gamma_k^{(1)/(2)}$ are the structure factors dictating the dispersion, and $a_k(b_k)$ are the magnon operators associated to the A (B) sublattice. The magnon energies are obtained

as:

$$\hbar\omega_{\mathbf{k}}^{\pm} = \mathcal{Z}_1 J_1 S + \mathcal{Z}_2 J_2 S \left(1 - \gamma_{\mathbf{k}}^{(2)} - \gamma_{-\mathbf{k}}^{(2)} \right) \pm |\mathcal{Z}_1 J_1 S| \sqrt{\gamma_{\mathbf{k}}^{(1)} \gamma_{-\mathbf{k}}^{(1)}}$$

We have also started to develop the formalism to calculate the magnon energy dispersion for the different anti-ferromagnetic phases found for the functionalized Cr₂C Mxenes.

Future Plans

We plan to simulate the electronic structure of magnetic lanthanide doped cerium orthovanadate and cerium orthophosphate for quantum transduction and evaluate the enhancement of microwave to optical quantum transduction by using cerium orthovanadate magnon modes. We shall then study magnon-mediated entanglement of magnetic lanthanide spin qubits to assess this framework's potential for entangling qubits and quantum memories and explore configurations and compositions that improve quantum transduction and quantum memories by quenching and or suppressing quantum noise. Despite the hypothesized enhancement of transduction via magnons, we will also calculate the magnon-induced linewidth of the RE ions. This will allow us to realistically assess the optimal situation that maximizes the transduction without substantially increasing the induced linewidth.

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Publications

None.

Optical Information Processing Through Jointly-Optimized Diffractive Surfaces and Electronic Neural Networks Aydogan Ozcan, Electrical & Computer Engineering, UCLA ozcan@ucla.edu

Keywords: Diffractive materials, Diffractive optical networks, Diffractive computing, Optical information processing, Deep learning

Research Scope: In this project, we are broadly exploring the science at the intersection of artificial intelligence, materials science and optics/photonics to harness the diffraction of light through structured materials composed of trainable surfaces (forming a 3D structured volume) that collectively execute a desired computational task, not achievable with standard optical design principles. These diffractive systems form optical processors that are passive (no external power), and operate at the speed of light, calculating the desired solution as the input light propagates through the physical diffractive system trained for a specific task. Benefiting from the scalability and parallelism of optics, diffractive processors and materials that are trained using e.g., deep learning, would create task-specific computational imagers and machine vision systems with various new capabilities. As part of our research, we will create the science and the physical design principles that will lay the foundations of diffractive information processors that are task-specific. As part of this research scope, we have been investigating the information processing capacity of trainable diffractive surfaces, to inquire a deeper understanding of the limits of their computational capabilities. Optical information processors created by trainable diffractive surfaces that are used as the front-end or back-end of electronic neural networks form hybrid information processing units. Our basic research aims a transformative advancement in our physical understanding of optical computing and information processing through trainable diffractive surfaces and materials that are jointly-optimized to work with electronic neural networks. We are exploring fundamental aspects of diffractive surfaces to bring a deeper physical understanding of their formulation for task-specific optical information processing systems, also creating unique interdisciplinary training opportunities for our graduate students. Recent Progress: High-resolution processing, projection, or transmission of visual information over a large field-of-view (FOV) is hindered by the restricted space-bandwidth-product (SBP) of wavefront modulators. Using jointly-optimized diffractive materials and electronic neural networks, we explored the design space of a deep learning-enabled diffractive image processor (Fig. 1) that synthesizes and projects super-resolved visual information using low-resolution wavefront modulators [1]. The digital encoder, composed of a trained convolutional neural network (CNN), rapidly pre-processes the high-resolution visual information of interest so that their spatial information is encoded into low-resolution (LR) modulation patterns, projected via a low space-bandwidth-product wavefront modulator. The diffractive decoder processes this LRencoded information using thin transmissive layers that are structured using deep learning to alloptically synthesize and project super-resolved image information at its output FOV. Our results demonstrated that this diffractive image processor design could achieve a super-resolution factor of ~4, demonstrating a ~16-fold increase in space-bandwidth-product. We also experimentally validated the success of this diffractive super-resolution visual processor using 3D-printed diffractive decoders that operate at the THz spectrum (Fig. 2).[1] This diffractive image decoder can be scaled to operate at visible and IR wavelengths and inspire the design of large spacebandwidth-product visual information processors that are compact, low-power, and computationally efficient.

This novel diffractive decoder designed by deep learning synthesizes and projects superresolved images at its output FOV by encoding each high-resolution visual information of interest into low-resolution representations with a lower number of pixels per image. As a result, the all-optical decoding capability of the diffractive material not only improves the effective SBP of the image processing system but also reduces the data transmission and storage needs since low-resolution wavefront modulators are used. The decoder network is an all-optical diffractive system composed of passive structured materials/surfaces and therefore does not consume computing power except for the illumination light. Similarly, the all-optically synthesized and processed images are computed at the speed of light propagation between the encoder plane and the diffractive decoder output FOV, and therefore the only computational bottleneck for speed and power consumption is at the inference of the front-end digital neural network encoder.

Unlike lens-based image processing systems that can, in general, be characterized through a spatially-invariant point spread function, the optical forward operation of a diffractive network is mathematically equivalent to the transformation of the complex-valued light field emanating from the input through a complex-valued (learnable/trainable) matrix that is not necessarily a Toeplitz matrix.[1-3] Stated differently, a diffractive decoder can implement any arbitrary complex-valued linear transformation between its input and output fields-of-view,



Figure 2: Experimental results of the diffractive PSR visual processor material with L=3 diffractive surfaces that are jointly optimized with an electronic neural network (front-end), where the encoded phase-only representations of the objects are obtained using the all-electronic encoder [1]. The all-optical diffractive decoder projects resolution-enhanced visual information. For comparison, low resolution versions of the same images using the same number of pixels as the corresponding wavefront modulator are illustrated at the bottom row of the figure.

covering any desired set of spatially-variant point spread functions, which forms a super-set of spatially invariant imaging systems. In fact, deep learning-trained diffractive networks were shown to all-optically perform an arbitrary complex-valued linear transformation, including space-variant operations such as permutation, with negligible error provided that the light modulation surfaces/materials forming the diffractive network contain a sufficiently large number of trainable diffractive features. In this sense, the presented diffractive PSR visual information processor can be viewed as a hybrid (electronic-optical) network system that is composed of an electronic encoder (front-end) followed by a complex-valued all-optical matrix operator (the diffractive back-end) that decodes the input encoded fields in a way that the light intensity distribution at the output plane approximates the high-resolution target image information. Note that the complex-valued linear transformation that is all-optically implemented by the diffractive decoder was not a priori known during the training phase since its mathematical function co-evolves along with the optimization of the encoder front-end neural network. In this joint optimization, the diffractive decoder evolves to implement the desired pixel super-resolved image synthesis at the output FOV based on the optimization of its physical features e.g., material thickness (Fig. 2), controlling the light phase at each diffractive feature, collectively performing the learned/optimized linear transformation at its output, in collaboration with the front-end electronic encoder.

Future Plans: We will continue our explorations and basic research on three distinct sets of transformations performed by diffractive material systems that are integrated and jointly-optimized with electronic neural networks: (1) space-to-space transformations, (2) space-to-time transformations and (3) time-to-space transformations. These physical transformations achieved through trained diffractive processors will form a powerful and mathematically rich symbiotic relationship between the optical information processor and the digital electronic network (jointly-trained) to achieve extreme advantages in terms of power-efficiency, frame-rate and classification speed for a given inference task.

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Light-matter interaction in nanoscale systems for energy applications

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Keywords: Nanophotonics, Photovoltaics, Radiative Cooling

Program Scope

The objective of this project is to advance the fundamental understanding of light-matter interaction in nanoscale systems. We aim to capitalize on our gained understanding to identify new opportunities for renewable energy applications. This objective will be accomplished by combined theoretical and experimental efforts.

Below we review some of our major results [Refs. 1-10 in the publication list]

Recent Progress

Atomic-scale control of thermal emission. Controlling the spatial and temporal coherence of

thermal radiation plays an important role in energy harvesting and thermal management. Conventional approaches for thermal radiation control rely on resonances in bulk thermal emitters, which usually have a large footprint and display little tunability. Here, in a collaborative work between the Brongersma and Fan groups [Paper 5 in the Publication List], we explore the control of temporally coherent thermal radiation at the atomic scale with 2D materials (Figure 1). We focus on using hexagonal boron nitride (hBN), which has a strong hightemperature phonon-





Figure 1. Thermal emitter with atomically thin hBN top layers. (a)-(f) Emissivity as a function of wavelength and ribbon width for different numbers of hBN atomic layers. By tuning the number of layers and the width of the hBN ribbon, the emissivity of the thermal emitter can be controlled.

polaritonic response in the mid-infrared spectral range. We show that, despite its atomic-scale thickness, thermal emitters made from single or a few atomic layers of hBN can generate a coherent emissivity spectrum with a peak emissivity comparable to bulk materials. The spectral

emissivity peak of phononic 2D-material emitters exhibits a much higher quality factor compared to the emissivity peak from emitters based on plasmonic 2D materials like graphene. We show that the radiative properties of the considered hBN thermal emitters depend sensitively on the number of atomic layers. Thus, this system provides a pathway to achieve atomic-scale control of thermal radiation.

<u>Nighttime electric power generation via radiative cooling.</u> A large fraction of the world's population lacks access to the electric grid. Standard photovoltaic (PV) cells can provide a renewable off-grid source of electricity but only produce power from daytime solar irradiance and do not produce power at night. In many rural areas dependent on mini-grid or off-grid systems, providing power during the nighttime often necessitates substantial additional battery



Figure 2. Nighttime power generation from radiative cooling of a photovoltaic (PV) cell. (a) Schematic showing the device configuration and the energy balance of the PV cell and the thermoelectric generator (TEG) unit. (b) Multi-day temperature and power measurements. (Top) Temperature measurements. (Middle) PV power generation. (Bottom) TEG power generation. Note the different scales used for daytime and nighttime.

storage installation, which adds significant system complexities and costs. Developing a mean to extract energy from existing PV cells at night would alleviate the daytime limitation of PV power generation and reduce or eliminate the need for battery storage in electrical power systems. Here, we show that a PV cell can be used to generate electricity at night. [Paper 8 in the

Publication List] The encapsulation layer of the PV cell is usually made of materials such as glass that is strongly emissive in the thermal wavelength range. The sky-facing PV cell therefore can undergo radiative cooling and reach a temperature below that of the ambient. We incorporate a thermoelectric generator to harvests electricity from the temperature difference between the PV cell and the ambient surrounding (Figure 2a). We achieve a power density of 50 mW/m² under a clear night sky, with an open-circuit voltage of 100 mV (Figure 2b). Our demonstrated power density is orders of magnitude higher as compared with previous demonstrations. During the daytime, the thermoelectric generator also provides additional power on top of the electric power generated directly from the PV cells. Our system can be used as a continuous renewable power source for both daytime and nighttime in off-grid locations.

Approaching the ultimate limit of solar energy harvesting with non-reciprocal photovoltaic cells. Understanding the fundamental limits of solar energy conversion and developing device configurations to reach these limits have been of central importance in the study of solar cells. When reciprocity is assumed, the solar energy conversion has an upper bound on its efficiency $\eta_M = 86.6\%$, known as the multi-color limit, assuming a solar temperature of $T_s = 6000K$ and a cell temperature of $T_c = 300K$. With the use of non-reciprocal components, one can further increase the efficiency beyond the multicolor limit to reach the Landsberg limit:

$$\eta_L = 1 - \frac{4}{3} \frac{T_c}{T_s} + \frac{1}{3} \left(\frac{T_c}{T_s}\right)^4 = 93.3\%$$

The Landsberg limit represents the ultimate efficiency limit of solar energy harvesting, as can be proven using fundamental thermodynamic considerations.



Figure 3. Configurations for reaching the Landsberg limit for the efficiency of solar energy harvesting. (a) A configuration proposed by Ries. (b) Our recently proposed non-reciprocal multiple junction cell. The cell consists of multiple semiconductor layers with varying band gaps. Each layer operates as a non-reciprocal semitransparent absorber.

The multicolor limit can be reached with use of a multi-junction solar cell, which consists of a stack of multilayers of semiconductors with different band gaps. Compared with the multijunction solar cells, however, the existing proposed configuration for reaching the Landsberg limit are far more complicated. The first proposal consists of an array of circulators and Carnot engines (Figure 3a). None of the proposed configurations has the conceptual simplicity of the multijunction solar cell.

We have proposed a non-reciprocal multijunction solar cell that can reach the Landsberg limit [Paper 7 in the Publication List]. In this configuration (Figure 3b), like the standard multijunction solar cells, the layers are semiconductors with different band gaps, with the larger band gap semiconductor placed closer to the front side of the cell facing the sun. Unlike the standard multijunction solar cells, however, each layer has a non-reciprocal semitransparent absorption/emission property. The absorber absorbs solely from one side but emits solely to the other. We have shown that this configuration, in the ideal limit with infinite number of semiconductor layers, can reach the Landsberg limit. We have also shown the nonreciprocal multijunction cell outperforms its reciprocal counterparts for any number of layers greater than one. We envision the study of non-reciprocal solar cells will open a new direction in the theoretical understanding of fundamental issues associated with solar and thermal energy harvesting.

<u>Structural color from a coupled nanowire pair beyond the bonding and antibonding mode</u>. The discovery of new mechanisms to create color have always been at the heart of human society—from colorful cave paintings in prehistoric times to advanced metasurfaces for solar cells, thermal radiation management layers, and displays with a wide color gamut. Compared to pigments, structural colors induced by optical resonances are chemically more stable and have highly designable spectra as well as the potential for dynamic tuning. Photonic crystals are well known to produce structural colors. However, a relatively large footprint is required to realize efficient color filtering due to the coherent interaction of the unit cells in photonic crystal.



Figure 4. (a) Experimental demonstration of structural color from Si nanowire (NW) pairs. (a) Cross-polarized reflection optical image of the fabricated Si NW pairs. All the NWs are 50 µm long and have the same 50 nm square size. (b) Top-view scanning electron microscope images of fabricated Si NW pairs. The separation distance between the NWs increases from 200 nm to 400 nm in steps of 50 nm. (c) Simulated scattering efficiency of the designed Si NW pairs on the sapphire substrate as a function of the incident wavelength under normally incident, TM-polarized illumination. The dispersion and absorption of Si are considered in the simulation. (d) Measured cross-polarized reflection spectra for the different fabricated Si NW pairs.

Here, we demonstrate both theoretically and experimentally that two identical neighboring silicon nanowires (NW) with different spacings form a new universal building block for structural color, while maintaining a subwavelength footprint [Paper 6 in the Publication List]. This is accomplished by exciting a series of Fabry-Pérot-like modes where light is repeatedly scattered between two NWs (Figure 4). The structural color results from these Fabry-Pérot modes can be tuned across the entire

visible frequency range by varying the distance between two NWs. Furthermore, the presented optical system provides a way to generate optical resonances in coupled nanostructures and expands the understanding of resonant coupling and the manipulation of light at the nanoscale.

Future Plans

We plan to focus on continued efforts towards understanding light-matter interaction in nanophotonic structures in the context of energy applications. We will continue our efforts towards enhancing radiative cooling based nighttime power harvesting schemes. We will also further develop the concepts of non-reciprocal solar cells for harvesting of solar and thermal radiation. The efforts include the use of non-reciprocal systems for thermophotovoltaic systems, and in electroluminescent cooling. In addition, we will develop new mechanisms to control thermal radiation using 2D quantum material engineering and space-time modulation. These works will deepen our fundamental understanding of light-matter interaction in nanoscale systems and open new opportunities for energy harvesting.

Ten Selected Journal Publications of DOE Sponsored Research in 2020-2022

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- 2. X. Yin, R. Yang, G. Tan, and S. Fan, "Terrestrial radiative cooling: Using the cold universe as a renewable and sustainable energy source," Science 370, 786–791 (2020).
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Fundamentals of Semiconductor Nanowires

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Keywords: Semiconductor nanowires, Optical properties, Phase transition, Structural dynamics.

Program Scope

The properties of semiconducting nanostructures are fundamentally defined by their morphology, and this has translated to the innovative design of optoelectronic devices. The controlled synthesis, advanced structural characterization, and theoretical modeling of the optical and electronic properties of semiconductor nanostructures will thus allow us to inform the design and control of nanoscale energy conversion and light-emitting systems with great precision. Specifically, we focus on semiconducting nanowires (NWs) because they are an excellent platform for studying emergent phenomena, such as structure-to-property relationships, phase transitions, and carrier dynamics. By studying NWs across three size regimes: 1) mesoscale, 2) nanoscale, and 3) molecularly thin, we will develop a holistic physical understanding of semiconducting NWs and their potential applications.

Recent Progress

1. <u>Mesoscale perovskite nanowires:</u> Ferroelectric semiconductors, characterized by a unique spontaneous polarization and visible light absorption, have emerged as an exciting class of materials for designing functional photoferroelectrics, such as optical switches and ferroelectric photovoltaics. Among these materials, our recently discovered two-dimensional CsGeX₃ (X = Cl, Br, I) perovskite, is the only class of inorganic halide perovskites with a noncentrosymmetric crystal structure that lead to ferroelectric properties¹. Specifically, the ferroelectricity of CsGeX₃ arises from the lone pair stereochemical activity in Ge(II) that promotes the atomic displacement of the metal cation, thus causing off-centering behavior that breaks the centrosymmetry of the crystal structure and giving rise to spontaneous polarization up to 10-20 μ C cm^{-2.1} This behavior marks CsGeX₃ as a next-generation ferroelectric semiconductor, a rare class of materials that can make a significant impact in solar-to-electrical energy conversion technologies. Single-crystalline CsGeBr₃ NWs can be synthesized via chemical vapor transport (CVT) methods. We have recently expanded approaches to grow these NWs on a library of substrates, including muscovite mica, Si, sapphires, MgO (Figure 1). The ability to engineer NW growth on a variety of substrates

allows us to tune both the NW growth orientation and the substrate interaction at the NWsubstrate interface. Both of these factors can potentially affect the structural distortion that generates spontaneous polarization, which in turn impacts the ferroelectric behavior. Current experiments involve further characterizing these NW-substrate interfaces with transmission electron microscopy (TEM) and understanding the size-dependent, dimensionality-dependent and substrate-dependent ferroelectric properties – such as the atomic-scale polarization distribution and domain microstructures of these NWs – using polarization-resolved scanning second harmonic generation microscopic imaging and piezo-response force microscopy. Extensive studies to correlate structural properties with nanoscale ferroelectric behavior in this scope will further our fundamental understanding of this new class of ferroelectric semiconductor and pave the way for applications in ferroelectric photovoltaic devices.

Furthermore, preliminary measurements to determine the electronic density of states and band structure in CsGeX₃ nanostructures with angle-resolved photoemission spectroscopy (nanoARPES) have been initiated at the Advanced Light Source beamline 7.0.2. Both CsGeBr₃ NWs and nanoplates have been directly grown on highly conductive silicon substrates and possess low resistance values on those substrates (generally below 1 k Ω), thus enabling more electrons to escape the material and be efficiently collected to generate sufficient nanoARPES signal. These nanoARPES measurement efforts will inform our understanding on probing the ferroelectric phase transition properties of CsGeX₃ nanostructures with tunable thicknesses from few nanometers to tens of nanometers. XUV transient absorption measurements on thin films of CsGeI₃ are in progress to understand the kinetic behavior on few-femtosecond timescales of the photo-generated electrons and holes. These carriers are being studied at the iodine N_{4.5} and Ge M_{4.5} absorption edges to provide mechanistic insight on the evolution of the carrier cooling and thermalization. Additionally, the XUV as a core-level probe is sensitive to



Figure 1. Scanning electron microscopy (SEM) images of (a) horizontal CsGeBr₃ NWs grown on muscovite mica (scale bar: 10 µm), (b) a network of CsGeBr₃ grown on muscovite mica (scale bar: 100 µm), (c) vertical CsGeBr₃ NWs grown on silicon (scale bar: 10 μ m), and (d) vertical CsGeBr₃ NWs grown on mplane sapphire substrates (scale bar: 2 µm).

lattice dynamics that may couple to the photo-generated carriers.

2. Nanoscale perovskite wires: The optoelectronic properties of semiconductor nanostructures are dominated by confinement when their thickness is smaller than that of the exciton Bohr radius. Consequently, a suite of structure-to-property relationships have emerged among perovskite materials, such as tunability of the bandgap, photoluminescence (PL) quantum yield, and



Figure 2. Representative TEM images of colloidal ultrathin CsPbBr3 nanowires, ~2.2nm diameter.

recombination lifetimes, central to engineering optoelectronic devices. In this program, our goal is to elucidate the photophysics of one-dimensional (1D) perovskite NWs, including CsGeX₃ and CsPbX₃, as a function of their thickness (Figure 2). A new perspective is that these NWs display greater diversity in their physical properties compared to their higherdimensional counterparts due to the ability to control the thickness of the NW. Their

absorption and PL spectra each contain intense excitonic resonances at room temperature, which redshift with increasing thickness. Such fine tuning of the optical bandgap with nanometer wavelength resolution will enable the study of nanomaterials under unprecedented levels of confinement, as well as the testing and revision of existing theoretical models that break down when describing electronic behavior in the weakly confined regime. For instance, the exciton-phonon and electron-phonon coupling may significantly impact the optical behavior of ultrathin NWs, and more-so with decreasing thickness, as already shown for two-dimensional CsPbBr₃ nanosheets, thus necessitating a more sophisticated understanding of photophysics in confined nanostructures and the contributions of long-range translational order afforded by the ionic perovskite lattice. The understanding of exciton-phonon coupling atomistically, allowing for understanding of the role of specific deformations on the nanoscale³. Theoretical understanding of the carrier dynamics will be aided by atomistic investigations of the nanowire electronic structure, including

trapping and exciton-phonon coupling, within a recently expanded semi-empirical pseudopotential framework. This work lays the foundations for a more detailed study of the exciton-phonon and electron-phonon coupling in 1D nanostructures, which will help to inform the design of optoelectronic devices, as well as highlight previously unexplored structural degrees of freedom to engineer the excited state dynamics of semiconductors.

3. <u>Single unit cell perovskite nanowires:</u> Single-unit-cell ultrathin perovskite NWs are challenging to synthesize, but their strong quantum confinement properties make them a high-interest topic in semiconductor optoelectronics research. A generalized bottom-up solution-based supramolecular assembly methodology was proposed to explore the synthesis and assembly of these NWs. The use of crown ether@alkali metal supramolecular cations was successful in stabilizing a



unique charge-neutral (crown ether@A)₂M(IV)X₆ dumbbell structure in solution, with highly tunable chemical composition. This lays the foundation for a new class of self-assembled optical materials (Figure 3a)⁴. The success of this approach warrants further exploration into the formation of 1D chain structures, such as an alternating crown ether-octahedra chain stabilized by a bridging divalent cation crowned by the crown ether (Figure 3b). To directly examine their electronic properties, we are exploring ways to stabilize such 1D molecular chains in solution. Moreover, investigation of the mesoscopic assembly of molecular wires via this supramolecular process may lead into interesting electronic coupling between these molecular wires.

In addition to the supramolecular assembly chemistry, encapsulation of halide perovskite into the carbon nanotubes (CNTs) can also achieve molecular wires with well-defined dimensionality down to the single-unit-cell level (Figure 4a & 4b)⁵. As known, halide perovskite materials are highly susceptible to electron beam damage. Therefore, previous study of halide perovskite transformation kinetics and mechanism were majorly probed by non-invasive imaging techniques such as PL microscopy, cathodoluminescence microscopy, and high-pressure Raman

spectroscopy. With the protection of CNTs, the perovskite NWs can maintain their structural integrity for longer times under the high-dose working conditions of TEM experiments. This opens up unprecedented opportunities to achieve *in situ* visualization of 1D perovskite NW

structural transformations and dynamics down to few- or single-unit-cell level. It further enhances the precision and control of 1D NW physical behaviors with high spatial resolution and temporal resolution. With combined efforts on synthetic advancement of CNTs-confined 1D halide perovskite NWs at single-unit-cell level, high-resolution phase contrast electron microscopy with *in situ* temperature control, and molecular dynamics simulation as well as novel atom tracing algorithms (Figure 4c), subsequent quantitative study of NW structural transformation is under way, such as temperature-dependent phase transitions of these highly confined halide perovskite NWs inside CNTs.

Future Plans

We will continue to draw fundamental connections between the structure and properties of the material systems showcased herein by leveraging our combined expertise in synthesis, characterization, and theory. We will continue the synthesis of novel 1D semiconductors with sizes from the



simulation of perovskite chain in CNT where Pb^{2+} , Γ , and Cs^+ atoms are colored in red, orange, and blue, respectively. (b) Low-does phase-contrast electron images of a CNT filled with halide perovskite lattice. (c) Real-time trajectories of cesium, lead, and iodine atoms (time interval is 53 ms).

meso- down to the molecular scale. Atomic resolution aberration-corrected TEM will be a powerful tool to quantify the lattice dynamics, thickness, and phase transitions of NWs. Furthermore, XUV and visible transient absorption spectroscopy will be used to probe the new ferroelectric semiconductors and unexplored carrier dynamics of NWs, respectively. Advanced computational methods are currently under development to handle the electronic structure calculations of large nanostructures, even exceeding 20 unit cells, which will model the observed excited state dynamics. The culmination of such work entails a comprehensive, physical understanding of 1D semiconductors.

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Ion Instabilities in 2D and 3D Metal Halide Perovskites Masaru Kuno and Prashant V. Kamat

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Keywords: Photosegregation, ion migration, phase segregation, metal halide perovskites, mixedanion, mixed-cation, transient spectroscopy.

Research Scope

To address near ubiquitous photosegregation in lead-based, mixed-halide perovskites, we have developed a band gap-based thermodynamic model that rationalizes nearly all experimental aspects of the phenomenon. At its most basic level, the model suggests that local band gap differences between parent mixed-halide alloys and stochastically-generated or light-induced iodine-rich regions provide a thermodynamic driving force to induce halide photosegregation. Band gap sensitivities appear in excess photocarrier energies that enable anion hopping within perovskite lattices. This, in turn, allows them to reduce their free energies by creating segregated iodine- and bromine-rich domains. In the absence of above gap excitation, the original lattice restores itself through entropically-driven, anion remixing. Spectroscopic studies have also been conducted to probe halide ion migration in two-dimensional (2D) and bulk, three-dimensional (3D) mixed halide perovskites with specific measurements conducted to modulate the extent of



Recent Progress

During current and prior funding periods, we have demonstrated that our band gap-based thermodynamic model¹ qualitatively and quantitatively explains: asymmetries in absorption and emission photosegregation response, excitation intensity (Iexc)dependent photosegregation rates/rate constants, temperature-dependent photosegregation rates/rate constants, Iexc-dependent terminal halide stoichiometries ($x_{terminal}$), existence of photosegregation I_{exc} thresholds ($I_{\text{exc,threshold}}$) below which no photosegregation occurs, and temperature-insensitive x_{terminal} . Figure 1 illustrates the predictions of our model and compare them to temperature-dependent x_{terminal} of other models. In more recent work, we have demonstrated that predicted x_{terminal} sensitivities to carrier diffusion length or nanocrystal size exist² and that our model can also be used to predict relative photosegregation sensitivities based on empirical Vegard's law expressions of composition-dependent band gaps.

ion migration using applied electrochemical bias.

In tandem, we have studied the photostabilities of two-dimensional (2D) mixed-halide and 2D/three-dimensional (3D) perovskite heterostructures.³ For the former, it has been proposed that 2D Ruddlesden-Popper (RP) perovskites exhibit suppress halide ion mobilities and, by extension, photosegregation tendencies. For the latter, passivating bulk 3D perovskite surfaces with RP perovskites stabilizes them against thermal- and moisture-induced degradation. This improves the stability of resulting (bulk) photovoltaic and light emitting devices.

Studies now suggest growing concern about unstable 2D/3D interfaces. This stems from cation or anion⁴ migration under illumination, under thermal stress or even during specimen aging. To address ion migration dynamics at 2D/3D perovskite interfaces, we have therefore recently undertaken photophysical studies of these materials, described below. A. Photoinduced phase segregation in BA₂PbBr₂I₂ films. When a BA₂PbBr₂I₂ film is subjected to



Figure 2. BA₂PbBr₂I₂ phase segregation under steady state irradiation. (A) Absorbance spectra, (B) difference absorbance spectra, and (C) photoluminescence spectra recorded during steady state irradiation with a 365 nm diode laser (I_{exc} =15 mW cm⁻²). (D) Absorbance change at 450 nm (black) and growth of emission at 510 nm (red) during photosegregation. Solid lines are monoexponential kinetic fits.

visible light excitation (either white light or continuous 400 nm diode laser), its 450 nm excitonic absorption decreases. This is accompanied by concurrent increases of observed absorption at 450 and 475 nm (Figures 2A and B). These changes reflect the formation of I- and Br-rich domains in BA₂PbBr₂I₂ due to photoinduced phase segregation. Upon stopping photoirradiation, films recover, illustrating that anion photosegregation is reversible.

Figure 2C shows corresponding changes to the emission during irradiation. Observed redshifting resembles that seen for bulk 3D perovskites. Namely, a redshifted 510 nm emission peak progressively grows as charge carriers accumulate in photogenerated I-rich domains. No absorption or emission changes are observed with corresponding pure bromide or pure iodide species. A monoexponential kinetic fit of absorption and emission data yield photosegregation rate constants of 2.2×10^{-3} s⁻¹

(absorption) and 2.4×10^{-3} s⁻¹ (emission). The similarity between these two kinetic rate constants establishes the close relationship between absorption and emission changes in BA₂PbBr₂I₂ due to photoinduced phase segregation.



Solid lines are exponential fits to obtain pseudo first order rate constants.

dichloromethane (DCM) halide ions are expelled. At early times, spectral behavior akin to above phase segregation is seen. Continued irradiation, however, leads to I⁻ expulsion as observed via a decrease of observed absorption at 450 nm (Figures 3A & B). Although bromide-related

absorption at 405 nm is retained initially, it ultimately succumbs to Br^- expulsion after prolonged photoirradiation. Triiodide (I₃⁻) formation in DCM confirms halide expulsion.

Despite Br⁻ and I⁻ existing in almost equal concentrations within BA₂PbBr₂I₂, their expulsion rates vary. Kinetic traces at 490 nm (iodide related), 450 nm (mixed-halide related), and 405 nm (bromide-related) in Figure 3C reveal rate constants of $k_{405}=5.01\times10^{-3}$ s⁻¹, $k_{450}=6.13\times10^{-3}$ s⁻¹, and $k_{490}=1.57\times10^{-3}$ s⁻¹. k_{450} is similar to k_{490} and is rationalized by loss of mixed-halide absorption

lid lines are monoexponential fit of absorption and ephotosegregation rate 4×10^{-3} s⁻¹ (emission). The similarity between thes are relationship between absorption and emission ch

B. I⁻ and Br⁻ expulsion from 2D perovskite films. When BA₂PbBr₂I₂ films are irradiated in

due to I⁻ expulsion. Between k_{405} and k_{490} , observed differences are attributed to different I⁻ versus Br⁻ mobilities. Specifically, charge accumulation in low bandgap I-rich domains, accompanied by large I⁻ mobilities, leads to initial I⁻ expulsion. Only when I/I⁻ expulsion is complete does charge accumulation in Br-rich domains result in eventual Br⁻ expulsion. C. Electrochemical Modulation of Iodine Migration and Expulsion. We have succeeded in modulating photoinduced I⁻ expulsion in mixed-halide perovskite films by applying



Figure 4. (A) Electrochemical bias-dependent I⁻ expulsion from MAPbBr_{1.5}I_{1.5} deposited atop electrodes under photoirradiation. Employed potentials range from 0.5 to -0.3 V vs. Ag/AgCl. (B) Schematic illustration of electrochemical modulation of the perovskite Fermi level and its influence on photoinduced I⁻ expulsion. Scanning electron microscopy images of biased and photoirradiated films to illustrate morphological changes induced on I⁻ expulsion.

electrochemical bias (Figure 4). Our prior work has shown that hole accumulation in Irich domains of mixed-halide perovskites plays an important role in inducing I⁻ migration.⁵ To illustrate, for MAPbBr_{1.5}I_{1.5} deposited atop electrodes, anodic potentials induce electron extraction. What then results is hole accumulation in the film, which, we observe leads to I⁻ migration in the perovskite. This is evident from apparent increases in I⁻ expulsion rate constants ($k_{\text{expulsion}} = 0.0030$

s^{\Box 1}). In contrast, under cathodic bias (-0.3 V *vs.* Ag/AgCl potential) electron-hole recombination (as opposed to extraction) is facilitated within MAPbBr_{1.5}I_{1.5} films. Under these conditions, I⁻ expulsion is suppressed by an order of magnitude, leading to dramatic reduction of I⁻ expulsion rate constants, i.e. $k_{\text{expulsion}} = 0.00018 \text{ s}^{\Box 1}$. Tuning the perovskite's Fermi level (E_{Fermi}) through external bias therefore modulates I⁻ migration and expulsion.

Future Plans

Going forward, we will focus on understanding anion dynamics in the limit of high excitation intensities. Here, it has been reported than an unusual photoremixing phenomenon exists wherein simply increasing incident light intensities *reverses* anion photosegregation. Of note is that photoremixing is not immediately predicted by any existing model of the phenomenon. In this regard, all existing anion photosegregation measurements and theoretical studies implicitly work in the limit of low carrier densities. Little is therefore known about metal halide perovskite anion dynamics at high carrier densities.

Our current results simultaneously highlight how differences in Br⁻ and I⁻ mobility influence the photostability of 2D and 3D perovskite films. Although incorporating 2D perovskites to passivate the surfaces of bulk 3D perovskites improves the photostability of corresponding perovskite solar cells, it remains to be seen how cation and anion instabilities influence the long term stability of 2D/3D heterojunctions. Controlling halide ion mobility at 2D/3D interfaces thus represents an ongoing challenge for stabilizing photoirradiated metal halide perovskites. Cation dynamics at 2D/3D perovskite interfaces will be addressed using concerted chemical, optical, photochemical, and electrochemical measurements. Specific cation imaging measurements will be conducted using a widefield, superresolution infrared absorption microscopy established with prior DOE support. Efforts entail high spatial resolution, hyperspectral imaging and spectroscopy of cation migration at 2D/3D interfaces, following visible light irradiation and/or electrical bias. This will be complemented with detailed photo- and electrochemical measurements.

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Discovery of Goniopolar Metals with Zero-field Hall and Nernst Effects

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Keywords: Goniopolar materials, zero-field Hall effect, zero-field Nernst effect, transport properties of solids, transverse thermoelectricity

Research Scope

This work focuses on the discovery of goniopolar materials, electronic materials that simultaneously have *n*-type conduction along specific crystallographic directions and *p*-type conduction along others. When such materials are cut so that the current flows at an angle vis-à-vis the principal crystallographic axes, the electrical resistivity, thermoelectric power, and thermal conductivity tensors have non-zero off-diagonal elements, zero-field Hall-like, Nernst-like and thermal-Hall-like effects. In such crystals, and also in the composites we will show, charge and heat flow at an angle vis-à-vis the applied electric field or thermal gradient, enabling applications in microwave and solid-state energy conversion devices. Hall plates can be used in non-reciprocal microwave isolators and circulators; so can goniopolar materials with a zero-field Hall effect. Similarly, like the Nernst effect enables transverse thermoelectric generators (TTEGs) and Ettingshausen transverse thermoelectric coolers (TTECs), so can their zero-field Nernst effect.

There are two mechanisms that lead to goniopolar behavior in single crystals, to which in this reporting period, we add a third, composite material with non-zero Hall and Nernst effects in the absence of external magnetic fields. The first mechanism, *single-Fermi Surface goniopolarity*,¹ is found in degenerately doped semiconductors and metals (e.g. NaSn₂As₂) that have a Fermi surface (FS) that is not 1-simply-connected and consists of a convex and a concave Gaussian curvature part. This type of Fermi surface occurs in electrically conducting solids in which the orbital nature of the electron wavefunction varies with the momentum vector in ways that differ along the different crystallographic directions. The second mechanism, *multi-Fermi Surface goniopolarity*,² occurs in degenerate semiconductors and semimetals in which the FS comprises an electron pocket and a hole pocket, (e.g. Re4Si₇) with different anisotropic mobilities; intrinsic semiconductors can also display this behavior, even though a FS is not developed. During this reporting period, a third mechanism was discovered that leads to non-zero Hall and Nernst effects in *magnetic composite materials*.³ It leads to completely three-dimensional anisotropic transport tensors with all off-diagonal terms non-zero at zero field.

Recent Progress

Re4Si7 was identified as being a *multi-Fermi Surface goniopolar* material during the previous period. It was also proven to have excellent longitudinal and transverse thermoelectric properties². A parallelepiped of goniopolar material, when cut at an angle such that the heat gradient is not along one of the principal axes along which the material is either n-type or p-type, has a thermoelectric tensor with non-zero off-diagonal components. This gives rise to transverse thermoelectric Nernst and Ettingshausen coefficients even in the absence of a magnetic field, which can be used in TTEGs and TTECs. TTEGs have two major advantages over conventional "longitudinal" thermoelectrics. First, they need electrical contacts only on the cold side of the TTEG, obviating the need for a semiconductor/metal contact technology at the hot side that must be robust to thermal degradation mechanisms. This property alone allows TTEGs to circumvent the major obstacle that stopped thermoelectric generators from being widely used commercially in spite of the large research effort that resulted in a tripling of the thermoelectric figure of merit zT of materials⁴. Second, TTEGs do not need to be shaped like thermopiles with multiple



elements connected in series, which cuts down on contact resistance losses. This work was expanded during this research cycle. First, it was realized that TTEG design criteria differ from those of

conventional longitudinal TEGs, in that the aspect ratio of the elements can result in a more "isothermal" heat injection (i.e. where the isotherms are parallel to the face of the sample where heat in injected/extracted) or a ore "adiabatic" heat injection (i.e. where one allows thermal Hall effects to appear). New measurement protocols were developed to document this difference, and the isothermal injection is proven more efficient. A review of the properties of all transverse thermoelectric devices, whether based on classic al Nernst-Ettingshausen, on the spin-Seebeck effect, or on goniopolarity is also published.⁴

Several new *multi-Fermi Surface goniopolar* goniopolar materials were discovered. The criteria included avoiding materials, such as Re, that are not earth-abundant. Most promising is WSi₂,

see Fig. 1. The other new system is NaSnAs. The third one is the elemental semimetal Bi, when it is p-type doped with Sn (manuscript in preparation), but unfortunately that is only goniopolar below 150 K.

Transverse thermoelectric devices have been constructed from semiconductor/metal and semiconductor/semiconductor multilayers cut at an angle⁵. We developed a new quench/anneal technique to prepare aligned MnBi/Bi composites (Fig. 2a).³ MnBi is a metallic high coercivity permanent magnet material. It is imbedded in the form of needles in Bi, a very high mobility semimetal with low carrier densities and high Hall and Nernst coefficients. The needles are single crystals with their easy axis along their length. When magnetized, their demagnetizing field exerts a Lorentz force on the electrons in the Bi. When cut at an





Fig. 2 Aligned Bi/MnBi composites. (a) micrograph of a Bi sample with aligned needles of MnBi, highly conducting permanent magnetic material. (b) schematic diagram of a sample cut out of such material with the needles in the (x,z) plane. Contacts are made to the sample to apply a current (I) or heat (Q) flux along x, and measure longitudinal (ρ_{xx}) and transverse electrical and thermoelectric properties along both y and z, i.e. ρ_{xy} and ρ_{xz}

angle vis-à-vis the direction of the

needles (Fig. 2b), this structure combines two transverse effects: (1) a "demagnetization Hall effect" arising from the Lorentz force on the electrons in the Bi, and a "multilayer" effect from the conductivity of the MnBi. With the current or temperature gradient applied along *x* (see Fig. 2b), the zero-field coefficient ρ_{xz} measures the multilayer effect, while the zero-field coefficient ρ_{xy} measures the Hall effect due to the demagnetizing field. The measurement, shown in Fig 3a, leads to the remarkable conclusion that the two Hall effects are of opposite polarity, making this a true goniopolar sample. The transverse resistivity ρ_{xz} is as large as the longitudinal ρ_{xx} . The two zero-field Nernst coefficients S_{xy} and S_{xz} (shown in Fig. 3b) are of the same polarity, but presumably the sign of S_{xy} can be inverted by poling the MnBi in the opposite direction. This results in a genuinely 3-dimensional transport tensor, in which all off-diagonal components are non-zero even in the absence of an external field.

Future Plans

Applications require goniopolar materials that are earth-abundant, air stable, non-toxic, and have a high resistivity and thermopower. The following ideas will be investigated.

1. A higher thermopower can be expected from *single-Fermi Surface goniopolar* materials with nested FSs, such as Nowotny Chimney Ladder phases. We will investigate. Mn₄Si₇, Mn₁₁Si₁₉, Mn₁₅Si₂₆, Mn₂₆Si₄₅ and NbAl_{0.6}Si_{1.4} which W. Windl

(private communication) calculates have nested FSs of the correct topology, as well as a higher thermopower.

- 2. Amongst the *multi-Fermi Surface goniopolar* materials, we first will investigate the Re₄Si₇ WSi₂ system, which should form solid solutions. Re₄Si₇ has much higher thermopowers than WSi₂. The alloy system is expected to maintain that while decreasing the amount of Re needed.
- 3. Research will be expanded in the *p*-type-doped Bi system to *p*-type $Bi_{1-x}Sb_x$ alloys, which are semiconductors for 0.09 < x < 0.22. They can be prepared to be intrinsic, because bismuth and antimony are isoelectronic. The hope is to drive goniopolarity in that system to room temperature.
- 4. The MnBi/Bi system will be investigated beyond the first data shown in Fig. 3. Independent variables that will be explored are the MnBi concentration and the able at which the composites are cut. An extension to the Bi_{1-x}Sb_x alloy system will also be tried.

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Properties, Electrochemical Activity, and Stability of Solid Oxide Cell Fuel-Electrode Materials

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Keywords: Electrolysis, Fuel cells, hydrogen, electrode materials, nanoparticle exsolution **Research Scope**

This project focuses on high-temperature ionically- and electronically-conducting oxide materials that have applications in solid oxide fuel cells, electrolyzers, and oxygen membranes. These solid oxide cells (SOCs) will play a crucial role in projected net-zero emissions pathways, especially H_2 production by electrolysis and utilization with fuel cells. The present project focuses on fundamental studies of a new class of SOC fuel electrode materials that was discovered under prior DOE-BES funding – oxide materials that exsolve performance-enhancing metallic nanoparticles during device operation. The research aims to: (1) determine the pathways of nanoparticle exsolution and associated oxide phase transformations; (2) measure oxide electronic transport properties; (3) ascertain how electrode electrochemical processes are affected by nanoparticle exsolution and associated oxide phase changes; (4) explore of the stability of the exsolution electrodes relative to electrolyte materials; and (5) explore the factors determining the long-term performance stability.

Recent Progress

Dynamics of (Ni,Fe) exsolution from Sr(Ti,Fe,Ni)O3-δ

High performance solid oxide fuel cell anodes have recently been achieved via the exsolution of bimetallic (Ni,Fe) particles from a parent Sr(Ti,Fe,Ni)O_{3- δ} (STFN) matrix. We have been studying the role of initial A-site deficiency and the effect of the change in perovskite stoichiometry during exsolution. In this study, the dynamics of exsolution are explored via thermogravimetric analysis (TGA), in-situ X-ray diffraction (XRD), and transmission electron microscopy (TEM). We have recently emphasized *in situ* techniques, since *ex situ* analyses have an inherent uncertainty: is the measured composition the same as that actually present in the electrode during operation at





temperature, or do the rapid cooling and changes in gas atmosphere significantly change it? *in situ* XRD studies are also being utilized to study intentional redox cycling, proposed as a method of "resetting" electrodes in the event of, e.g., exsolved particle coarsening, phase change towards
higher Fe, and/or coking (possible for electrode operation in a hydrocarbon fuel). The aim is to elucidate the timescale and phases involved in the exsolution and redox cycling of STFN, and then to link these to changes in electrochemical characteristics.

An example of *in situ* XRD observations during exsolution from S_1TFN (at 700 C in humidified hydrogen) is shown in Figure 1. The decomposition of the perovskite to the Ruddlesden-Popper phase along with Ni-Fe alloy exsolution are linked and the process appears to have enough time to reach an equilibrium under these conditions.

Stability of STF fuel electrodes

 $Sr(Ti_{1-x}Fe_x)O_{3-\delta}$ (STF) with x = 0.7 has been demonstrated to be a compelling MIEC electrode material both in oxygen and fuel environments. As an oxygen electrode, it can be constituted with a small percentage of Co in order to create low polarization resistance for intermediate temperature SOFCs. On the fuel electrode, percentages of both Ru and Ni have been substituted in order to allow exsolution of the reducible cations into metallic active sites for hydrogen adsorption.

In recent work, STF with other x values has been explored as an oxygen electrode, with the x = 0.7 confirmed to provide the fastest overall oxygen transport. STF characteristics in fuel environments (a variety of fuel-gas H₂/H₂O compositions), including stability of the perovskite phase, conductivity, and electrode polarization resistance. Stability against Fe exsolution is important to determine the range of fuel conditions that can be utilized in application. It is also of special interest because it helps to determine the composition of exsolved particles when dopant atoms such as Ni or Ru are added to STF. Conductivity is also of practical importance for electrode applications.

ALD-based surface area measurement technique

We have developed a novel method for measuring surface areas of materials with much higher sensitivity compared to conventional BET surface area measurements. Surface area determination is a characterization goal broadly needed, *e.g.*, in catalysis, to compare area-specific activity. However, for SOC materials, which are sintered complex ceramic oxides, typical specific surface areas are on the order of 1-10 m²/g with typical weights of ~10 mg per sample, resulting in absolute surface areas well below 1 m², a practical lower limit for conventional BET surface area measurements.

The new method is conceptually similar to BET, which uses gas physisorption to extract surface area, instead using self-limiting chemisorption of a chemical precursors used in atomic layer deposition (ALD). That is, ALD allows deposition of a known surface coverage over all the internal surfaces of a porous sample, and when the volume of the deposited species is ascertained either gravimetrically or, more sensitively, by digesting the ALD overcoat in a solution for measurement by plasma spectroscopy, an absolute surface area is obtained. Sensitivity is a factor of ~ 100 times higher than BET.

Infiltrated PrOx surface area loss over time

The above ALD-based surface area determination method is sufficiently sensitive to characterize nano-scale features present in state-of-the-art solid oxide cell electrodes. For example, electrodes with nanoparticles introduced through infiltration or exsolution are susceptible to coarsening at SOC operating temperatures. One infiltrated species in particular, PrO_x , has emerged as a compelling candidate for oxygen electrodes. Ionic scaffolds as well as mixed ionic/electronic

conducting (MIEC) scaffolds infiltrated with PrO_x have shown extremely competitive polarization resistances at low-intermediate temperatures (550°C). In a recent study,¹ coarsening was assessed qualitatively using STEM-EDS mapping. Here we have quantified coarsening by analyzing PrOx infiltration within lanthanum strontium manganite (LSM)/Gd-doped Ce (GDC) composite electrodes. Figure 2 shows the measured electrode surface areas over a 1000 h life test. The PrO_x surface area increase is readily detected. Furthermore, the decrease in surface area after 1040 h due to coarsening is observed. It is otherwise difficult to quantify such small changes in electrode surface area. The results also correlate well with observed changes in electrochemical characteristics observed during the life test. Carbon Capture Fuel Cell Vehicles



Figure 2. Specific surface area of the pristine LSM/GDC and the PrOx-infiltrated LSM/GDC at an early stage and after a later stage of aging. Results are shown for two different samples.

Although battery electric and hydrogen fuel cell vehicles hold great promise for mitigating CO₂ emissions, there are still unaddressed sectors for electrified transport, e.g., the heavy-duty and long-range global shipping industry. We have examined the viability of CO₂-neutral transportation using hydrocarbon or alcohol fuels, in which the CO₂ product is captured on-board the vehicle. This approach takes advantage of the unparalleled energy density of carbon-based fuels as needed for these energy-intensive applications. A concept is developed considering the power technologies, infrastructure, and fuels required. Storage volume and mass requirements are calculated for a wide range of vehicle types and compared with those for other CO₂-neutral options, namely hydrogen fuel cell vehicles (H2FCVs) and battery electric vehicles (BEVs). Efficiency is considerably improved over H2FCVs by avoiding the need to first convert such fuels to hydrogen and then compress and transport. As illustrated in Figure 3, the CO₂ captured on vehicles can be returned to a CO₂ distribution network where, after sequestration, the cycle is CO₂neutral for fossil fuels and CO₂-negative for biofuels. Another route, recycling the CO₂ back into fuel via electrolytic processes, is also possible. This so-called Carbon Capture Fuel Cell Vehicle (CCFCV) can function on a variety of fuels including hydrocarbons and alcohols. The key advantage of the solid oxide fuel cell is that it combusts fuels with pure oxygen, resulting in a CO₂/H₂O-rich mixture that is nearly sequestration ready (The water is easily separated from the CO₂ upon cooling the exhaust.) The total volume for a given fuel and pressure can be reduced by utilizing a single adjustable tank versus separate fuel and CO_2 tanks; moderate CO_2 pressurization to 250 bar results in storage volumes that are not much larger than that of fuels such as ethanol and diesel, and substantially lower compared to hydrogen or batteries.



Figure 3. Schematic illustration of a Carbon Capture Fuel Cell Vehicle (CCFCV) and associated infrastructure. The vehicle includes a solid oxide fuel cell (SOFC) for efficient electrical generation from hydrocarbon or alcohol fuels. Fueling is with any of biofuels, fossil fuels, or electrolytic fuels produced using renewable electricity. The captured CO_2 can be stored in a separate tank or in a unified tank with a movable partition, as shown, to minimize net storage volume. After offloading, the CO_2 can either be used in electrolytic fuel production or sequestered. Different infrastructure designs and fuel choices can yield an overall CO_2 impact ranging from mitigatory to net negative.

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Session IX

Light-matter interaction phenomena using subwavelength engineering of material properties

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Keywords: Metamaterials, nanophotonics, light-mater interaction, semiconductors, nonlinear optics

Research Scope

Nanostructured materials offer new opportunities to rewrite the laws of light-matter interaction as they are customarily applied to bulk materials. This project focuses on such emergent behavior, with an emphasis on metamaterials coupled to semiconductors. Our hypothesis is that nanostructured "meta-atoms" that tailor electromagnetic fields for desired interactions with judiciously chosen materials can lead to metamaterials and metasurfaces with new types of optical behaviors or with improved behavior for optical emission, nonlinearities, or response to external stimuli. Our efforts have been focused on two main themes. *Novel Light-Matter Interactions at the Nanoscale for Next Generation Nonlinear Metasurfaces* investigates the rich nonlinear optical physics that can be obtained when the unique electromagnetic behaviors of metasurfaces are combined with nonlinear materials.. *Ultrafast Spatiotemporal Phenomena in Metamaterials* explores novel transient behavior such as modulation, beam steering, and frequency conversion

that can be achieved through ultrafast spatial and temporal modulation of the meta-atom optical properties.

Recent Progress

1. Generation of Terahertz Waves using Nonlinear Semiconductor Metasurfaces: Previously, we used novel semiconductor metasurfaces to demonstrate large enhancements of second harmonic generation (SHG).¹ The "zero"-frequency counterpart of this second-order nonlinearity is optical rectification, where either nonlinear instantaneous material polarization or photocurrent is induced within the metasurface.

Metasurfaces can overcome the fundamental limitations of optical rectification in bulk materials for three reasons: 1) a metasurface can control the magnitude and orientation of the electromagnetic field vector; 2) an ultrathin metasurface layer can enhance light absorption; 3) the metasurface geometry can modify the transport of photoexcited charge carriers. We exploited both the metasurface photonic resonances and the resonant semiconductor material response (i.e. the interband transitions in semiconductors such as InAs and GaAs) to



Figure 1: Illustrations of THz pulse generation in: (*top*) nonlinear metasurfaces and (*bottom*) a nonlinear THz metalens that simultaneously generates and focuses THz pulses

control optical rectification and to maximize the nonlinear response.

Narrow-bandgap InAs has different wavefunctions in the ground and the excited states; thus, optical excitation induces instantaneous polarization in the crystal. When this effect, known as shift currents, occurs on a sub-picosecond timescale, the currents lead to radiation of terahertz (THz) pulses, which reflect the temporal dynamics of nonlinearities and enable a range of THz applications. Typically, this effect is overshadowed by the photo-Dember effect; however, our

investigations revealed that the nonlinear response caused by shift currents can become dominant in an InAs metasurface, i.e. the metasurface design enables activation and suppression of selected nonlinear processes through the metasurface geometry.² Consequently, the shift current nonlinearity allowed us generate remarkable THz pulses in a 130 nm thick InAs metasurface, exceeding the power produced by a 1 mm ZnTe crystal by 10 times.² Additionally, the activation of different generation mechanisms and control of the induced polarization allowed us to structure the THz beam; thus, our team became the first to generate reversed-polarity THz pulses using a thin InAs metasurface. We use this concept to develop and demonstrate a binary-phase proof-ofconcept InAs metalens that simultaneously generates and focuses THz pulses.²

2. Giant Nonlinear Optical Response Using Intersubband Polaritonic Metasurfaces: Plasmonic metasurfaces coupled to intersubband transitions (IST) where a resonant nonlinearity can be engineered, offer a giant *effective* nonlinear response. However, plasmonic or metallic structures



Figure 2: a) Schematic of an all-dielectric intersubband metasurface fabricated on top of a sapphire substrate. b) Formation of intersubband polaritons at ~ 70 THz in all-dielectric intersuband metasurfaces. The different curves correspond to metasurfaces with cylinders of different sizes. c) Experimentally measured SHG efficiency at ~ 8 μ m using an all-dielectric intersubband metasurface.

are traditionally not preferred for nonlinear optics because of their higher losses and lower damage thresholds. Additionally. the evanescent coupling mechanisms also significantly limit the ability to control the light-matter coupling strength because fields decay exponentially from the surface of the photonic structure. Thus, we Mie-type explored using semiconductor metasurfaces to realize intersubband polaritonic metasurfaces. Mie-type

semiconductor metasurfaces have lower loss and higher damage thresholds, and offer the ability to support modes with a diverse spatial distribution of electromagnetic fields, polarization, and field enhancements, making them extremely attractive for nonlinear optics, as they offer many degrees of freedom for optimizing the nonlinear response.

To that end, we first developed Mie metasurfaces where the InGaAs/AlInAs quantum wells (QW) that support quantum-engineered ISTs are embedded within individual semiconductor resonators (Figure 2.a). Using this new type of semiconductor polaritonic metasurface, we achieved a first-time demonstration of a strong-light matter interaction and the formation of intersubband polaritons in a semiconductor metasurface, with tunable Rabi splitting as large as $\sim 10\%$ (Figure 2.b). We also demonstrated that the strength of light-matter coupling can be controlled, either through the design of the semiconductor heterostructure or by optimizing the Mie resonator to support Mie photonic modes with different spatial distributions of the out-of-plane polarized electric fields.

Next, we utilized the novel semiconductor polaritonic metasurfaces to enhance nonlinear generation efficiency by designing the heterostructure such that two asymmetric coupled QWs support two ISTs at 4 μ m and 8 μ m (i.e. equally separated in energy) and utilized the metasurface for SHG.³ The asymmetric-coupled QW design helped us to break the inversion symmetry and maximize the transition dipole moments to generate a gigantic second-order material nonlinearity $\chi^{(2)} \sim 200 \text{ nm/V}$. Since the only non-zero component of the $\chi^{(2)}$ tensor in these heterostructures is $\chi_{zzz}^{(2)}$, we designed the semiconductor resonators to support a magnetic dipole (MD) mode that induces relatively large field enhancement for the *z* component of the electric fields to increase the coupling of pump light to the ISTs and maximize the SHG efficiency. Figure 2.c shows an

experimentally measured SHG efficiency of ~ 0.5 mW/W^2 for the novel metasurface, orders of magnitude higher than the previous state-of-the-art SHG efficiency for semiconductor metasurfaces.³

3. Generation of quantum light via spontaneous parametric down-conversion (SPDC) using

nonlinear semiconductor *metasurfaces*: conventional In nonlinear crystals and waveguides, parametric down-conversion processes require strict momentum involved conservation for the photons, which strongly limits the versatility of the states that they produce. However, our subwavelength-thick metasurfaces relax the momentum conservation requirement. In addition. our photonic design of high-Q optical resonances in metasurfaces enhances the vacuum field with enhancements proportional to the 0 of the resonance. In metasurfaces, O-factors be can especially high for bound states in the continuum (BIC) resonances,⁴



Figure 3: a) Conceptual diagram of multiplexed entangled photon resonances in metasurfaces enhances the vacuum field fluctuations at certain wavelengths, with enhancements proportional to the Q of the resonance. In metasurfaces, Q-factors can be especially high for bound states in

which are discrete-energy modes whose energy levels overlap with a continuous spectrum of radiating modes. In symmetry-protected BIC metasurfaces, the outcoupling of radiation in the normal direction is forbidden by symmetry.⁴ Consequently, the quality factors of these modes can be infinite and could, in theory, infinitely enhance the spontaneous emission of photons and photon pairs. In practice, the enhancement is finite due to symmetry breaking (quasi-BICs) but can be still as high as 10²-10⁴. Using our semiconductor nonlinear metasurfaces, we showed a spectacular demonstration of these effects,⁵ showing that quasi-BIC resonances enhance both degenerate SPDC *and non-degenerate SPDC* (Fig. 3.a).

The semiconductor metasurfaces used in this demonstration⁵ were based on our 2018 photonic design,⁴ which breaks the symmetry of cubic-resonators by adding a perturbation to the cubical resonator (Fig. 3.b,c). Thus, this design creates quasi-BIC resonances that correspond to out-of-plane electric and magnetic dipole modes. Every time this metasurface is pumped at ½ of the quasi-BIC resonance wavelength, the rate of photon-pair generation is enhanced by 3 orders of magnitude compared to unpatterned films. More surprisingly, even when these metasurfaces are pumped at a different wavelength, we still observe non-degenerate photon pairs with wavelengths consistent with energy conservation (i.e. signal and idler) (Fig. 3d). Even detuning the pump by tens of nanometers, the efficiency of non-degenerate SPDC remains quite constant. We attribute this non-degenerate process to enhancements of the local density of optical states at either idler/signal wavelengths (or potentially both). Wavelength-localized enhancement of the SPDC photons can provide the basis for more complex quantum states ⁵ and this type of multiplexing highlights the uniqueness of nonlinear metasurfaces for quantum applications, because the effect has no equivalence in macroscopic nonlinear optics. These experimental results therefore open up immense discovery territory for fundamental studies in the area of quantum optical metasurfaces.

Future Plans

Our activities will proceed along the two main following directions:

i) Increasing efficiency of Spontaneous Parametric Down Conversion and enabling new degrees of freedom with new types of quantum optical metasurfaces (QOM): We aim to increase the efficiency and enable new functionality in quantum light by generating biphotons through parametric down-conversion from metasurfaces. To do so, we will develop new material approaches that will enable several orders of magnitude increase in photon pair generation rates and serve as a foundation for creating QOMs with new functionalities. In parallel, we will also leverage the capacity for metasurface resonances to control the polarization of far-field radiation to create quantum light sources with additional degrees of freedom, such as orbital angular momentum.

Theme 2: Tailoring metasurface-mediated light-matter interactions in sparse quantum dot systems: Following preliminary work done by our team over the past year, we propose to expand our research on embedding, with high spatial precision, local-droplet etched (LDE) quantum dots into metasurfaces and topological cavities, which enhance and control the local density of states (LDOS) at the emitters, enabling tailorable light-matter interactions. Moreover, this platform may offer multiple pathways for entangling light emission from QDs, while providing high brightness. **References**

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Metamaterials

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Keywords: Broadband metamaterial, Multi-resonant metasurfaces, Dark-state surface lasers

Program Scope

Metamaterials are artificial materials that enable the realization of novel optical properties unattainable in nature. This project explores the fundamental theoretical understanding, analysis, development, fabrication, and experimental characterization of metamaterials, and investigates their feasibility for innovative applications. Our work targets current, fundamental problems and opportunities in controlling light with matter and matter with light: We will enhance nanoscale light-matter interactions and overcome dissipative loss by coupling to quantum gain, enabling undamping of resonances, amplification, and coherent collective radiation, to devise novel lasers and coherent dark near-field sources. We will control radiation damping, manipulate the radiative electromagnetic vacuum seen by quantum emitters in metasurfaces to obtain fundamental improvements to metasurface-based coherent THz sources and nonlinear photon energyconversion. We will overcome the inherent bandwidth limitations in resonant metasurfaces, creating arbitrarily large phase and group delay and potentially replacing bulk optics with surfaces. We investigate optical forces at the nanoscale for control of matter with light and create coherent opto-mechanical coupling, exploiting macromolecular mechanical and electromagnetic states in novel metallized DNA-templated meta-molecules. The proposed work will expand our physical understanding of the interaction of light with both classical and quantum matter and will facilitate further development of modern metamaterials. It aligns with the 2007 BES Grand Challenge as well as the recent 2015 BESAC report on how to exploit coherence in light and matter, and leverages major theoretical and experimental expertise within the FWP and interdisciplinary collaboration between FWPs available at Ames Laboratory.

Recent Progress

Dark-state surface lasers: The quest for versatile subwavelength coherent light sources has led to the exploration of dark-mode based metasurface lasers, which allow for independent adjustment of the lasing state and its coherent radiation output. Here, lasing, i.e. stimulated emission into a macroscopically populated dark electromagnetic surface state, constitutes a dielectric analog of lasing into dark plasmon-polaritons and allows to design ultra-thin, large-aperture lasing dielectric surfaces, with control over directionality and shape of the out-coupled laser beam. We report a proof-of-concept dark-state metasurface laser fabrication, experimental demonstration, and characterization with our external collaborators in Finland. Our recent theoretical work suggests using direct lasing into dark surface states to construct surface-emitting lasers that conceptually allow for independent implementation of the lasing state and its coherent radiation output. We experimentally demonstrate lasing in dark resonant states of a metasurface laser and controllable coherent out-coupling of radiation with the aid of a tightly coupled, weakly

radiative metasurface. The laser is implemented using a thin, low-loss dielectric film supporting surface mode-like dark dielectric bound states and the coupling metasurface is composed of small nonresonant scatterers that controllably but weakly perturb the dark mode and turn it partially bright. We identify and demonstrate distinct far-field signatures that are observed experimentally for both dark and bright lasing. The scalability of our design, here implemented for lasing in the near-infrared, enables large-aperture ultra-thin coherent light sources with controllable emission from the infrared to the visible. [1]

Understanding coherent versus incoherent illumination in measurements of scattering amplitudes in metamaterials: The characterization of metamaterials relies on determination of scattering parameters like transmittance and reflectance. While, numerically, coherent plane wave scattering amplitudes for infinite perfectly periodic samples are readily accessible, experimental measurements necessarily involve scattering of possibly incoherent optical probes with finite-size illumination spots on finite sample surfaces that need to serve as a proxy for the true plane wave scattering amplitudes. In some situations, but not always, this difference can lead to substantially different observed scattering spectra. We analyze the observable effects on the measured scattering spectra originating from coherent versus incoherent optical probes, finite



Fig. 1: Experimental demonstration of dark-mode metasurface laser. For low pump (a,b) the luminescence footprint marks the dark mode parabolic dispersion. For strong pump (c,d) the excited states collapse into a single lasing dark mode; without the scatterer, for an infinite system the lasing mode should be completely dark, however due to leakage from the edges of the finite-size metasurface, dark mode lasing can be identified in the far-field as a double lobe pattern. With the scatterer present, the dark mode is controllably turned into bright, and lasing into the dark mode is identified in the far-field as a single lobe pattern due to intentional outcoupling.

illumination spot size, magnifying imaging systems, as well as beam shaping optical elements. We show the relation to the wave vector content of the illumination and the sample's spatial dispersion properties, and demonstrate that this can result in qualitatively significant deviations of observed scattering spectra from true plane wave scattering, which must be taken into account to understand experiments and allow comparison with simulations. [2]

Experimental achromatic multi-resonant metasurface for broadband pulse delay: Resonant response in metamaterials is desirable because it generates strong light-matter interaction, and enables negative response functions, required, e.g., for negative refractive index materials, that are not possible in non-dispersive materials. But, it also renders resonant metasurfaces inherently narrow bandwidth, a strong limitation for their usefulness with technologically relevant signals. By implementing multiple sharp resonances on a single metasurface, we can combine the strong delay of constituent resonances along with the broad aggregate bandwidth of the resonance ensemble, "tricking" the delay-bandwidth limit. Ensuring a spectrally constant group delay across the aggregate bandwidth, we can (in principle) achieve arbitrary delay of arbitrarily broadband pulses without distortion. We demonstrate experimentally a proof-of-principle achromatic time delay metasurface in reflection, fitting five resonant meta-atoms in a subwavelength unit cell to create an ultra-thin ($\lambda/19$) implementation of a constant-groupdelay broadband metasurface reflector. This highlights the practical potential of metasurfaces for applications that rely on large and broadband phase delays. [3]

Future Plans

Nanoscale light-matter interactions at THz wavelengths: We develop initial theory and simulations for deeply sub-wavelength, nanometerresolution THz SNOM-type Time-Domain Spectroscopy imaging experiments using the THz "nano-scope" instrument developed Jigang Wang's



Fig. 2: (top) Photograph and schematic design of the fabricated multi-resonant metasurface. (middle) Intercalated trains of electric and magnetic resonances in the effective sheet conductivities of the metasurface that enable broadband response and the 5π linear phase delay not possible with a single resonance. (bottom) The delayed, undistorted reflected signal pulse in time domain.

lab. It is particularly challenging to probe deep sub-wavelength electric field distribution (at length scales of 10's of nanometers) under electromagnetic wave coupling (100's of um wavelength) at individual nano-junctions and correlate them with structural imperfections from interface and boundary, ubiquitous in Josephson junctions used in transmon qubits. Conventional microscopy tools are incapable of measuring simultaneous at nanometer and terahertz, "nano-THz" scales, which often associate with frequency-dependent charge scattering in nano-junctions. Our goal is a comprehensive scattering and imaging theory that will allow a *quantitative* interpretation of these experiments. We further develop approaches to manipulating deeply subwavelength THz lightmatter interaction, radiation damping, and local near-field with metasurfaces as a means to enhance

nonlinearity and coupling to quantum processes in materials, enabling next-generation technology for sensing and THz generation.

Breaking the bandwidth limit with multi-resonant metasurfaces: We extend our theory on multi-resonant broadband metasurfaces to "beyond linear" phase modulation with broadband chirped metasurfaces for group-delay dispersion control and compensation. We demonstrate how ultra-thin metasurfaces with a specific multi-resonant response can enable simultaneously arbitrarily-strong and arbitrarily-broadband dispersion compensation, pulse (de-)chirping, and compression or broadening, overcoming the fundamental trade-off between conventional, non-resonant (bulky) and modern, singly-resonant metasurface (narrowband) approaches to quadratic phase manipulations of electromagnetic signals. We will further pursue broadband multi-resonant metasurfaces as general spatio-temporal "meta"- boundaries, which enable mode shaping and vacuum-matching in wave guiding applications, e.g., for phased arrays.

Functionalized output dark-state metasurface lasers: We further develop theory and darkstate surface laser designs to enable emission non-trivial beams, such as focusses emission without external lenses and direct coupling into surface modes, e.g., plasmons on graphene. In particular, to understand & control the spatial phase response along a realistic patterned surface, we will develop a simple theoretical model for co-scattering of dark surface modes and propagating radiated fields in dark-surface-mode/radiating-metasurface sandwich structures.

Resonant meta-atoms from metallized DNA-templated meta-molecules: We continue to understand metallized-DNA self-assembled meta-atoms; Characterization of orientational and spatial distribution-based disorder in realistic bio-templated surface structures. We study optical forces and opto-mechanical coupling in articulating metallized-DNA nano-resonators as non-trivial optical forces at the nanoscale for control of matter with light; create and exploit coherent opto-mechanical coupling mediated light-matter interaction. Understand non-periodic metasurfaces and limitations & benefits arising from spatial and morphological disorder, taking advantage of synergies with bio-inspired metamaterial fabrication.

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Overcoming Optical Selection Rules in Materials by Extreme Localization of Light Hayk Harutyunyan, Department of Physics, Emory University, Atlanta, GA 30322

Keywords: nanophotonics, metamaterials, nonlinear optics, ultrafast optics, materials physics

Research Scope

The main scope of this program is to study the new physical phenomena in light matterinteractions that arise due to the nanoscale confinement. Typically, the optical interactions in nanoscale materials are determined by the material composition and the geometric properties nanostructures. In this conventional approach, the quantum transitions and carrier dynamics are governed by the electronic structure of the constituent materials. Nanoscale modification of the material structure and geometry can add a new way of controlling electronic transitions due to e.g. carrier confinement or carrier injection across heterogeneous interfaces. However, typically, the role of the specific properties of the optical modes are overlooked when studying the mechanisms of photo-assisted transitions.

The goal of this program is to study the optical properties adopting a different approach and try to control the light-matter interactions by manipulating the properties of the excitation light itself. To this end, we use nanostructured materials to design special interfaces and nanocavities with desired optical properties. These structures support optical modes with tunable spatial and

temporal parameters such as field enhancement and localization, field gradients and quality factors. By using optical spectroscopic methods we engineer and study fundamentally novel types of optical interactions at the nanoscale.

Recent Progress

One approach for achieving unprecedented control over the lightmatter interactions is centered on the idea of time-varying metasurfaces. In a recent work, we used amorphous Ge to fabricate semiconductor metasurfaces comprising of an array of sub-wavelength resonators. These structures form cavities trapping the excitation light with a resonant peak in the mid-infrared spectral region at ~3.3 μ m. Typically, the light matter interaction in the cavities are controlled by their geometric and



Figure 1.(a) Experimental change in transmittance for different pump-probe delay times. (b) Extracted carrier concentration as a function of time. (c) Experimental transmittance at $\tau = 0$ ps for various fluences. (d) Simulated data at $\tau = 0$ ps for the same fluence values as in (c).

material properties such the mode volume, cavity losses etc. However, using our approach of modifying the optical interaction by controlling the properties of the light itself we achieve unprecendented control of the ultrafast optical properties of materials.

We used ultrafast pump-probe spectroscopy where the femtosecond laser pulse at abovebandgap energies is used to modify the refractive index of the cavity by generating electron-hole plasma via single photon absorption. In such experiments, the ultrafast metasurface platform exhibits all-optical switching with a low activation power and high-contrast amplitude on femtosecond timescales, Fig .1a. The combination of such desirable characteristics in one optical nanosystem has been elusive so far. We have demonstrated a relative change in transmittance of $\Delta T/T \approx 1$ with picosecond (down to $\tau \approx 0.5$ ps) free carrier relaxation rates, obtained with very low pump fluences of 50 µJ cm⁻² (Fig 1(c), 1(d)). These observations are attributed to efficient free carrier promotion, affecting light transmittance via high quality-factor optical resonances, followed by an increased electron–phonon scattering of free carriers due to the amorphous crystal structure of Ge (Fig 1(b)).

Another interesting platform that was proposed by us to study the light confinement effects in the current project period was metal-insulator-semiconductor (MIS) systems. We have used these structures to explore nonlinear and ultrafast optical properties at the nanoscale. Interestingly, such geometries give rise to bound states in the continuum (BIC) which exhibit unusually narrow spectral quality factors. These tunable spectral features allow unprecedented control of light-

matter interaction such as harmonic generation or twophoton absorption. BICs are localized wave states that exist in the continuous spectral region but do not exchange energy with free space. This leads to infinitely high quality factors that can be attractive for variety of application including nonlinear optical labels and converters. Typically, demonstrating quasi-**BIC** resonances requires fabrication





of sub-wavelength resonators with a broken spatial symmetry to allow radiation leakage. The degree of asymmetry determines the coupling strength to free space enabling ultimate control over the quality factors of the resonance. However, the accurate control of the degree of asymmetry makes their fabrication very challenging. By employing MIS geometries we were able to demonstrate the emergence of BIC modes in symmetric Si nanopillars, without the need of inducing spatial symmetry breaking, Fig. 2 (a). The coupling of the magnetic dipole (MD) to its image in the Au mirror induces cancellation of far field scattering resulting in a BIC resonance. The evolution from ideal BICs to quasi BICs is controlled by metasurface-mirror distance or the size of Si pillars (Fig. 2 (b-c)) which are easily controlled in conventional fabrications, without need of the broken geometric symmetry. The resulting quality factors of the

resonances are more than an order of magnitude larger that typically observed in metallic and dielectric nanophotonic systems, Fig. 2 (d). The unique features of our photonic platform enable a record-breaking third harmonic generation (THG) efficiency from the metasurface benefiting from the strongly enhanced electric field at high-quality resonances, Fig. 2(e-f). We observe not only 7 orders of magnitude enhancement compared to an unpatterned Si film but also a record conversion efficiency compared to the state of the art.

Recently, phase-change materials have emerged as a novel platform for controlling the optical properties of photonic platforms. In particular, germanium-antimony-tellurium Ge₂Sb₂Te₅ (GST) alloy has proven to be a reliable material for tuning the optical properties via strong nonvolatile changes of the real and imaginary parts of the refraction index corresponding to amorphous-crystalline phase change. We have used these remarkable properties of GST to achieve tunability of the nonlinear response in photonic structurers and metasurfaces (Fig. 3. top). Using GST-based asymmetric Fabry–Perot cavity we have shown broadband-tunable third harmonic generation (THG). Similarly, by using GST-based hybrid metasurface featuring a gap-surface plasmon resonance we have demonstrated switching of second harmonic generation (SHG) by actively controlling the crystalline phase of GST (Fig. 3. bottom). Importantly, such approaches can be combined with ultrafast and compact heating processes using indium tin oxide (ITO) Joule heaters, providing electrical control of the optical properties of materials.



Figure 3. Tuning of the nonlinear signal in GST-based photonic systems. The dependence of the THG on the crystallinity of GST in Fabry-Perot cavities (top). The dependence of SHG on the crystallinity of GST in plasmonic metasurfaces (bottom)

Future Plans

In our future research, we will explore novel type of optical absorption processes in the presence of strong field confinement. On the example of intraband absorption in noble metals we aim to demonstrate that strong field gradients induce large-momentum transitions resulting in non-thermal hot electron distribution in metals. We will use nonlinear PL spectroscopy to study this effect which serves as a sensitive probe for excited state carrier distribution. The origin of the emission in plasmonic structures is typically attributed to energetic, or "hot", electron generation in metal conduction band leading to a radiative recombination process [1]. Thus, hotcarrier PL measurements serve as a sensitive tool for understanding the optical absorption mechanisms at the nanoscale. For excitation above the interband transition threshold, downconverted PL is known to result from recombination of sp conduction-band electrons with dband holes. When the incident photon energy is below the interband energy such as for NIR excitation, direct single-photon interband absorption is impossible necessitating multi-photon nonlinear absorption to observe PL. Indeed various studies on rough gold films have demonstrated this effect however the power-law-exponent observed in these works have ranged from 1 to 2, even including non-integer values [2-3]. This was attributed to enhanced plasmonic absorption leading to the formation of transient hot electron distribution which leads to the formation of equilibrated Fermi carrier distribution. However, no signatures of non-thermal carrier distributions have been observed so far. Unlike rough films, isolated single nanostructures can provide a better insight into the origins of physical mechanisms at the nanoscale by removing any potential averaging effects. To this end, studies on the origin of broadband

emission from single plasmonic structures such as nanoparticles have been indeed carried out, however the universal origin for the observed emission has remained inconclusive. While the dimensions of isolated colloidal particles can reach the limit needed to induce direct intraband transitions leading to non-thermal carrier distribution, their geometric properties can still show great variability masking the origin of the broadband PL emission. In our future research, we plan to study the nonlinear PL emission in precisely fabricated metal-dielectric-metal nanogaps, to controllably probe the degree and onset of the breakdown of dipole approximation leading to the formation non-thermal hot electron distribution.

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Study of modified Planck's law in both the near field and far field

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Keywords: Hyperbolic Phonon Polariton, Near-Field Energy Converter, Radiative Recombination, Thermoradiative Cell, Thin Films

Program Scope

For a semiconductor diode, the emission and absorption of photons with energies exceeding the bandgap energy are associated with the radiative recombination and photogeneration processes. From a thermodynamics point of view, the Bose-Einstein statistics need to be modified to include the photon chemical potential, which equals the difference between the quasi-Fermi levels of the electrons and holes. Consequently, the traditional Planck's law for spontaneous emission from a blackbody must also be modified to describe the electroluminescent processes, which are important for light-emitting diodes, thermoradiative (TR) cells, electroluminescent refrigeration, and thermophotovoltaic (TPV) systems. This project aims to study various practical semiconductor devices, including heterojunctions and degenerate semiconductors, for potentially improved performance. A comprehensive examination of the radiative recombination processes and "spontaneous" emission under nonequilibrium conditions (such as voltage biasing) will be carried out to better understand the interactions between photons and semiconductors. The proposed method will be used to study electroluminescent emission, for which only a few experiments exist that support modified Planck's law.

Recent Progress

Modeling radiative recombination is crucial to the analysis of radiative energy converters. Here, we use fluctuational electrodynamics (FE) to connect the external luminescent emission to a local radiative recombination coefficient. A thin-film InAs cell is modeled in free space as well as in a TPV setup with or without a back gapped reflector (BGR). The doping effect on the local radiative recombination coefficient of the cell is considered using an electroluminescence coefficient, which enables the distinction between thermal and nonthermal radiation above the bandgap energy. The effect of the electroluminescence coefficient on the performance of a TR cell is quantitatively examined.

Consider a near-field radiative energy converter shown in Fig. 1. The cell or active region receives incoming thermal radiation from both the upper and lower regions (denoted by A+ and A-, respectively). It also gives out photons through thermal emission (B+ and B-) and luminescent emission (C+ and C-). Depending on the temperature and voltage bias conditions, Fig. 1 could represent a power generator or refrigerator [1]. FE establishes the relation between the resulting electromagnetic field and the random fluctuation of charges at thermal equilibrium [2]. Considering a direct bandgap semiconductor, the emission may be divided into a nonthermal portion due to interband transitions (ib) that is affected by the chemical potential and a thermal portion due to other transitions, such as free-carrier transitions (fc) and lattice vibrations (la) [3]:

$$W(\omega, z') = \varepsilon_{\rm ib}''(\omega) \Psi(\omega, T, \mu) + \left[\varepsilon_{\rm fc}''(\omega) + \varepsilon_{\rm la}''(\omega)\right] \Theta(\omega, T)$$
⁽¹⁾



Fig. 1. Schematic of a thin-film radiative energy converter [3]. The cell or active region is on a substrate and separated with the upper region by a vacuum (or air) gap of distance d, which may be in the near or far field. The processes A, B, and C (along with the superscripts + and –) are explained in the text.

In Eq. (1), $\varepsilon'' = \varepsilon_{ib}'' + \varepsilon_{fc}'' + \varepsilon_{la}''$ is the imaginary part of the dielectric function, where the subscripts denote different contributions, $\Theta(\omega, T)$ and $\Psi(\omega, T, \mu)$ are the mean energy of Planck's oscillator and the modified expression considering a photon chemical potential μ . Note that ε_{ib}'' is nonzero only above the bandgap and the ratio $\phi(\omega) = \varepsilon_{ib}''(\omega) / \varepsilon''(\omega)$ is called the electroluminescence coefficient, which is less than unity for heavily doped semiconductors.

A near-field TR cell is considered by reversing the previously studied TPV-BGR configuration, as shown in the inset of Fig. 2(a). The emitter (consisting of the InAs film with a BGR structure) is fixed at 600 K, and the heat sink (made of tungsten with an ITO coating) is fixed at 300 K. The dielectric function of the cell is modeled using p-type InAs with a dopant concentration equal to the effective density of states of the valence band $(N_{\rm v})$ at 600 K. The luminescent emission and thermal emission spectra for a bias voltage $V = \Box 0.052$ V are shown in Fig. 2(a). The reverse bias voltage gives rise to a negative photon chemical potential: $\mu = eV = -0.052$ eV, corresponds to the maximum power condition of this TR device. The ideal assumption with $\phi = 1$ treats all the above-bandgap absorption as due to interband transition and overpredicts the luminescent emission. At a given frequency, thermal emission is scaled to $\varepsilon_{\rm fc}''(\omega)\Theta(\omega,T)$. The difference between the ideal and acutal luminescent emission is scaled to $\varepsilon_{fc}^{"}\Psi(\omega,T,\mu)$, which is smaller than $\varepsilon_{fc}^{"}\Theta(\omega,T)$ when $\mu < 0$ as in this case. Therefore, the sum of thermal and nonthermal emission with the actual ϕ exceeds the luminescent emission for $\phi = 1$ at certain frequencies. At the photon energy of 0.274 eV, corresponding to the bandgap energy at 600 K, thermal emission exceeds the electroluminescent emission. At the photon energy increases, the fraction of thermal emission goes down rapidly. This quantitiatively distinguished the abovebandgap thermal radiation from the luminescent emission. The total luminescent emission calculated with the ideal ϕ assumption is 7.4 kW/m², which is 11% higher than that with the actual *\u03c6* determined by considering free-carrier contributions. A comparison of the power density and efficiency at the operating point (based on maximum TR power output) are shown in Fig. 2(b). The assumption of $\phi = 1$ would cause more than 10% overprediction of both the maximum power density and the efficiency of the TR cell. Though the results are based on a structure that is not optimized for a TR application and some simplifications have been made in the calculations, the findings provide evidence of the effect of thermal emission with high dopant concentrations. Hence, the geometric and doping effects must be considered for thin-film near-field radiative energy converters [3].



Fig. 2. (a) The net spectral heat flux due to thermal and nonthermal emission for a TR cell configuration (inset), along with the net spectral heat flux with an ideal electroluminescence coefficient, and (b) Power density and efficiency as functions of the bias voltage [3].

In another project, we proposed an InSb-hBN TR device with a nanoscale vacuum gap down to 10 nm [4]. This device, as illustrated in the inset of Fig. 3, has the potential to achieve efficient waste heat recovery using solid-state technologies. The analysis is based on fluctuational electrodynamics considering photon chemical potential [5]. The spectral heat flux at the short-circuit scenario is shown in Fig. 3. There are two peaks due to hyperbolic phonon polaritons in the hBN film. The peak near 0.1 eV does not result in a significant heat flux. One the other hand, the peak between 0.17 and 0.2 eV is much larger and broader. This peak is located above the InSb bandgap energy of 0.11 eV at 550 K. Hence, it creates a strong coupling between the interband transition in InSb and the hBN hyperbolic phonon polariton modes. The net heat flux is 18 folds of that between two blackbodies at the same temperatures, and concentrated in a narrow band .

The performance of such a near-field TR device is evaluated with or without considering losses. For the ideal case without nonradiative losses, as the negative bias being built up by thermally driven emission, the output power exhibits a maximum value of 0.77 W/cm² when V = -0.042 V, and the corresponding efficiency reaches to 18.5%. When the magnitude (absolute value) of the increases, voltage bias the radiative recombination is suppressed due to the low concentrations of free carriers. Nevertheless, the emitted power is also suppressed. Therefore, the efficiency of the TR device reaches its maximum value of 36% at V =-0.124 V; this is almost 80% of the Carnot efficiency. The corresponding output power is 0.19 W/cm². The effects of nonradiative losses were also considered in this study [4].



Fig. 3. Spectral heat flux of the near-field TR device and two blackbodies with the same temperatures. The inset is the schematic of the TR device with an InSb emitter and hBN receiver [4].

Future Plans

Genetic algorithms and machine learning have also been extensively applied to design materials and micro/nanostructures with engineered properties as well as to optimize devices. The PI plans to use machine learning to design and optimize TPV and TR devices, along with electroluminescent cooling devices in both the near-field and far-field regimes. We have recently received a spectral radiometer that is transferred from another lab for measuring the directional spectral irradiation in the wavelength region from 1 to 6 µm, which is complimentary with our current Fourier-transform infrared spectrometer system. We will develop a temperature controlled stage to hold a semiconductor p-n junction and measure the emission spectrum as a function of current or voltage bias. In order to measure the absolute luminescent spectrum, comparisons with a high-temperature blackbody will be made and the emissometer facility. The blackbody spectra will be taken at various temperatures to calibrate the responsivity of the FTIR or the spectral radiometer. The absolute intensity emitted by the diode will be measured at each wavelength. For an InGaAs diode, the emission peak is 1.55 µm wavelength. The spectral radiometer is mostly suitable. For an InSb diode, the peak wavelength will be located around 10 µm, which is covered by the FTIR emissometer facility. Materials properties will be used to perform a comprehensive modeling that considers multiple reflection, total internal reflection, etc.

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Collective Energy Transport of Excitons in Two-dimensional Materials

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PROGRAM SCOPE

Collective behavior describes the rich physical phenomena that emerge in ensembles with large numbers of interacting particles. Such behavior goes beyond the independent particle picture that is commonly used to describe a vast majority of solid state physics phenomena, including the transport of quantized carriers of charge and heat in solids. While collective behavior gives rise to superconductivity at low temperatures, signatures of collective behaviors in both charge and heat transport appear at rather high temperatures in several recent studies of low-dimensional materials.

The thermoelectric figure of merit of excitons (bosonic) have been predicted to exceed that of electrons and holes (fermionic) due to the collective behavior of bosons. The formation of excitons (i.e., bound electron-hole pairs) is pronounced in two-dimensional (2D) materials, such as transition metal dichalcogenides (TMDCs), with exciton binding energies far exceeding $k_{\rm B}T$ at room temperature. Recent theoretical calculations suggest that inter-layer exciton-driven thermoelectric devices may have high thermoelectric figure of merits due to the spin degeneracy and valley degeneracy, which result in an increased entropy per carrier.

In this DOE-funded project, we explore thermoelectric measurements to obtain unique insights into the unusual collective energy transport behaviors of inter-layer excitons, which cannot be captured by electronic transport measurements alone. In particular, our exploratory device is based on the so-called "counterflow" measurement configuration illustrated in Figure 1b.



Figure 1. Schematic diagrams of (a) traditional *pn*-thermoelectric device and (b) counterflow interlayer exciton thermoelectric device suggested by Wu *et al.* (Physical Review Applied, 2, 054013 (2014)).

RECENT PROGRESS

During the current funding period, we have fabricated and tested several sets of exciton counterflow thermoelectric devices, as illustrated in Figure 2. This device fundamentally consists of a WSe₂/BN/MoSe₂ stack with separate bottom contacts to both bilayer WSe₂ and bilayer MoSe₂ as illustrated in Figures 2a and 2b. In a lateral temperate gradient applied by the heater, the bound interlayer excitons diffuse from hot to cold producing an *n*-type thermoelectric voltage in the MoSe₂ layer and a *p*-type thermoelectric voltage in the WSe₂ layer. By connecting these layers in series, as illustrated in Figure 2a, these thermoelectric voltages sum additively in the so-called "counterflow" geometry. The BN layer is necessary to prevent short circuiting between the two layers and enable the two thermoelectric voltages to be summed additively. However, the thickness of the BN layer is critical. That is, it needs to be thin enough to support stable interlayer exciton

formation yet thick enough to prevent quantum mechanical tunneling between the bilayer MoSe₂ and bilayer WSe₂. In addition to the WSe₂/BN/MoSe₂ stack, the actual device has top and bottom gates, i.e., graphene/BN/WSe₂/BN/MoSe₂/BN/metal, as illustrated in Figures 2b and 2c. These gates provide independent control over the charge density and type in the MoSe₂ and WSe₂ layers. Overall, this device requires 4 precisely-aligned transfers of the constituent 2D materials and 4 electron beam lithography steps. In addition, the main difficulties that have limited the device yield are associated with making low-resistance ohmic contacts to these 2D materials. In addition to global top and bottom gates, we have patterned individual gates for each electrode in order to improve the contact resistance.



Figure 2. (a,b) Diagrams and (c) optical microscope image illustrating the exciton counterfow thermoelectric device structure.

With a heating current (I) applied to the heater line, the temperatures of the two resistance thermometer lines are measured together with the thermoelectric voltage drop along the MoSe₂ sample. The measured thermoelectric voltage increases linearly with the temperature drop, as shown in Figure. 3c.



Figure 3. Measured thermometer temperature rises $\Box T$ (a) and thermoelectric voltage along the MoSe₂ layer (b) as a function of the heater current. (c) The measured thermoelectric voltage increases linearly with the temperature difference between the two thermometer lines.

For electrical injection of electrons and holes as bound exciton pairs into the $MoSe_2$ and WSe_2 layers, respectively, the chemical potentials of their respective metal contacts need to be aligned with the exciton energy levels, as shown in Figure 4a. This optimum biasing condition is searched in our experiments with the application of two voltage biases (V_h and V_e) of opposite polarities to the WSe₂ and MoSe₂ layers, as illustrated in Figure 4b. In this configuration, the top gate and bottom gate are grounded.



Figure 4. (a) Energy band diagram and (b) biasing conditions of the top gate/BN/WSe₂/BN/MoSe₂/bottom gate structure.

We use electrical transport measurements to understand the band alignments at different biasing conditions. During this measurement, a floating electrical current is used to measure the electrical conductance (\Box) of the MoSe₂ layer at different V_h and V_e potentials applied to the WSe₂ and MoSe₂ layer, respectively, see Figure 5a. A small kink appears in the line plots of Fig. 5b at V_e near -0.6 V, where the chemical potential (\Box_e) of the metal contact to MoSe₂ is expected to be near the conduction band edge (E_c). In addition, the MoSe₂ conductance starts to depend on V_h applied to the WSe₂ layer at V_h above about 0.6V, where the chemical potential (\Box_h) of the metal contact to the WSe₂ is expected to be near its valence band edge (E_v) for hole injection.

As shown in Fig. 5c,d, the magnitude (-S) of the measured Seebeck coefficient (S) initially increases approximately linearly as V_e is increased from -0.8 V to -0.6 V, where an abrupt increase in (-S) is observed when \Box_e is lowered below E_c . However, a peak amplitude is reached at V_e near -0.55V. For a semiconductor with approximately symmetric electron and hole bands, the S magnitude reaches a peak value and starts to change sign when the chemical potential is close to the midgap. Because the bandgap is well over 1 eV for MoSe₂ bilayer, it is unlikely that \Box_e is already reduced from E_c to the midgap when V_e is varied from -0.6 V to -0.55 V. Instead, the observed peak feature is attributed to the injection of electrons at states below E_c of the MoSe₂ layer. The peak magnitude increases as V_h is decreased toward 0.55 V to reduce hole injection into the valence band of the WSe₂ bilayer. Detailed measurements and theoretical analysis are currently employed to understand this observed feature and its relationship with excitonic transport.



Figure 5. Measured electrical conductance (a,b) and Seebeck coefficient (c,d) of the MoSe₂ layer at different biases V_h and V_e applied respectively to the MoSe₂ and WSe₂ layers.

FUTURE PLANS

Having solved many of the difficulties associated with sample fabrication, we are now poised to complete the measurement with full control over the top and bottom TMDC materials. This will enable us to bias and gate the device under conditions that are favorable for excitons to dominate the transport. During the next reporting period, we will continue this collaborative work to complete thermoelectric transport measurements of MoSe₂/barrier/WSe₂ heterostructures. This interlayer exciton structure enables us to evaluate Bosonic (i.e., excitons) thermoelectric transport as distinctly different from Fermionic (i.e., free electrons) thermoelectric transport.

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Molecular Heterogeneous Multiferroics

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Keywords: Magnetoelectrics, molecular crystals, magnet, two-dimensional materials

Research Scope

This project aims to explore a new class of molecular heterogeneous multiferroics towards room temperature stimuli-responsive magnetoelectricity by untangling the complex interplay between molecular magnets and molecular ferroelectrics. The hypothesis of this project is to test if the rational design and molecular engineering of hydrogen-bonded molecular heterogeneous multiferroics will enable rapid proton-transfer between molecular ferroelectric and magnetic components to control its ferroelectricity, magnetism, and intramolecular spin and dipole interactions, a promising pathway toward room temperature magnetoelectric coupling.

Recent Progress

1) Chemical-tuning Meets Two-Dimensional Molecular Magnets

Two-dimensional (2D) magnets that provoke a surge of interest in large anisotropy in reduced dimensions, promise for next generation information technology where dynamically magnetic tuning is essential. The 2D molecular hard magnets have been a long-standing missing member in the 2D magnet family, which is promising for next generation information technology due to its large anisotropy and saturation magnetization. Therefore, an intense effort has been explored in 2D molecule-based alternatives to conventional magnets. Until recently, the crucial metal-orgainc

magnet $Cr(pyz)_2 \cdot xLiCl \cdot yTHF$ with considerable high coercivity and hightemperature magnetic order opens up a new platform to control magnetism in metalorganic materials at room temperature.

We present the chemical tuning and exchange coupling to control roomtemperature magnetism in the 2D molecular Cr(pyz)₂·xLiCl·yTHF hybrid (LCPC) magnets.¹ Magnetic ordering temperature above 510 K and high anisotropy in LCPC magnet are resulted from the lithiation in the 2D layered $Cr(pyz)_2Cl_2$ redox-active precursor materials, on which we report the insitu electrochemical lithiation to dynamically control the degree of lithium coordination (Figure 1a). The lithiation control transforms the octahedral coordination of Cr into coplanar Cr-pyrazine framework, which forms the 2D layered structure with LiCl layer (Figure 1b). Besides, the movement of THF molecule allows the tuning of LCPC lattice during solvation and desolvation for further optimization of magnetism (Figure 1c). The above room-temperature magnetism



Figure 1. 2D molecule-based $Cr(pyz)_2 \cdot xLiCl \cdot yTHF$ (LCPC) magnet. a) Schematic of electrochemical lithiation of precursor $Cr(pyz)_2Cl_2$ shows lithium cations penetrate into octahedral Cr^{3+} coordination framework in a two-electrode electrochemical cell. b) Lithiated LCPC magnet features 2D layered structure consisting of LiCl and $Cr(pyz)_2$. c) The shematic of the solvation/desolvation of THF molecule in LCPC lattice. d) LCPC magnet with strong magnetism is attracted by permanent magnet.

originates from high lithiation level to reduce Cr^{3+} cations, while the desolvation of THF molecule controls the interfacial exchange coupling. The control of lithiation and solvation in the coordination networks enables LCPC magnet for a high coercivity (H_c) of 8500 Oe (Figure 1d), and a high saturation magnetization of 28 emu/g.

Figure 2a illustrates the control of the coordination structure on the spin configuration of Cr cation. The initial octahedral Cr^{3+} cation in $Cr(pyz)_2Cl_2$ precursor is coordinated with two Cl atoms and four N atoms from pyrazine molecules, presenting a magnetic order below. After lithiation, Cr^{3+} is reduced to Cr^{2+} cation, leading to a coplanar framework with four pyrazine molecules and the occupancy of four Cr 3d orbitals (d_{yz} , d_{xz} , $d_x^{2-y^2}$ and d_z^2). Due to the reduction from Cr^{3+} (t_{2g}^3 , S=3/2) to Cr^{2+} ($t_{2g}^3e_g^1$, S=2), the ferrimagnetic coupling between chromium and pyrazine is shown to achieve room-temperature spin order and high coercivity/magnetization.^{2,3} The control of magnetic performance is realized by tuning lithium stoichiometry through both electrochemical and chemical lithiation reactions. The origin of room-temperature magnetism in LCPC magnets lies on the reduction of Cr cation from Cr^{3+} to Cr^{2+} during lithiation process which is evidenced through X-ray photoelectron spectroscopy (Figure 2b-2c) and cyclic voltammetry measurements.

The deconvolution of XPS curves separates the contributions from Cr³⁺ and Cr^{2+} in Cr 2p3/2 peaks of precursor and LCPC. From the fitting results, Cr²⁺ shows a larger proportion of 54.2% in LCPC than 29.5% in the precursor, indicating the reduction of Cr^{3+} into Cr^{2+} . Figures 2d and 2e present the magnetization as a dependence of magnetic field and temperature (M-H & M-T), respectively, with an increasing the nominal ratio x of lithium to chromium. The saturation magnetization $M_{\rm s}$ is largely dependent on the lithiation (x = 0.17, 0.90) from 0.42 emu/g to 5.8 emu/g, while H_c is increased from 527 Oe to 2638 Oe. The M-H loops show a pronounced increase on both $M_{\rm s}$ and H_c at x = 1.46 and 2.92 (Figure 2d) with 18 emu/g and 8500 Oe, while T_c is increased to above 510 K (Figure 2e). The magnetic performance of H_c and T_c are summarized in Figure 2f by increasing lithium stoichiometry x, confirming the lithium stochiometric effect on magnetic properties of LCPC magnet.



Figure 2. Lithium stoichiometric effect on magnetic properties of Cr(pyz)₂·xLiCl·yTHF (LCPC) magnet. a) The octahedral Cr³⁺ cation is reduced to coplanar Cr²⁺ with spin configuration transformed from $(t_{2g}^{3}, S = 3/2)$ to $(t_{2g}^{3}e_{g}^{1}, S = 2)$. b-c) The deconvolution of XPS curves were conducted to separate the contributions from Cr^{3+} and Cr^{2+} in Cr 2p3/2 peak. d) Magnetization versus magnetic field curves of LCPC magnets exhibit the growing magnetic hysteresis loops as increasing lithium nominal stoichiometry x (atomic ratio of lithium to chromium) through electrochemical lithiation (x = 0.17 and 0.90) and chemical solvation (x = 1.46 and 2.92). e) Temperature dependent magnetization presents transition temperature is tunable up to over 510 K by an increasing lithium stoichiometry. f) The coercivity and transition temperature are summarized as the dependence of lithium stoichiometry x, indicating high-temperature magnetism

2) Proton Switching Molecular Magnetoelectricity

A reversible 29% magnetization control at ferroelectric phase transition is observed in such multiferroic heterogeneous macromolecule with a broad thermal hysteresis region of 160 K (between 192 to 352 K).⁴ More importantly, a room-temperature reversible magnetic modulation

is realized at a low electric field stimulus of 1kV/cm (Fig. 3a and inset of Fig. 3a). Based on these unique characteristics of macromolecular magnetic and ferroelectric building blocks, a new proton mediated magnetoelectric (ME)coupling mechanism is proposed. As shown in Fig. 3b, the electric dipole of molecular ferroelectrics can be switched by external electric field, which can interact with protons in molecular electrostatically. magnet This electrostatic interaction together with the coupling of proton with magnetism in molecular magnet enables the ME coupling in molecular heterogeneous multiferroics.



heterogeneous solid. a, Selected multiferroic composites. Processing temperature is plotted against the driving field (ferroelectric coercivity), as technological important parameters. The low driving field in this work results from the primarily non-covalent bond (i.e. hydrogen bonding) in molecular ferroelectrics which is weaker than the strong ionic/covalent bonds in polymeric and inorganic ferroelectrics. Inset shows the schematic figure for the free energies of molecular, polymeric and inorganic ferroelectrics. b, Schematic diagram for the proposed proton mediated ME coupling in molecular heterogeneous solid.

Temperature dependent magnetization and dielectric measurements (Fig. 4a) show the coupling between the dielectric and magnetic order parameters in the IM-VH heterogeneous solids. This is manifested as a distinct 29% decrease in the magnetization at the first-order structure transition of molecular ferroelectric phase (232 K). In contrast to the sharp change in magnetization during the cooling process, the magnetization of IM-VH shows a step-like transition with a broad thermal hysteresis width of 160 K (from 192 K to 352 K). The transition is repeatable as shown in the first and third cycle temperature dependent magnetization measurement results. Temperature dependent dielectric measurement further suggests the role of protons on magneto-dielectric coupling in IM-VH. As shown in Fig. 4b, the dielectric transition shifts to a higher temperature with increasing magnetic field while decreasing the dielectric constant. To provide a mechanistic understanding of magnetoelectricity in IM-VH heterogeneous solids, we further examine temperature dependent Raman spectra on the C≡N stretching modes (Fig. 4c), which are sensitive to the bonding mode of the cyanide and to the valance state of the metallic ions coordinated to the C≡N bridge. We observe such mode shifts to a high frequency from 200 to 290 K. More importantly, a significantly pronounced shift is observed at the dielectric and magnetic transition region. The Raman spectra indicates that an interfacial interaction induced charge transfer effect has occurred in the metallic ions coordinated C=N bridge. A proton mediated ligand-metal charge transfer is proposed here to illustrate such an effect. The interfacial interaction between IM and VH ensures that the surface electric field effect of IM could be effectively applied to the VH phase. According to the literature, such surface electric field of ferroelectrics could reach up to 1V/nm⁵, coupling the dipole of IM and protons of VH. The VH is surrounded by IM phase under ferroelectric field effect (Fig. 4d). During the cooling process, the dipole order is disrupted in IM at 232 K with a first-order phase transition which would induce the proton charge transfer and structure distortion of VH, causing an abrupt magnetic transition. As shown in Fig. 4e, a metastable weak magnetization state can be created. This state is not stable and can be reversed back through thermal induced transition close to T_c (Fig. 4f). In addition, lithium-ion control of magnetism study shows that the control of magnetism based on electrochemical redox reaction requires a long switching time (over 1,000 s) as shown in Fig. 4g. The short switching time via proton compared

with other ionic control could result from its small-sized Proton mediated proton. coupling between dipole of IM and protons of VH suggests the possibility of electric field control of magnetism at room temperature. As shown in Fig. electric field 4h. tuning coercivity of IV-VH through proton transfer shows a strong electric field dependence and anisotropic characteristics. A large coercivity change of around -45% is obtained at a low field of 4 kV/cm. The electric field tunable coercivity suggests field-controlled electric magnetism at room temperature (Fig. 4i) in proton mediated IM-VH heterogeneous solids.

Future Plans

The future plan focuses on molecular multiferroic orders of molecular heterogeneous materials, consisting of high temperature molecular ferroelectric and magnetic building blocks with the control



Figure 4. Proton mediated ME coupling. a, Temperature dependence of magnetization (M) at 10 Oe and dielectric constant (1kHz) for IM-VH. b, Temperature dependence of dielectric constant (1kHz) at different magnetic fields for IM-VH. The inset shows the measured pyroelectric current during the cooling process. c, Temperature dependence of Raman shift for IM-VH. The inset shows the Raman spectra for IM-VH at 200 and 240 K, the smooth lines are fitting results. d-f, Schematic diagrams for proton mediated strong coupling between dipole of IM and magnetism of VH. g, Lithium-ion battery control of magnetism of VH. h, Room-temperature angle dependence of coercivity change for IM-VH solid at different electric fields. 0° means that the applied electric field is parallel to the magnetic field. The x-axis shows the angle value between the applied magnetic field and magnetism for IM-VH.

of their ionic tuning. The detailed experimental plan includes:

1) Molecular heterogeneous magnetoelectric material growth with the control of material composition and structure;

2) Study chemical ion-controlled magnetism and polarization of molecular magnetoelectrics;

3) Mechanistic understanding of ion mediated magnetoelectric coupling properties in molecular crystals.

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Understanding the Role of Defects to Accelerate Wadsley-Roth Niobates for Long-Duration Energy Storage

Morgan Stefik, University of South Carolina (Principal Investigator) Hanno zur Loye, University of South Carolina (Co-Investigator) Christopher Sutton, University of South Carolina (Co-Investigator) Ming Hu, University of South Carolina (Co-Investigator) Scott Misture, Alfred University (Co-Investigator) Keywords: Wadsley-Roth, Niobate, Battery, Diffusion, Transport

Research Scope

We are developing systematic design guidelines for Wadsely-Roth (WR) niobates that connect composition and disorder/defect tailoring to transport mechanisms and properties with the aim of enabling extremely durable batteries. The Long Duration Storage Shot aims to decrease energy storage costs by 90% in the next decade, where a 10x increase in battery lifetime enables this lifetime cost target. The classes of materials with the potential for extreme durability minimize strain upon intercalation (C1), avoid first order phase transitions (C2), operate within the stability window of typical carbonate electrolytes (C3), and exhibit excellent ionic and electronic transport characteristics to minimize or eliminate the need for additives (C4). Many niobate intercalation materials satisfy criteria C1-C3, specifically the rich diversity of XaNbbOc WR phases. WR niobates are the ideal platform for understanding and tailoring ionic and electronic transport mechanisms since each occurs within distinct intrinsic crystalline regions (ion transport along blocks and electron transport along shear planes). For example, trial-and-error experiments identified Nb₁₆W₅O₅₅ with remarkably high ionic and electronic conductivities (C4) that led to state-of-the-art power and energy densities. Going beyond equilibrium phases, recent examples show the potential of tailored disorder/defects to enable enhanced conductivities in WR niobates. A clear knowledge gap is understanding the connections between composition, disorder, and defects upon transport. The study of defects within WR phases, however, has been broadly limited by the complexity of addressing disorder in both atomic structure characterizations and transport modeling. Furthermore, there is a historic challenge of ambiguity in transport measurements due to a lack of access to tailored porous architectures that can be examined one-variable at a time. Our methodology includes two approaches for modifying transport: 1) prediction and discovery of new equilibrium WR phases (X_aNb_bO_c and X_aY_bNb_cO_d) and 2) non-equilibrium tailoring of disorder/defect chemistries including grain boundaries, substitutions, and vacancies. This work includes inverse design where machine learning (ML) accelerates experimental work by identifying promising new WR compositions. Diverse synthetic methods are being used to realize

these phases with diverse defect structures that may enable novel transport mechanisms. The inclusion of comprehensive atomic structure characterizations and systematic transport measurements that deconvolve ionic and electronic constraints will enable multiscale transport modeling that connects transport characteristics to the underlying disorder/defects chemistries.

Recent Progress

The present experimental work is focusing on understanding how disorder/defects (Misture) in known WR phases (Nb₁₆W₅O₅₅ and TiNb₂O₇) affect transport properties (Stefik). Importantly, tailored porous architectures are being synthesized to remove ambiguity when analyzing convolved transport processes.^{1,2} We have developed a synthetic route to achieve the Nb₁₆W₅O₅₅ composition with block polymer templates. Much recent experimental activity has focused on the high temperature stability of these nanostructures during the crystallizing of WR phases which

typically form between 800-1,100 °C. Whereas this porous oxide tends to collapse below 800°C, we have found improved thermal stability after integrating carbon precursors which *in situ* form a hard scaffold that supports the nanostructure at high temperatures. Several alternative routes to support the oxide nanostructure during crystallization are currently being examined. Separately, the synthesis of micron scale particles of these two niobates are being developed using a spray drier with subsequent thermal crystallization. Since this synthetic route is not nanostructured, it is not subjected to challenges of thermal collapse and is thus a generalized low-risk strategy for these studies. To date, the spray drying efforts have yielded TiNb₂O₇ particles after crystallization with XRD patterns consistent with this well-known WR phase. The spray dried particles are suitable for initial studies of transport characteristics while the nanostructured analogs continue to be refined.

Initial computational work is seeking to identify new WR compositions (Sutton) and understand their transport characteristics (Hu). In our project, we are using computational highthroughput screening (HTS) to quickly evaluate many new possible compounds for stability before synthesis. Our starting point was a compilation of Nb-oxide based WR crystal structures reported in the literature, resulting in a set of 9 compounds with different formulae. A large chemical space was generated from these compounds by replacing the cation sites of the known compounds with 33 elements chosen for their likely oxidation states and coordination environments. This led to 2,326 new compounds that are currently being evaluated for stability using density functional theory (DFT). Of these 2,326 new compounds, only 20 are tabulated in the Materials Project database, 12 of which are stable within 100 meV of the convex hull. As likely new WR niobate compounds are identified, they will be validated first by solid state synthesis (zur Loye) before examining transport and defect characteristics later in detail. Our computational efforts are also presently seeking to understand the transport characteristics of WR Nb₁₆W₅O₅₅ for comparison to previously reported transport studies.

Future Plans

The short term future plans for the rest of the first project year are as follows. Stefik is continuing to develop diverse synthetic methodologies for $Nb_{16}W_5O_{55}$ and $TiNb_2O_7$ to enable transport and defect studies within the first project year. A 16 channel battery cycler was delivered in January which will accelerated these upcoming electrochemical studies. Misture is applying for synchrotron and neutron beam time at national facilities to support defect measurements for this project in the coming months when his new postdoc becomes available. Zur Loye is testing the solid state synthesis of a library of possible WR niobates that are continuously being identified by Sutton. Zur Loye is then providing these compounds to Stefik for electrochemical screening to see if they are suitable for further study. Sutton is continuing HTS of candidate WR compositions, focusing on ternary (XNbO) compounds before elaborating to more complex quaternary compounds. Hu is continuing to model lithium transport in Nb₁₆W₅O₅₅ computationally as a testbed before examining transport in the same phases with deliberate addition of defect structures that mimic experimental conditions.

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Publications

Not applicable yet.

Fermi Surface Tuning of MX₂ Compounds for Hydrodynamic Transport **Fazel Tafti**

Electron hydrodynamics, Electron-phonon coupling, Fermi surface, Transition-metal tatralides **Research Scope**

The project's goal is to achieve a hydrodynamic regime of electron transport in solid-state materials. The fundamental design principle is to grow crystalline materials in which the momentum-conserving scattering rates (el-el and phonon-drag) exceed the momentum-relaxing scattering rates (defect scattering and umklapp phonon scattering). Only then, could the hydrodynamic regime replace the conventional diffusive regime of electronic transport in metals [1,2].

Hypothetically, the momentum-relaxing mean free path Figure 6: Fermi surface of MX_2 compounds can be dramatically increased via an interplay of four factors: short metallic bonds, phonon-drag effect,

topological band structure, and correlations. Over the past six months, the PI has focused on the short metallic bonds and phonon-drag effects in transition-metal tetralides (MX₂ compounds in Fig. 1), where evidence of a strong electron-phonon coupling has been found by his group [3]. The coupling between electrons and phonons can be modified by systematically tuning the electron and phonon band structures, which is achieved in the MX₂ family, where M and X are transitionmetal and group IV (tetralide) elements. Transport experiments were performed both at the PI's lab and at the National High Magnetic Field Laboratory (NHMFL). One student has been trained on the project. She has calculated the Fermi surfaces of MX₂ systems shown in Fig. 1 and performed the quantum oscillation measurements discussed in the next section.

Recent Progress

High-quality crystals of four MX₂ compounds (NbSi₂, NbGe₂, TaSi₂, and TaGe₂) were grown by the PI's student and characterized at both BC and NHMFL. The in-lab resistivity data in Fig. 2 show extremely low residual resistivities in all four samples indicating negligible impurity scattering in the high-quality crystals.

These crystals were taken to the NHMFL at Tallahassee for de Haas-van Alphen measurements of quantum oscillations. A summary of the Fourier transform of quantum oscillations at different temperatures are presented in Fig. 3a. These data were then used to (i) confirm the calculated Fermi surfaces (Fig. 1) from DFT, and (ii) extract the effective mass of electrons. Figure 3b shows two different behaviors between the silicides and



Figure 7: Extremely small residual resistivity in four MX_2 crystals grown by PI's group.

germanides. In the silicide materials (NbSi₂ and TaSi₂), The experimental effective masses are comparable to the value computed by DFT and do not show any frequency dependence. In contrast, the experimental effective masses in germanides (NbGe₂ and TaGe₂) are at least three times larger than the calculated values and increase with increasing Fermi surface size (proportional to the oscillation frequency). Since DFT calculations use a non-interacting single-particle model, the enhanced effective masses are likely due to strong electron-phonon coupling in the germanide



with M = Nb, Ta and X = Si, Ge.

systems. Such a strong el-ph coupling has been proposed as a mechanism of electron hydrodynamics [2].

The field dependence of quantum oscillations (not shown here) can be used to extract the quantum lifetime of charge carriers in MX_2 compounds. We found this tunable system as an excellent platform to modify both electron and phonon band structures, and enhance the momentum-relaxing mean free path to achieve a hydrodynamic regime. A manuscript is currently under preparation to summarize these effects and explain how tuning the Fermi surface alters the details of el-ph coupling, effective mass, and quantum lifetime.

Future Plans

The next step is to go beyond the el-ph interactions and understand the effect of el-el interactions on the transport properties of highly conducting metals. To this end, the PI has identified a



Figure 8: (a) Fourier transforms of the quantum oscillations in MX_2 systems. (b) Effective masses of carriers extracted from a Lifshitz-Kosevich fit to the temperature dependence of quantum oscillation amplitudes as a function of temperature.

magnetically ordered material FeP, which has a Néel temperature of 120 K and residual resistivities comparable to MX₂ compounds. Single crystals of FeP has been grown via chemical vapor transport. A new student is being trained to look into details of transport measurements in that system. Also, the PI is sending crystals of both MX₂ and FeP compounds to his collaborator, Dr. Philip Moll at the Max-Planch Institute (Hamburg), for the fabrication of mesoscopic devices which will then be characterized at BC.

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Publications

A manuscript is under preparation currently.

Probing the Distribution of Plasmonic Hot Carriers via Single Molecule Quantum Transport

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Keywords: Plasmonics, Hot Carriers, Single-Molecule Junctions, Charge Transport

Research Scope

The efficient generation of non-equilibrium hot carriers in plasmonic nanostructures holds promise for the development of a range of emerging energy-related applications, including catalysis, solarenergy harvesting, and photodetection.^[1-4] Despite the rapidly growing interest in utilizing plasmonic hot carriers for clean-energy applications, deep understanding about the formation of these non-equilibrium hot carriers has been hampered due to technical difficulties in directly characterizing their spatial and energy distributions at the nanoscale. The overarching goal of the proposed research is to experimentally probe and understand the steady-state spatial and energy distributions of plasmonic hot carriers generated in noble metal plasmonic nanostructures (PNs). Our research is motivated by the hypothesis that single molecules with appropriate transmission

characteristics can act as efficient energy filters (and sensors) to access plasmonic hot carriers generated on the surface of a noble metal PN.^[5] Therefore, the steadystate distributions of plasmonic hot carriers can be probed via measuring charge transport through single molecules deposited on the PN surface (Fig. 1). We aim to develop an experimental platform that combines scanning tunneling microscopy (STM)-based quantum transport through single molecule junctions with nanoplasmonics excitation method to systematically investigate the steady-state hot carrier distributions in PNs. It is also important to understand the impact of PN material and geometry on the hot carrier distributions. In this



Figure 1. a) Schematic illustration of the STM-based single molecule transport measurements for probing hot carrier distributions on a PN surface. b) Energy profiles of the single molecule junction in a with (top) and without (bottom) plasmonic excitation.

project, STM break junction technique^[5-6] will be employed to construct PN-molecule-tip tunnel junctions and quantify electrical current contributed by hot carriers flowing through single molecule junctions (Fig. 1b). This novel experimental platform will provide detailed insights into the generation of hot carriers in a variety of plasmonic systems and further boost the development of plasmonic hot carrier-based technologies for energy conversion and harvesting.

Recent Progress

As a new research lab founded amidst the COVID-19 pandemic in 2021, we have brought on board two graduate students who have been heavily involved in our initial research outcomes. We have made progress in three research thrusts despite the impacts due to COVID-19 on delay of instrument delivery, visa processing, and hiring and training of personnel.

The first thrust focus on developing an experimental platform for stable and repeatable single molecule transport measurements on the noble metal surface (eventually the PN surface). We developed and implemented a custom-built STM break junction (STMBJ) platform capable of stably trapping single molecules between STM tip and the metal substrate for charge transport measurements. We performed single-molecule conductance measurements on a variety of analyst molecules, including alkanethiol molecular series, to verify the stability of the system. Single-molecule junction stability was also tested with additional mechanical manipulation of the tip position (compression and elongation). For all molecules tested, we observed excellent junction stability (<1 angstrom drift for the period of 800ms) and that the tip location can be mechanically controlled with angstrom-level precision, which is critical for subsequent measurements. The junction length agreed well with the molecular length, indicating a robust characterization of single-molecule transport.

The goal of the second thrust is to identify and characterize molecular candidates with



Figure 2. a) Schematic of the STMBJ setup. b) Structure of the open shell conjugated oligomer systems. The red circles at the two terminals of the molecule are the chemical linkers for forming covalent bond between the molecule and the gold electrode. c) 1D (left) and 2D (right) conductance histograms for the oligomers with n=3. d) 1D (left) and 2D (right) conductance histograms for the oligomers with n=6. e) The conductance response of single oligomer (n=6) showing 100-fold conductance enhancement upon mechanical compression.

suitable transmission characteristics for accessing hot electrons and hot holes. To serve as an efficient energy filter, only molecules with a sharp transmission resonance close to the Fermi level of the metal PNs are suitable for this research. We designed and characterized a group of open-shell conjugated oligomers composed of donor-acceptor units in the monomer structure (Fig. 2b). From our single-molecule measurements, unprecedentedly high conductance (~1E-1.5G₀) was observed over a wide range of molecular length. The observed high conductance is a good indication that the molecules possess a transmission resonance close to the Fermi level of the gold electrodes, making them suitable for this study. One crucial advantage of the molecular systems reported here is that the charge transport has a rather weak dependence on the molecular length. As shown in Fig. 2c and d, the conductance of such a molecular system has an ultra-efficient charge transport across a molecular length. Such unique transport properties are ideal for probing plasmonic hot carriers as it allows one to decouple the potential plasmonic excitation on the STM tip by performing the transport measurements when the STM tip is placed relatively far (>5nm) from the PN surface. This helps to isolate the contribution of hot carriers generated on the

PN substrate. The ability to further tune the transmission of the molecule is also important. As shown in Fig. 2e, we further demonstrated that delicate mechanical perturbation (sub-nanometer compression) of the molecular conformation could enhance the molecular conductance by almost 100-fold. This is attributed to the shift of molecular transmission resonance even closer to the gold Fermi level. Such ability to fine tune the transport properties under low junction bias will help us access hot carriers at different energy levels in the subsequent studies of this project.

The third thrust focuses on the fabrication of noble metal plasmonic nanostructures and integrating them into the STM setup for single molecule transport studies. Given the limited scanning area of a STM tip and the need for optical access, it is critical to fabricate samples with desired noble metal plasmonic nanostructures covering a large area on a transparent conductive substrate. In this regard, we started with gold nanostructures and fabricated gold nanotriangle structures on ITO substrate using the nanosphere lithography method. The fabrication schematic is shown in Fig. 3a. We were able to produce of gold nanotriangle arrays covering large area (>20um x 20um) with controlled thickness on transparent ITO substrate. The fabrication processes were verified at each step with SEM and AFM characterizations. The results will serve as the basis for the planned studies of the single molecule quantum transport on various PN surfaces.

Future Plans

Building on the progress, we will continue pursuing the proposed activities. In Thrust 1, we will measure single-molecule transport properties under plasmonic excitation using the

identified molecular candidates. In Thrust 2. combining theoretical simulation and experimental characterization. we will continue to optimize and characterize new molecular for systems suitable the proposed study. In Thrust 3, we will continue to optimize the fabrication of large area gold plasmonic nanostructures in different geometries on ITO substrate. This will allow us to initiate Thrust 4 of the research which investigates the impact of PN geometries. We will integrate these nanostructures into STMBJ setup for systematic single molecule transport study under dark and illuminated



Figure 3. a) Schematic illustration of the nanosphere lithography technique. b and c illustrate the assembly of polystyrene nanospheres on ITO surface characterized by SEM and AFM, respectively. d) AFM image of gold nanotriangle arrays covering a large area of ITO substrate.

conditions. We will adopt both the *break junction* and *blink junction* methods. Meanwhile, we have started and will continue developing experimental approaches based on single-molecule thermoelectric measurement to probe local heating effect caused by plasmonic excitation, which is part of Thrust 5 of the project.

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Molecular Insights for Fine-Tuned Hydrogen Interaction Control: MXenes as a Model System

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Keywords: hydrogen, MXene, density functional theory, isothermal adsorption, kinetics

Research Scope

Greater insight into the variety of surface characteristics, which promote dissociation and recombination of hydrogen on a material surface and the behavior of subsurface hydrogen species, is key to lower energy pathways for the storage and release of hydrogen. MXenes are a recently discovered class of 2Dmaterials which have demonstrated potential as a hydrogen storage medium. The objective of this .⊆ Change ir research is to provide an in-depth analysis of the interactions between **MXenes** and hydrogen. Bv systematically evaluating the influential factors that are responsible for hydrogen binding, dissociation. and recombination in MXenes we can provide a greater understanding of how



Figure 9. Illustration highlighting methodologies for MXene tunability

these interactions can be controlled and manipulated. Utilizing a theory-guided experimental approach, we are systematically evaluating the most promising candidate features of Ti-based MXene materials to shed light on the nature and mechanistic behavior behind the interactions of hydrogen with these materials. Herein, we present preliminary results highlighting the theoretically predicted binding sites and spectroscopic signatures within Ti-based MXenes and the experimentally evaluated influence of particle size on hydrogen uptake kinetics in $Ti_3C_2T_x$.

Recent Progress

Based on first-principles density functional theory (DFT) calculations, we have carried out a systematic study on Ti_3C_2 derivatives (e.g. bulk, monolayers, multilayers, surfaces) related to hydrogen adsorption. To model $Ti_3C_2T_x$ MXenes (i.e. T_x represents surface terminations in MXenes) which are closely aligned with experimentally synthesized materials, $Ti_3C_2T_x$ which are F, O, OH-terminated are considered in DFT simulation based on PBE functional with the DFT-D3 Van der Waals energy correction description. Among the F, O, OH-terminated Ti_3C_2 monolayers, the O-terminated Ti_3C_2 monolayer is found to be the most energetically favorable, followed by F-terminated and OH-terminated. Our preliminary results predict hydrogen is likely stored in $Ti_3C_2T_x$ in two possible ways; 1) Kubas-type hydrogen molecules adsorbed on the surfaces/edges and 2) intercalated hydrogen atoms within the Ti_3C_2 lattices as shown in Figure 2.

From ab initio molecular dynamics (AIMD) simulation, the intercalation of hydrogen



Figure 10. Radial distribution function (RDF) results of Ti₃C₂T_x MXenes (left) and illustration of hydrogen interactions with Ti₃C₂T_x MXenes (right) with various termination groups

atoms within the lattice was evaluated when Ti_3C_2 edges are partially O-, F-, Cl-, OH-terminated and exposed to 1 atm H₂ gas at temperature range of 300 K – 500 K. In addition to latticeincorporated atomic hydrogen, AIMD simulations predict Kubas-bound hydrogen molecules at terminated edges as illustrated in other work. [1] As shown in Figure 2, these Kubas-type hydrogen molecules are generally present with an elongated H-H bond ~ 0.80 – 0.85 Å, in contrast to noninteracting or physiosorbed H₂ molecules with a bond length of ~ 0.72 - 0.75 Å. According to DFT-PBE-D3 calculations, intercalated H₂ molecules in Ti_3C_2 lattices and interlayers are not favorable, and only the intercalated atomic hydrogen atoms are energetically favorable. Based on DFT-PBE-D3 phonons calculation, the presence of these intercalated hydrogen atoms can be identified through the infrared (IR) spectra at frequency range ~ 1000 –1700 cm⁻¹, which is distinguishable from pure Ti_3C_2 lattice vibration modes that is below 800 cm⁻¹ as highlighted in Figure 3.



Figure 11. IR vibrational mode predictions in hydrogen incorporated Ti-C MXenes

In parallel to these theoretical efforts, wide а series of elements (i.e. group I, II. III. IV and VII) as an adatom on **MXenes** monolavers been have explored by means of DFT calculations. Based on our recent studies on adatom decorated on Sc₂C and Sc₂CO₂ monolayers, it is found that sparse adatoms on Sc₂C show stronger adsorption energies and less preference on the

adsorption sites compare to those on Sc_2CO_2 monolayer. The electron density of states (e-DOS) and band structures analysis indicates that the major contribution of electronic states around the Fermi level are from the MXene layer for the Sc_2C adsorption and the adatoms barely modify its electronic structure. While for Sc_2CO_2 monolayer, it is more susceptible to the adatoms, and significant changes and impurity states attributed to the presence of adatom around the Fermi level can be found. This implies that single atom adatom could be a plausible route to manipulate surface chemistry of MXene monolayer, especially for the oxygen-terminated functionalized surface, such as Sc_2CO_2 .

 $Ti_3C_2T_x$ (where T is F, OH, or O) MXenes were produced with various particle size distributions. Isothermal adsorption measurements were carried out of the various particle sizes of MXenes to gain further insight into the diffusion pathways for hydrogen uptake (i.e. basal plane vs. edge



Figure 12. Isothermal absorption of MXenes with different particle sizes at 30 °C at 60 bar H₂ (left) and the particle size distributions of the MXenes evaluated (right)

preference). Preliminary data suggests a significant influence in uptake kinetics between MXene flakes with an particle size distribution center around 1 μ m versus MXenes which are smaller in flake size as shown in Figure 4. These MXenes demonstrate a reasonably high gravimetric hydrogen capacity of 2.0-2.5 wt. % at nearly room temperature (30 °C) and moderate pressures (60 bar).

Future Plans

Additional computational efforts will continue to focus on systematically evaluating hydrogen sorption/diffusion in $Ti_3C_2T_x$ monolayers and multilayers along the basal planes and edges and elucidating the influence of termination groups on the nature of interactions with hydrogen. In addition, the effects of Ti- and C-vacancies in the $Ti_3C_2T_x$ system will be explored. These computational efforts will be utilized to guide and confirm experimentally obtained results.

In-situ vibrational spectroscopy techniques will be leveraged to provide additional insight into the nature of hydrogen bonding within the MXene materials. Additionally, in-situ powdered x-ray diffraction will be used to provide supporting information related to bulk lattice changes upon hydrogen incorporation. Scanning tunneling microscopy and atomic force microscopy will be leveraged to visualize and identify defects and modification made to MXene materials. Hydrogen isothermal absorption measurements and pressure composition isotherms will be continued to provide valuable kinetic and thermodynamic information related to the hydrogen interactions with the MXene materials of interest.

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Session XI

Nanocrystal-based Dyads for Solar to Electric Energy Conversion David H. Waldeck, Chemistry Department, University of Pittsburgh David N. Beratan, Chemistry Department, Duke University,

Self-identify keywords to describe your project: chirality, spin-filtering, charge transfer

Research Scope

The project team at the University of Pittsburgh, Duke University, and the Weizmann Institute of Science is designing, creating, and studying supramolecular nanomaterials that perform chargeand spin-transfer. During the last funding period, our team explored the unusual electronic and magnetic properties, including electron spin filtering and charge transfer, of chiral molecules and nanostructures, which arise from a phenomenon that we call the chiral induced spin selectivity (CISS) effect. Having demonstrated that CISS correlates with the chiro-optical response of chiral molecules and materials, we have focused on developing a better understanding of the underlying electronic interactions through which chiral molecules imprint a chiro-optical response on the electronic structure of materials. Below we describe our recent findings along three interrelated thrusts: the elucidation of mechanisms to imprint electronic chirality on semiconductor nanoparticles, the use of chiral inorganic structures for spin-selective redox chemistry, and the investigation of magneto-electronic effects in chiral molecular films and chiral metal-oxides.

Recent Progress

<u>Chiral Imprinting in Nanoparticles</u>. By combining circular dichroism (CD) and ¹H NMR studies, we showed that the CD response of methylammonium lead halide perovskite nanoplatelets (NPLs) saturates at high coverage of chiral phenylethyl-ammonium (PEA) surface ligands as shown in Figure 1C. Through density functional theory analysis and statistical modeling (Fig. 1D), we showed that this behavior arises from the overlap of the chiral ligands' electrostatic potential and



Figure 1 Panel A illustrates the methylammonium lead halide perovskite NPL structure, with chiral Sphenylethylamine (S-PEA) ligands and achiral octylamine (OA) ligands. X- denotes Cl- or Branions (red), methylammonium cations are teal, and the Pb²⁺ cations are gray. Panel B shows circular dichroism (CD) spectra for X = Br NPLs synthesized with S-PEA:OA ratios between 0.05 (dark green) and 0.35 (light green). Panel C plots the CD strength at the first exciton transition as a function of PEA:OA ligand ratio for X = Br (green) and X = Cl (blue) NPLs, with a fit by a Boltzmann function to guide the eye. Panel D shows computational results for the dependence of rotational strength on the PEA:OA ratio and the exciton edge length (dotted, 1.8 nm; dashed, 2.4 nm; and solid, 3.0 nm).

the exciton size. In concert with the NPL studies, we developed a new methodology for doping CsPbX₃ nanoparticles and for studying how the circular dichroism (CD) intensity varies with nanoparticle size (exciton size) for quantum confined sizes of CsPbBr₃ perovskite nanoparticles (NPs). We find that as the NP size increases and crosses the quantum confinement threshold, the dominant mechanism of chirality transfer switches and becomes dominated by surface effects, as found by others. See papers 1, 5, 8, and 9 in the publication list.

<u>Chirality and Magnetoelectric Effects.</u> Because mirror symmetry breaking in chiral matter manifests in a magneto-electrical response, we have examined how chiral symmetry may be used to manipulate magnetic properties on the nanoscale. For example, we used a Hall bar device to

demonstrate that an applied electrical field acting on a chiral monolayer film generates a magnetization in the molecular layer;¹ and correspondingly that an applied magnetic field on those films changes the contact potential difference.² Kelvin-probe atomic force microscopy (KP-AFM) studies show electrostatic potential differences as large as 100 mV, which is enantiospecific, i.e., they depend on the chiral molecules' handedness. These responses are significantly greater than kT at room temperature and underscore the promise of using chiral symmetry breaking for applications. In related investigations, we collaborated with Professor Dali Sun's group at NCSU to study photogenerated magnetization at the interface of two-dimensional, chiral hybrid organic–inorganic perovskites (chiral-HOIPs) and a permalloy substrate using magneto-optic Kerr effect (MOKE) studies.³ The MOKE signal shows a linear dependence of the response on the magnetic field, and its sign is controlled by the chirality of the HOIPs. That is, the incident light generates an enantiospecific magnetization at the permalloy interface.

Current magnetic memory sizes are limited to 30-50 nm because the magnetization and magnetic orientation become susceptible to thermal fluctuations and stray magnetic fields for



Figure 2 The left column illustrates the device design, in which a Hall bar sensor is used to sample the magnetization state generated by a film of chiral quantum dots (the QDs have first exciton transitions at 532 and 405 nm). The center panel shows a logic tree, in which the operational parameters control the magnetization state of the device. The nine multilevel logic state Hall response for a D-cysteine QD coated device is shown on the right. The numbers constitute the digital bit associated with the response level. A positive (negative) signal response is represented by a positive (negative) integer. The individual numbers are representative of the readout of the Hall device.

smaller size domains. In the last funding period, we showed how chiral quantum dots (QDs) could be used to create a 9-state flash memory.⁴ By assembling a double QD architecture on the active area of a Hall sensor we demonstrated an optical nine-state readout which arises from the modulation of the electron transfer rate by the QD chirality and the light polarization. Because chiral QDs spin filter electrons, they generate a magnetization that is proportional to the current density. This gives rise to four magnetization states, defined by the chirality (left versus right) of the QD and the polarization of the light (clockwise versus counterclockwise). In addition, the device shown in Fig. 2 uses two differently sized QDs, which allows for modulation of the magnetization with light wavelength and gives rise to 8 different magnetization states (two different excitation wavelengths times the four combinations from the chirality and light polarization); the dark condition gives the 9th magnetization state. This study exemplifies how one can reimagine the operation of spintronic memory by employing chiral materials.

<u>Chirality Effects in Redox Chemistry</u>. To examine the importance of chiral materials for electrocatalysis, we studied how spin-selective chiral nanostructures might prove useful for electrocatalysis of important energy-related chemical reactions. The oxygen evolution reaction

(OER) is widely known to exhibit kinetic sluggishness (requires high overpotentials), and its improvement promises to impact the efficiency of water electrolysis. We examined the performance of chiral cobalt oxide electrocatalysts and showed that chirality reduces the reaction overpotential by 65 mV at 10 mA/cm², increases the oxygen yield by 1.4-fold at pH 10, and decrease the production of hydrogen peroxide by 4.0-fold as compared to its achiral analogue.⁵ Moreover, we showed that paramagnetic chiral electrocatalysis, under an applied external magnetic field, displays even superior performance. The oxygen reduction reaction, which is important for clean energy technologies, should have similar spin constraints to that of OER– as the reaction proceeds by converting triplet oxygen into singlet state products. We examined the electron transfer efficiency of oxygen reduction at chiral electrodes and found that it is superior to that at the analogous achiral electrodes; see publication 4.

Future Plans

The activities proposed for the next funding period aim to develop design principles to guide the development of chiral nanomaterials and the transport of change and spin in these structures. The proposed studies involve a rich interplay of theory and experiment. Major themes of that effort will be

<u>1. Probing spin transport through inhomogeneous homochiral nanoparticle (NP) networks</u> We will elucidate the differences between the transport of an electron's spin and that of its charge by quantifying the dependence of chirality induced spin filtering and the more traditional charge transport on the properties of the NP (their shape, size, and band gap) and on the properties of the networks, including distance and connectivity between NPs, chirality of NPs and their linkages, energy disorder of the NPs, and spatial disorder of the NPs in the network. In parallel with these experimental studies, we will develop a tunneling pathway model for electron transport in nanoparticle assemblies and construct a network model for the spin and charge transport. Beratan has previously built empirical models to describe electron tunneling through proteins and this approach will provide a starting point to develop the required theoretical description. The experimental and theoretical studies will proceed from well-ordered NP films to disordered NP:polymer composites.

2. Chiroptical and chiromagnetic properties of doped NPs. The doping of semiconductor NPs with transition metals and/or lanthanide ions is known to endow them with novel optical and magnetic properties, yet systematic investigations into the benefits of such doping for chiral NPs are lacking. We will explore the promise of coupling chiral symmetry with dopant effects along two lines: chiroptical properties and chiromagnetic properties. We will extend our earlier theoretical and experimental studies of chiral imprinting on the electron absorption properties of NPs to study circularly polarized luminescence (CPL) of chiral NPs and chiral doped NPs. On a different tack, we will investigate the magnetic properties of chiral NPs doped with paramagnetic (or ferromagnetic) ions, with the goal of exploring how a chiral NP's matrix impacts superexchange couplings between ion dopants and affects the magnetic responses. This line of research will build upon our recent investigations into Mn-doped chiral oxides and $Co_{3-x}Fe_xO_4$ structures. The studies will use magnetometry and MOKE methods to reveal effects of the lattice on the electron spin population's orientation.

<u>3. Spin-filtered currents for coherent and correlated spin processes.</u> The generation of spin-filtered currents in chiral matter and the promise of spin transport over micron length scales is largely uncharted, however the potential applications can be revolutionary. For example, the use of electrodes that spin filter electrons are providing a wholly different approach to spin-selective electrocatalysis. We will explore how chiral materials can be used to effect multi-electron processes through the electrodeposition of metal films, in order to direct energy flow in

multichromophore arrays, to construct ultrathin "spin wires" of length exceeding several micrometers, and to manipulate spin coherence in "spin wires".

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Exploring the Impact of the Local Environment on Charge Transfer States at Molecular Donor-Acceptor Heterojunctions

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Self-identify keywords to describe your project: Excitons, charge transfer states, disorder,
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Research Scope

Charge transfer from a donor-type to an acceptor-type system forms the basis for the photovoltaic effect observed within excitonic systems. The charge transfer (CT) state is a Coulombically-bound charge pair that serves as an intermediate state for both charge generation and recombination processes. In organic semiconductors, the binding energy of the CT state is much larger than k_bT and therefore must be overcome in order to produce a free electron and hole. While much has been learned about the role of CT states in limiting open-circuit voltage, there remains a lack of fundamental knowledge regarding what controls CT state energy, dissociation efficiency, and recombination rate. The goal of this research program is to comprehensively investigate the various nanoscale environmental factors that determine CT state behavior (dielectric, structural, dynamic, and energetic), as well as to quantify their spatial extent and density of states (DOS) energetic distribution.

Our team is addressing this challenge through the use of sensitive spectral response measurements, impedance spectroscopy, X-ray scattering, and spectroscopic ellipsometry to probe the structure and optical response of donor-acceptor heterostructures. Surface-sensitive techniques such as ultraviolet photoelectron spectroscopy (UPS), inverse photoelectron spectroscopy (IPES), and X-ray photoelectron spectroscopy (XPS) are used to measure energy levels. Finally, time-resolved and steady-state photoluminescence (PL), electroluminescence (EL), electroabsorption, and pump-probe spectroscopy measurements are used to probe CT state energetics and dynamics, enabling us to link basic material properties to the CT-related energy loss that occurs in the photovoltaic process.

Recent Progress

We will discuss our recent work¹ that shows that a substantial portion of voltage loss in organic solar cells stems from an energeticallydisordered distribution of CT states. In terms of energy loss, Marcus theory of electron transfer, which only considers Franck-Condon vibrational broadening, cannot completely interpret the experimental CT state luminescence and absorption data, especially in the case of highly disordered donor-acceptor blends. We will present the framework that we have developed for extracting the disorder in the CT state DOS. Shown in Fig. 1 are examples of two different donor:acceptor systems, both of which have identical CT energies, but very different disorder parameters. And because the disorder impacts the CT DOS via the functional form of $\frac{\sigma^2}{2k_BT}$, it is necessary



Figure 13. Trend of CT energy for two different donor:acceptor systems, as a function of temperature. The slope reflects the disorder inherent to each system, and the y-intercept at high temperature reflects the actual CT energy.

to perform temperature-dependent optoelectronic measurements (e.g. photocurrent spectra or emission) to find the true CT or reorganization energy through extrapolation to *high* temperature. This contrasts with most literature methods and practice up until this work where either room temperature or low temperature measurements were utilized.

Building upon the disorder framework described above, we will present our recent work showing how disorder influences the energy loss of organic solar cells.² Prior to this understanding, it was always observed that energy loss was approximately 0.5-0.6 eV, but it turns out that this definition did not account for here disorder approximately definition.

did not account for how disorder can manipulate the definition of CT state energy. In this work, we correct the issue, and show unequivocally that disorder increases the energy loss in organic solar cell operation. Furthermore, we show a quadratic dependence of energy loss on disorder (see Fig. 2). This work implies that the best organic solar cells will feature either completely ordered, crystalline systems (as our team has demonstrated previously³) or completely disordered systems. Any heterogeneity (mixture of order and disorder) increases the disorder parameter immensely, which has a negative impact on energy loss.



Figure 3. Modulation response of CT state electroluminescence (EL), demonstrating that CT emission on the blue side of the inset spectrum responds faster to the current modulation than CT emission on the red side.

Another aspect that is impacted by disorder is the assumption of quasiequilibrium which, in essence, means that electrons and



Figure 14. Trend of increasing voltage loss with increasing CT state disorder follows a quadratic trend. Minimal non-radiative voltage loss can be expected to be approximately 0.3 eV, like what our consortium has demonstrated for a crystalline rubrene-based organic photovoltaic.

holes relax within their respective DOS much faster than all other charge transport and recombination timescales. Quasi-equilibrium is assumed for nearly all solar cells; however, we recently found that it breaks down for organic solar cells. Specifically, we reported the first experimental proof that the distribution of *CT states does not exist in quasi-equilibrium*, and thus cannot be described by a Boltzmann-like distribution. This result, which is based on the modulation response

of CT electroluminescence (Fig. 3), is all the more surprising because it is obtained for electrical injection in the dark. It is significant because it challenges the widespread use of reciprocity-based methods to determine basic CT state properties, and it implies that the distribution of CT states under illumination (i.e. under normal conditions of solar cell operation) is even farther from quasi-equilibrium than in the dark.

One process that reduces open-circuit voltage is the process of nonradiative recombination, and yet there is a lack of microscopic descriptions of non-radiative recombination mechanisms at organic interfaces. Recently, we reported on the discovery of a new nonradiative recombination mechanism⁴ that involves an intermolecular CT state resonantly transferring its energy to a nearby charge carrier, or polaron (shown in Fig. 4). Basically, a CT state is de-excited and a charge carrier is temporarily excited (the lifetime of an excited polaron is very short). This can be thought of in loose analogy to Auger recombination in the monomolecular limit (i.e. at high doping or carrier injection) where a collision of two carriers results in the creation of a temporarily hot carrier and a recombination event.



Figure 4. Schematic diagram of the new nonradiative recombination process discovered by the PIs during our last funding round, involving energy transfer from an intermolecular CT state to a shortlived polaron.

Future Plans

Our future work will explore the breakdown of quasi-equilibrium at

donor/acceptor interfaces to understand the implications for organic solar cell operation and modeling, as well as to determine whether non-thermal CT state and free carrier distributions can be exploited to improve performance. If successful, our future work will provide a scientific basis for reducing voltage loss in organic solar cells.

Also, we will explore the generation mechanism that is a complement to the recombination mechanism discovered recently and described above (cf. Fig. 4). In the field of semiconductor physics, it is well established that recombination mechanisms have their counterpart in a corresponding generation mechanism (e.g. radiative recombination and absorption, defect-mediated (aka SRH) recombination/generation, and Auger recombination with impact ionization). Given this precedent, we hypothesize that the new non-radiative recombination mechanism we recently described will have its counterpart generation mechanism, and that this generation mechanism is responsible for the reverse saturation current in organic diodes. We describe this mechanism as a thermally excited polaron transferring energy to an intermolecular CT state, generating an electron-hole pair in the process of charge separation (efficient under the reverse bias conditions inherent to diode saturation current).

In addition to organic-organic heterojunctions, we will explore new CT state physics in hybrid systems consisting of organic molecules paired with two-dimensional perovskite and transition metal dichalcogenide semiconductors. These systems provide a unique platform to study the factors that influence CT state binding energy by controlling the dimensionality and spatial extent of the underlying electronic states, and may also enable new, hydrogenic intra-CT state transitions that exhibit strong optical nonlinearity in the mid-infrared.

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Tailoring Photophysical Energy Transfer for Selective Separations of Critical Lanthanides

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rare earths • photochemistry • photophysics • excited state kinetics • light-harvesting ligands

Research Scope

To overcome limitations of cation-size based separations of critical rare earth elements (REEs),¹ we aim to develop a novel approach that exploits the *unique and discontinuous electronic structures* of well-shielded 4*f* orbitals of the individual lanthanide ions,² via *dynamic and element specific photo-induced modifications of the chemical environment* surrounding them. This concept is built on computational chemistry calculations and multi-modal transient spectroscopy-guided

synthesis of ligands with the desired chemical and physical motifs (Fig. 1).³⁻⁴ These designer ligands will ultimately enable demonstration of efficient solutionphase separations via control of (i) large, dynamic excited-state perturbations of the photophysical properties of the complexes or (ii) sensitization of ligand-centered photo-chemical reactions. This work will expand our understanding and manipulation of excited-state energy flow in lanthanide complexes, to enable control of lanthanide complex solubility and separation, by:

 Developing chemical descriptors of ground-state alectropia structure & excited



Fig. 1. Schematic illustrating the combined experimental-theoretical approach that will yield fundamental understanding to enable novel photophysical and photochemical lanthanide separations.

electronic structure & excited-state dynamics

- Probing energy transfer between lanthanide ions and surrounding coordination ligands
- Inducing lanthanide-selective photophysical/photochemical changes in the coordination sphere
- Evaluating changes in the strain and solubility within the coordination complexes

Recent Progress

1. *The Role of pKa and Ligand Dipole on Extraction Strength:* We have synthesized several asymmetric arylvinyl phosphonic acid (AVPA) mono 2-ethylhexyl esters (Fig. 2a) as prototypes for target photoswitchable ligands to understand the potential steric and electronic impacts of incorporating conjugated photoswitchable groups into the traditional dialkylphosphonic phosphonic acid extractant platform.

Spectroscopic measurements of this class of extractants suggest they form similar complexes with REEs as conventional dialkylphosphonic acids, but are much stronger RE extractants (Fig. 2a). This suggests similar steric contributions to intra-RE selectivity. Much of the increase in the extraction strength can be attributed to the stronger acidity (decreasing pKa) of the AVPA mono 2-ethylhexyl esters as compared to dialkylphosphonic acids. However, the extraction strengths of two of the new phosphonic acids do not follow the order expected purely from the pKa's. The extraction strength for rare earths should increase with decreasing pKa because the earth cations increasingly rare are competitive with protons for the phosphonic binding acid site with increasing acidity. Instead, computations suggest that the detailed order of extraction strengths for the asymmetric AVPA mono



Fig. 2. (a) Data illustrating that extraction strength for europium increases with the magnitude of the ground state dipole moment for several novel asymmetric AVPA extractants and (b) Schematic illustrating the photoinduced change in the magnitude of the dipole moment (orange arrow) for the spiropyran/merocyanine isomers.

2-ethylhexyl esters track the order of the dipole moments of the extractants. This observation points to potentially new chemical design principles for tuning the strength of rare earth separating ligands, via control of the acidity and dipole moment. Furthermore, we are currently exploring strategies aimed at light-induced dynamic control over these chemical properties, using photoswitchable chromophores (Fig. 2b).

2. *Ligand-Ligand Interactions in Rare Earth Complexes with AVPA Ligands:* We subsequently explored the photophysics in the extracted Eu-AVPA complexes using steady-state and transient spectroscopy. Pairs of ligands functionalized with CF_3 groups at the para position in the styryl moiety pre-associate in the ground state according to calculated geometry optimizations (Fig. 3a, compared to Fig. 3b) and steady-state absorption measurements (data not shown). Consequently, the Eu-CF₃Styryl complexes undergo faster and more efficient ligand excimer formation upon electronic excitation of the ligand, characterized by the narrow and intense excited-state absorption at ca. 525 nm in pump-probe experiments (Fig. 3c, compared to Fig. 3d). The emission intensity from CF₃Styryl-complexed Eu³⁺ after energy transfer (ET) from the ligand depends on the degree



complex and (b) Eu-Styryl complex (ethylhexyl groups and hydrogen atoms removed for clarity). Transient absorption maps showing strong excimer feature for the (c) Eu-CF₃Styryl complex compared with the (d) Eu-Styryl complex.

of aggregate photoselection at the excitation wavelength; weaker emission suggesting excimer formation hinders the typical ligand-RE ET pathway.

The excimer formation pathway shows some dependence on the RE identity. For example, Dy-based complexes show predominately excimers with styryl AVPA ligands, as opposed to the excimer-dominated Eu-CF₃Styryl complexes described above. The exact conditions that determine this behavior need to be better understood, but control of the bifurcated excited state pathway ligand through design and complexation with different RE elements may provide a simple route to photodriven separation of critical materials.

3. *Triplet-mediated Photochemical Reactions Modulated by Rare Earth Excited States:* Triplet excited states that readily form on organic ligands in proximity to heavy metals have lifetimes that depend on ligand-metal electronic coupling. This coupling can be modulated by geometric effects

or by energetic offsets tailored through ligand design and RE identity (Fig. 4a). We synthesized the complexes $RE(hfac)_3(NMMO)_2$ (RE = Dy³⁺, Y³⁺, hfac = hexafluoroacetvlacetonate, NMMO = 4methylmorpholine-N-oxide). Using ¹H- and ¹⁹F-NMR spectroscopies, we monitored the rates of oxygen-atom transfer (OAT) to triphenylphosphine under ultraviolet (UV) irradiation, showing that the photochemical reactivity in the Dy complex is strongly reduced (Fig. 4c). Ultrafast transient pump-probe spectroscopic measurements (Fig. 4b) show that the ligand excited state lifetimes are significantly longer for the Y complex allowing for the diffusion-controlled OAT reaction to take place. In contrast, competing sensitization pathways lead to excited-state deactivation in the Dy complex through energy transfer to the Dy 4f-electron manifold, which ultimately slows the OAT reaction. The measured rate differences between the open-shell Dy³⁺ and closed-shell Y³⁺ complexes demonstrate that using established principles of 4f-ion





sensitization may deliver new, selective modalities for differentiating the REEs that do not depend on cation size.

Future Plans



Fig. 5. Multi-disciplinary approach to produce novel multi-functional ligands systems designed to undergo photochemical reactions mediated by the electronic structure of the target RE ions (here for a representative coumarin-functionalized DO3A-macrocycle platform), allowing for light-driven dynamic chemical separability.

We plan to build upon our understanding of excited state interactions between these multifunctional ligand systems and the RE ions through a multidisciplinary approach (Fig. 5). This will involve not only tailored ligand synthesis, but development of advanced spectroscopic and computational techniques to track excited state evolution and photochemistry from the moment of photoexcitation through reaction completion. Our plans include:

- (i) Mapping the excited state potential energy surfaces in RE coordination complexes
- (ii) Developing in-situ spectroscopic tools to probe excited states in photoswitchable ligands
- (iii) Excited state-mediated ligand photochemistry

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Project Title: Design, Synthesis, and Atomic Scale Characterization of Rare-Earth Based Supramolecular Nano-graphene and Nanoribbons

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Research Scope

This project seeks to advance fundamental understanding on the physics and chemistry of rare earths in well controlled environments and development of novel materials using molecular design and new synthetic approaches. In these structures, rare earth ions are caged in organic complexes whose electronic properties can be tuned by changing ligand design or by an external stimulus. Atomic scale characterization of individual rare earth ions in the proposed structures are performed with the most advanced instrumentation: The elemental, and chemical, properties of rare earth ions in the network are determined simultaneously using synchrotron X-ray scanning tunneling microscopy, while tunneling spectroscopy is used to measure the electronic structure of the caged rare earths on one ion-at-a-time basis. Low temperature electron paramagnetic resonance methods are used to probe the spin structures of the 4f electrons while excitation and energy conversion studies are carried out using advanced magneto-optical spectroscopy techniques. Taken in concert, these experiments provide unparalleled atomic level information of the rare earth ion environment within these novel structures. This, in turn, is used to develop theoretical frameworks to describe accurately the electronic properties of the constituent 4f rare earth cations and rational blueprints for the design and synthesis of new structures with improved functions.

Recent Progress

Atomically Precise Control of Rotational Dynamics in Charged Rare-Earth Complexes on a Metal <u>Surface¹</u>: Complexes containing rare-earth ions attract great attention for their technological applications ranging from spintronic devices to quantum information science. While charged rare-earth coordination complexes are ubiquitous in solution, they are challenging to form on materials surfaces that would allow investigations for potential solid-state applications.



Fig.1. (a) STM image of a rotating Eu complex on Au(111). **(b)** Controlled rotations are performed by supplying electrical energy from an STM tip. **(c)**, **(d)** Before and after rotation of a complex, respectively. The dashed circle indicates the counterion.

Here we form rare-earth complexes by coordinating a positively charged europium (Eu) -(pcam)₃ molecule with negatively charged CF₃SO₃ counterions on a Au(111) surface (Fig. 1a). Electronic and structural properties of these complexes are then investigated on a one complex at-a-time basis using scanning tunneling microscopy (STM) and tunneling spectroscopy methods. Although they are composed of multiple units held together by electrostatic interactions, we show that an entire rare-earth complex can be rotated like a single unit (Fig. 1b) when electrical energy is supplied from a scanning tunneling microscope tip² with precise control of their rotational dynamics at the atomic scale (Fig. 1c to 1e). Despite the hexagonal symmetry of the gold surface, a counterion at the side of the complex guides three-fold rotations, and 100% control of their rotational directions is achieved using a negative electric field from the scanning probe tip. This work demonstrates that counterions can be used to control dynamics of rare-earth complexes on materials surfaces.

<u>Microcavity-Modified Emission from Rare-Earth Ion-Based Molecular Complexes³</u>: Despite the remarkable optical properties of rare-earth ion materials, their applications as light sources and in quantum technologies are often hindered by their long lifetimes and weak emission. Leveraging



Fig. 2. (a) Eu complexes coupled to a microcavity exhibit stimulated emission. (b) Complex structure. (c) Fourier image of the molecule-cavity system. (d) Cavity length-dependent emission intensity of the molecule-cavity system.

the natural compatibility of rare-earth ion molecular complexes with photonic structures, we modify their photoluminescence properties by coupling them to a flexible open Fabry-Perot cavity (Fig. 2). The in situ tunability of the Fabry-Perot cavity enables' fine control over its cavity modes leading to achieve resonant coupling between the rare-earth ion emission and the cavity modes. This configuration allows achieve further а maximum us to photoluminescence enhancement factor of 30 and the decay rate of up to two orders of magnitude on a Eu DPEPO-TTA complex (Fig. 1b, ac, and 1d). Our pump-power-dependent spectroscopic studies of the emitter-cavity suggest that the cavity-modified system emission is primarily caused by amplified spontaneous emission.

These results further highlight that integrating rare-earth ion molecular complexes with photonic structures could be a viable approach for the effective tuning of their optical properties. This

natural compatibility, together with their versatile molecular structures and the resultant electronic states, renders rare-earth ion complexes a potential alternative material platform for lighting and quantum applications.

<u>Characterization of Just One Atom using Synchrotron X-rays</u>: Since the discovery of X-rays by Roentgen in 1895, its utility has been ubiquitous from medical and environmental applications to materials sciences. X-ray characterization requires a large number of atoms and reducing the



Fig. 3. (a) STM image of a single $[Tb(pcam)_3]_2$ complex measured with the SX-STM set-up. **(b)** Corresponding model. **(c)** STM-NEXAFS signal of Tb ion. **(d)** M₅ absorption edge signal of a single Tb ion from (a).

material quantity is a long-standing goal. To date, attogram amount of sample can be detected by X-rays however, it is still in the range of $\geq 10^4$ atoms or more and gaining access to a much smaller sample is becoming extremely arduous. Here, we show that X-rays can be used to characterize the elemental and chemical state of just one atom. Using a specialized tip as a detector, X-ray excited currents generated from an iron and a terbium atom coordinated to organic ligands⁴ are detected. The fingerprints of a single atom, the $L_{2,3}$ and $M_{4,5}$ (Fig. 3) absorption edge signals for iron and terbium respectively, are clearly observed in the X-ray absorption spectra. The chemical states of these atoms are characterized via near edge X-ray absorption signals where X-ray excited resonance tunnelling is dominant for the iron atom. The X-ray signal can be sensed only when the tip is located directly above the

atom in extreme proximity, which confirms atomically localized detection in the tunnelling regime. Rare-earth metals have tantalizing electronic and magnetic properties for high technological applications due to their well shielded 4f electrons. This is clearly observed in our one-atom measurements where the 4f orbitals of the Tb ion are isolated and are not involved in chemical bonding with the ligands (Fig. 3c) while the 3d orbitals of the Fe ion are heavily hybridized with its surrounding environment. This work connects synchrotron X-rays with a quantum tunnelling process and opens future X-rays experiments for simultaneous characterizations of elemental, and chemical properties of materials at the ultimate single atom limit.

Light and Chemical Doping Induced Magnetic Behavior of Eu Molecular Systems: Owing to its narrow emission bands and high light purity, Eu is used as a red phosphorus (Eu^{3+}) in many solid-state applications including upconversion and light emitting diodes, while high energy broad blue emission of Eu^{2+} is used for broad excitation in white light emitting diodes. Here, we explore magnetic properties of different oxidation states of Eu complexes and assess their conversion from non-magnetic to paramagnetic state as sensors of their redox environment. We find that while Eu(III) chelating complexes are diamagnetic, simple chemical reduction results in the formation of paramagnetic species. In agreement with the distorted D_{3h} symmetry of Eu complexes studied here, the electron paramagnetic resonance spectrum of reduced complexes shows axially signals. Illumination of water-soluble complex $Eu(dipic)_3$ at 4K led to the ligand to metal charge transfer



Fig. 4. (a) A model of Eu(dpic)-CB7. (b) STM image of Eu(dpic)-CB7, and (c) EPR spectra of Eu(dpic)3. (d) dI/dV tunneling spectra of Eu(dpic)-CB7.

that resulted in the formation of Eu(II) in a rhombic environment. Existence of ligand to metal charge transfer affects luminescence of Eu(dipic)₃, and pre-reduction of the complex to Eu(II)(dipic)₃ reversibly reduces red luminescence with appearance of a weak blue luminescence. Absence of carboxylate groups in complex Eu(pcam)₃ also prevents ligand to metal charge transfer, and makes it stable upon illumination. Furthermore, encapsulation of a large portion of the dipic ligand with Cucurbit[7]uril (CB7) (Fig. 4), a pumpkinshaped macrocycle, inhibited ligand to metal charge transfer preventing formation of Eu(II) upon illumination. This work not only demonstrates the ligand to metal charge transfer in Eu compounds leading to turn on magnetic behavior in the complexes, but also show a way to prevent it if it is the desired outcome.

Future Plans

Following our success on one atom level characterizations of rare-earth ions and control of their environment, we plan to extend our investigations on mixed rare-earth ions within molecular complexes. Different rare-earth metals will be incorporated into our molecular complexes, and by linking on materials substrates, we plan to form two dimensional networks of rare-earth complexes. Our key interest is to understand behaviors of rare-earth ions in these complex networks that would enable tailoring their properties for potential applications spanning from emission, upconversion, energy harvesting, to separation, spintronics and quantum information applications.

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Poster Sessions

Physical Behavior of Materials Principal Investigators' Meeting

Poster Session I

Wednesday, March 15, 2023

- 1) "Quantum Metamaterials" David Awschalom, Argonne National Laboratory
- 2) "Light-Matter Quantum Control: Coherence and Dynamics" Jiang Wang, Ames National Laboratory
- 3) "A Nonlinear Approach to Weyl Transport" Kenneth Burch, Boston College
- 4) "Photon-mediated interactions in superconducting circuits as a new tool to study emergent phenomena far from equilibrium" Hakan Tureci, Princeton University
- 5) "Coherent control of strongly interacting spins in the solid-state" *Jeffrey Thompson, Princeton University*
- 6) "Atomistic and Mesoscopic Study of Metallic Glasses" Takeshi Egami, Oak Ridge National Laboratory
- 7) "Metamaterials as a Platform for the Development of Novel Materials for Energy Applications" Willia Padilla, Duka University

Willie Padilla, Duke University

- 8) "Study of Materials and Interface Properties for High-Efficiency Spin Injection" Jing Shi, University of California, Riverside
- 9) "Materials, Physics, and Nanostructures for Next Generation Spintronics" Chia-Ling Chien, Johns Hopkins University
- 10) "Spin Functionality Through Complex Oxide Heteroepitaxy" Yuri Suzuki, Stanford University
- 11) "Elucidating Chirality-induced Magnetism and Magnetoelectric Functionalities in Layered Chiral Hybrid Metal Halide Perovskite" Dali Sun, North Carolina State University
- 12) "Unique optical excitations in topological insulators " Stephanie Law, University of Delaware

Physical Behavior of Materials Principal Investigators' Meeting Poster Session II

Thursday, March 16, 2023

- 1) "Electronic Materials Program" Ali Javey, Lawrence Berkeley National Laboratory
- "Digital Synthesis: A Pathway to Create and Control Novel States of Condensed Matter" Anand Bhattacharya, Argonne National Laboratory
- 3) "Characterization of Functional Nanomachines" Michael Crommie, Lawrence Berkeley National Laboratory
- 4) "Extraordinary Resp. Magnetic Rare Earth Materials" Yaroslav Mudryk, Ames National Laboratory
- 5) "Hot Carrier Dynamics in Low-Dimensional Systems" Ian Sellers, University of Oklahoma
- 6) "Quantum Coherence of Moiré Excitons in Transition Metal Dichalcogenide Twisted Homobilayers" Elaine Li, University of Texas, Austin
- 7) "Stimuli-Responsive Materials from Mesoscale Self-Assembly of Plasmonic and Quantum Nanoparticles" Ivan Smalyukh, University of Colorado Boulder
- 8) "DNA-Controlled Dye Aggregation A Path to Create Quantum Entanglement" William Knowlton, Boise State University
- 9) "Super-Ionic Clusters Structure, Stability, and Energy Applications" Puru Jena, Virginia Commonwealth University
- 10) "Photoelectrochemistry of Halide Perovskites: from Stability to Chirality" Yiying Wu, Ohio State University
- 11) "Microscopic understanding of growth, substrate engineering, and proximity coupling in two-dimensional organic/inorganic hybrid systems" Pengpeng Zhang, Michigan State University
- 12) "Semiconductor nanoshell quantum dots for energy conversion applications" Mikhail Zamkov, Bowling Green University

- 13) "Control of Light-Matter Interactions in Hybrid Structured Environments with Novel Nanomaterials of Different Dimensionalities"
 - Anton Malko, University of Texas, Dallas
- 14) "Excitons in Low-Dimensional Perovskites"" William Tisdale, Massachusetts Institute of Technology
- 15) "Electron Spin Polarization in Large Electric Fields" Vanessa Sih, Michigan University

Physical Behavior of Materials Principal Investigators' Meeting Poster Session III

Friday, March 17, 2023

- 1) "Plasmon and Photon Excitations in Layered Heterostructures" Harry Atwater, California Institute of Technology
- 2) "Quantum Nanoplasmonics Theory" Vadym Apalkov Georgia State University
- 3) "Control of light-matter interaction with epsilon-near-zero homogeneous alternative plasmonic materials" Alexandra Boltasseva, Purdue University
- 4) "Plasmonic Photoconductive Nanostructures for High-Power Terahertz Wave Generation" Mona Jarrahi, University of California, Los Angeles
- 5) "Uncovering and Surmounting Loss Mechanisms in Nitride Light Emitters" Chris Van de Walle, University of California, Santa Barbara
- 6) "Response of Gallium Oxide to Pressure, Temperature, and Alloying" Matthew McCluskey, Washington State University
- 7) "Fundamental Studies on Heat Conduction in Polymers" Svetlana Boriskina, Massachusetts Institute of Technology
- 8) "Extreme Thermoelectric Behavior in Low-Dimensional Oxide Conductors" Joshua Cohn, University of Miami
- 9) "Probing Coherence in Nanoscale Energy Transport with High Spatial-Temporal Resolution" Bolin Liao, University of California, Santa Barbara
- 10) "Singlet and Triplet Exciton Interaction and Dynamics in Molecular Crystals" Ivan Biaggio, Lehigh University
- 11) "Novel Physical Behaviors Driven by Magnetostructural Phase Transitions" Shane Stadler, Louisiana State University
- 12) "Weyl Semimetals for High-Thermopower Transverse Thermoelectric Transport " Sarah Watzman, University of Cincinnati
- 13) "Orienting Strained Interfaces designed to Direct Energy Flow Bodies" Dongkyu Lee, University of South Carolina, Columbia
Poster Abstracts

Quantum Nanoplasmonics Theory

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Keywords: spaser, topology, graphene, TMDC **Program Scope:**

Major goals of this Program is in theoretical research devoted to new phenomena in two dimensional (2D) materials and metal nanostructures subjected to strong ultrafast optical fields. We consider such novel and promising 2D systems as graphene (a 2D semimetal), transition metal dichalcogenides (2D semiconductors), and surfaces (2D boundaries) of three-dimensional topological insulators. We focus on effects in the reciprocal space that are related to topological properties of the Bloch wave functions: Topological curvature, Berry phase, valley polarization, etc. These properties are protected by fundamental symmetries of nature: time reversal (Tsymmetry) and spatial reflection (P-symmetry), which are in the focus of this Proposal.

Recent Progress

TMDC-Based Topological Nanospaser: Single and Double Threshold Behavior

We theoretically study a topological nanospaser, which consists of a silver nanospheroid and MoS₂ monolayer flake of a circular shape [1]. Such a topological nanospaser consists of two main components: a metal nanospheroid and a TMDC, i.e., MoS₂, monolayer flake of a circular shape. The nanospheroid functions as a plasmonic nanoresonator with two relevant plasmonic modes, which rotate in the opposite directions and are characterized by azimuthal quantum numbers m =+1. The MoS₂ monolayer is a gain medium with nontrivial topology. It is placed atop a nanospheroid and has two chiral valleys, K and K'. The system is pumped by a circularly polarized light, which populates the conduction band states of only one valley, say the K valley. We show that the topological nanospaser has very rich dynamics[1], which strongly depends on the radius of the gain medium (TMDC nanoflake). If the radius of TMDC is less than the radius of the metal nanospheroid, then the K and K' valleys are mainly coupled to the co-rotating plasmonic modes, e.g., the K valley is coupled to the m = 1 mode. In this case, the nanospaser has one threshold, g_{th} , so that if the gain is larger than g_{th} then the co-rotating plasmon mode is generated. For a larger radius of nanoflake, the valleys of TMDC become also strongly coupled to the counterrotating modes, and the nanospaser has two thresholds, $g_{th,1}$ and $g_{th,2}$, so that if $g_{th,2} > g > g_{th,1}$ then only the co-rotating mode is generated, while if $g > g_{th,2}$ then both co-rotating and counterrotating modes are generated, see Fig. 1. For even a larger radius of TMDC, the two thresholds merge into one and the nanospaser has only one regime when two modes, m = 1 and m = -1, are cogenerated. In this case the number of counterrotating plasmons is larger than the number of co-rotating ones. Because of that property, the far-field radiation of nanospaser shows interesting behavior. Namely, by changing the gain strength, one can change the handedness of the far-field radiation from left to right and vice versa.



All these unique properties of topological nanospaser make it an extremely viable option for several nanoscopic applications. The main areas are near-field spectroscopy and sensing where a plasmon frequency of a nanospaser can be tuned to work at the required condition. However, the topological nanospaser can also be used in optical interconnects and probing.

Ultrafast electron dynamics of graphene quantum dots: High harmonic generation

Nonlinear optical properties of graphene quantum dots (QDs) placed in a field of a short and strong linearly polarized optical pulse strongly depend on the dephasing processes in quantum dots [2]. One such nonlinear optical response is the high harmonic generation (HHG), which was studied theoretically in Ref. [2] for a graphene QD consisting of 24 atoms. Due to dimensional quantization, a graphene QD has an intrinsic band gap, which depends on the size of the dot. As a result, in QDs of small size, ultrafast electron dynamics in the field of a strong optical pulse can be both reversible and irreversible, depending on the frequency of the pulse. If the frequency of the pulse is much less than the band gap of the QD, then the electron dynamics is almost reversible, i.e., after the pulse, the electron system returns to its initial state. But if the frequency of the pulse is comparable to the band gap, then the electron dynamics is highly irreversible, i.e., the residual population of the excited OD states is almost the same as their maximum population during the pulse. The reversibility of electron dynamics is strongly affected by the dephasing processes [2]. To introduce the dephasing into the model, the density matrix approach has been used in Ref. [2]. The dephasing is introduced through the relaxation of the nondiagonal elements of the density matrix. The dephasing processes make the electron dynamics incoherent and more irreversible. Since the electron dynamics completely determines the nonlinear optical response of the system, such as HHG, then the nonlinear optics of graphene QDs strongly depends on the dephasing processes.

The dephasing affects both the intensities of the high harmonics and the harmonic cutoff. With increasing the relaxation time, i.e., when the electron dynamics becomes more coherent, the intensities of harmonics increase. This can be attributed to the fact that for coherent dynamics, more paths can contribute to the formation of high harmonics coherently, resulting in larger intensity.



The effect of relaxation on the harmonic cutoff is also related to the reversibility of electron dynamics, namely, with increasing the relaxation time the electron dynamics becomes more reversible with less population of the highly excited QD levels. As a result, the harmonic cutoff decreases with increasing relaxation time, see Fig. 2. As a function of the field amplitude, the harmonic cutoff shows almost linear dependence at small frequencies of the pulse when the corresponding energy cutoff is less than the energy range introduced by the lowest and highest energy levels in the QD. When this energy range becomes comparable to the energy cutoff, which happens at large frequencies of the pulse, then the cutoff shows a saturated behavior as a function of the pulse amplitude.

Ultrafast valley polarization of graphene nanorings

In graphene-like systems with two valleys, the valley polarization can be induced only through the processes which break the time-reversal symmetry. For example, such polarization can be introduced in systems interacting with a circularly polarized pulse. Here, ultrashort optical pulses are particularly interesting since they allow control of the valley degree of freedom at a femtosecond time scale. The valley polarization can be induced by such an ultrashort circularly polarized pulse in monolayers of graphene-like materials only if they have broken inversion symmetry. The broken inversion symmetry also introduces a finite band gap in the system. Thus, in pristine graphene, which has inversion symmetry, no valley polarization can be generated by any short optical pulse. To resolve such a problem, a graphene monolayer with broken translational symmetry, e.g., graphene nanoring, was considered theoretically by us in Ref. [3]. Such a graphene nanoring is placed in the field of an ultrashort optical pulse. For an optical pulse, with a duration of just a few femtoseconds, the electron dynamics is coherent and is described by a time-dependent Schrodinger equation. If the optical pulse is circularly polarized, then two valleys of graphene are populated differently, resulting in a finite valley polarization of the system after the pulse. Such valley polarization is a unique property of graphene nanoscale systems, while for a graphene monolayer, a circularly polarized pulse does not produce any valley polarization. The valley polarization of the graphene nanoring depends on the parameters of the system, such as inner and outer radii. With the system's size increasing, the valley polarization monotonically decreases,

converging to its zero value for the infinite graphene monolayer. At small pulse amplitudes, F_0 , the valley polarization quadratically increases with F_0 , while at large values of F_0 , the valley polarization shows a saturated behavior. Such saturation is related to the finite number of nanoring levels considered in the effective model of nanoring.

The energy spectrum of graphene nanoring consists of bulk states with a finite band gap between the valence and the conduction bands and in-gap edge states. Such in-gap states are mainly responsible for the generation of finite valley polarization of graphene nanoring.

Future Plans

A topological nanospaser consists of a metal nanospheroid and a TMDC nanoflake. The dynamics of such a nanospaser strongly depends on the size of the gain medium, i.e., the TMDC system. Namely, for the relatively large size of the TMDC nanoflake, the spaser dynamics has a two-threshold regime, when the transition from the generation of only one plasmonic mode to the simultaneous generation of two modes occurs. We will study in detail how the dynamics of topological nanospaser depends on the initial conditions, i.e., the initial number of plasmons. We expect that the spaser dynamical regime can be switched from one to another by changing the initial number of plasmons. We will also address the problem of the generation of plasmonic excitations in topological nanospaser by applying a strong femtosecond-long circularly polarized optical pulse to a nanospaser. Such a pulse will generate a population inversion of the TMDC nanoflake, which will be transferred to the surface plasmons.

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Plasmon and Photon Excitations in Two-Dimensional and Layered Materials

Harry A. Atwater, California Institute of Technology

Research Scope

Light-matter interactions in layered and two-dimensional materials allows one to achieve extreme optical confinement approaching the atomic scale, enabling exploration of new materials phenomena. Layered narrow bandgap and zero bandgap materials, such as black phosphorus and graphene, support unusual and intriguing quantum-confined electronic states in thin layers and surface electronic states. The incomplete screening of applied electrostatic fields in ultrathin materials permits the exploration of light-matter interactions at high electric fields and over a wide range of carrier densities in a single sample, facilitating exploration of the optical and plasmonic properties of ultrathin and layered materials under electrochemical potential control. We seek to understand the nature of optical interband and intraband plasmon excitations in layered materials such as graphene, black phosphorus, molybdenum diselenide, and molybdenum ditelluride.

Recent Progress

In 2022-2023, we focused intensively on photophysical properties of confined excitons at black phosphorus (BP) edges and Rydberg excitons in molybdenum ditelluride (MoTe₂), resulting in submission of four major papers (in review), which reported three key discoveries:

- Discovery of quantum-confined excitons localized at the edges of monolayer black phosphorus two-dimensional crystals. We find strikingly different optical properties for "edge excitons" compared to "interior excitons" in the interior of the BP crystal, including dramatically narrower linewidth and single photon emission from some edge exciton states.
- Observation of an excitonic Rydberg series in monolayer MoTe₂, up to 3s states, in an experimental investigation of excitonic luminescence properties. We observe a strongly gate-tunable exciton-trion interplay for all the Rydberg states governed mainly by free-carrier screening, Pauli blocking, and band-gap renormalization, in agreement with the results of first-principles GW plus Bethe-Salpeter equation approach calculations.
- Observation of excitonic phase modulation and beam steering in monolayer MoSe₂ patterned as metasurfaces, indicative of modulation of scattered light amplitude and phase via exciton density control.

1. Rydberg excitons and trions in monolayer MoTe2

Like the hydrogen atom, excitonic optical resonances in transition metal dichalcogenide (TMDC) semiconductors can exhibit an entire Rydberg series of resonances. Excitons have been extensively studied in most TMDCs (MoS₂, MoS₂, WS₂ and WSe₂), but detailed exploration of excitonic phenomena has been lacking in the important TMDC material molybdenum ditelluride (MoTe₂). We reported an experimental investigation of excitonic luminescence properties of monolayer MoTe₂ to understand the excitonic Rydberg series, up to 3s levels.

We characterized the optical properties of electrostatically gated monolayer MoTe₂ via photoluminescence measurements (Fig. 1(b)). Combining high-quality heterostructures and a resonant back-reflector geometry, we identified optical transitions corresponding to the excitonic Rydberg series, revealing semiconductor-like behavior with quantitative estimation of zero-temperature energies and Rydberg exciton-phonon coupling strengths. We observe exciton-trion interplay for all the Rydberg states governed mainly by free-carrier screening, Pauli blocking, and band-gap renormalization (Fig. 1(c) and (d)) - in good agreement with the results of first-principles

calculations. By controlling the charge density in the monolayer MoTe₂ from charge neutrality up to electron/hole densities of $\sim 10^{12}$ cm⁻² we find strong modulation of optical transitions and continuous tuning of the ground and excited state excitonic manifold. First-principles calculations

based on many-body perturbation theory (MBPT) revealed the properties excited-state of monolayer MoTe₂ (Fig. 1(a)). First principles GW plus Bethe Salpeter equation (GW-BSE) calculations with a new plasmon pole model show that the strong tunability attributed is to enhanced screening of the excitonic from states the increased electron density as well as phase space filling which leads to Pauli blocking of optical transitions. With increasing doping density, calculations predict (i) a reduction in the exciton oscillator strength and (ii) a near-constant (mild blueshift) exciton of the energy, in agreement with experimental measurements (Fig. 1(e) and (f)).



Figure 1 (a) Excitonic energy landscape of Rydberg series in monolayer MoTe₂ with the quasiparticle band structure, exciton state energies Ω^{S} , and exciton binding energies E_{b}^{S} obtained using GW-BSE calculations. (b) device geometry with hBN encapsulated monolayer MoTe₂ on Au substrate (c), (d) Derivative of the PL spectra, $\frac{dPL}{dE}$, of different neutral excitons and trions as a function of gate voltage near the 1s and 2s/3s resonance, respectively. (e) the variation in exciton energy $\Delta\Omega^{S}$ (black curve), the exciton binding energy ΔE_{b} (blue curve), and the renormalization of the QP band gap ΔE_{g} (red curve) for the ground A1s exciton, (f) the oscillator strength for the A1s, A2s and A3s states. (inset) Same as (c) plotted in semi-log scale on the y-axis.

2. Quantum confined excitons in monolayer black phosphorus edges

In recent work, we discovered that certain edges of monolayer black phosphorus act as excellent candidates for quantum confinement of the intrinsic, interior quasi-1D excitons, resulting in discrete spectral emission lines with a nearly 10x reduction in linewidth, as shown in Fig. 2(a-d). We found through GW+BSE calculations that such edge-excitons can exist under specific conditions of atomic reconstruction at a physical edge. Using DFT theory we scanned lowest energy reconstruction configurations, selected 5 promising candidates with direct bandgap energies near the intrinsic exciton resonance. We found two structures (namely ZZ4-i and AC12-i) that yield bright, optically active excitons that match our experimental observation, and which are polarized along the principal armchair axis. Upon integration into a gate-tunable heterostructure, we demonstrated electrical switching of the edge excitons, with a highly symmetric gate-dependence, turning off upon electron and hole injection.

Future Plans

1. Full Poincaré sphere nanophotonics with twisted bilayer black phosphorus metasurfaces

In our previous work, we demonstrated that excitons in black phosphorus can be electrically tuned to generate programmable birefringence due to the anisotropic nature of the optical transitions along zigzag and armchair crystal axes. By injecting electrons or holes in trilayer black phosphorus, excitons are screened strongly which reduces their oscillator strength and induces a modulation of the refractive index. Upon integration into resonant optical cavities (Fabry-Perot) we showed that a tunable electro-optic polarization modulator can be realized. We are currently working to expand the scope of this work by: i) integration of black phosphorus into a metasurface structure using MIM-type gap plasmon modes to reduce the footprint an order of magnitude compared to previously realized polarization control from ~500nm to ~50nm; and ii) using twisted layers black phosphorus with two unit cells of black phosphorus twisted by 90 degrees, combined with dual gates that individually control the charge density in each layer, allowing for complete control of optical anisotropy and accessing nearly every state on the Poincaré sphere.



Figure 2 (a) Schematic of emission mechanisms originating from bulk (red) excitons and edge (yellow) excitons. (b) Normalized PL spectra from an edge and the interior of a monolayer BP sample. (c) PL spectrum from one edge location vs. polarization. (d) Comparison of the interior exciton orientation versus the edge states. Blue, orange, and yellow points correspond to the first, second and third peak observed in the same spot. Optical absorption spectrum computed from first-principles GW-BSE calculations for the AC12-i (e) and ZZ4-i (f) structures. (g), (h) Computed GW-BSE band structure for reconstruction configurations shown in (e) and (f), respectively. (i) PL spectrum from an edge region, normalized for each voltage to the maximum emission feature. (j) PL intensity variation for the three features marked in (c) and (d) in yellow (bulk contribution) and red and blue (edge contribution).

2. Excitonic beam steering in monolayer molybdenum diselenide

Two-dimensional transition metal dichalcogenides (2D TMDCs) are promising candidates for ultra-thin active nanophotonic elements due to their strong tunable excitonic resonances that dominate their optical response. We previously demonstrated over 200% modulation in both the real and imaginary part of the complex refractive index in monolayer MoSe₂ by tuning the exciton resonances. The large electrical tunability of the optical properties is accompanied by large changes in reflectance amplitude and phase, enabling us to explore van der Waals metasurfaces with tunable reflection phase gradients that rely solely on the intrinsic excitonic resonances of the monolayer MoSe₂. In Figure 3, we experimentally showed a reconfigurable metasurface for dynamic beam steering based on a 2D van der Waals heterostructure. Our structure is comprised of a monolayer MoSe₂ encapsulated with hBN on top of an array of addressable electrodes. Our experiments show reflected light steering to angles between -30° to 30° at three different resonant



Figure 3. Excitonic beam steering from monolayer MoSe₂. (a) Microscope image of metasurface device. (b) Measured voltage and spectral dependence of the experimental steering efficiency at 30°. Three distinct peaks corresponding to the B exciton (X_B), A exciton (X_A), and trion (T) are observed. (c) Simulated voltage-dependent reflectance and (d) phase at the A exciton wavelength of 757 nm for different radiative efficiencies. (e,f) Simulated reflected angular far field intensity for $\eta = 0.25$ and $\eta = 0.5$, respectively, under different applied voltage gradient profiles and corresponding steered angle.

wavelengths corresponding to the A exciton, B exciton, and trion (Figure 3b). Monolayer MoSe₂ acts simultaneously as a strong resonant scatterer and a tunable material, revealing that intrinsic material resonances can perform light manipulation. Figure 3c and d are simulated gate voltage dependent reflection amplitude and phase of our metasurface for various MoSe₂ quantum yields, $\eta = \gamma_r / (\gamma_r + \gamma_{nr})$, corresponding to sample quality. Figure 3e and f show the far field intensity pattern of seven different periodic voltage configurations V(x) that steer the reflected beam between -30° to 30° for $\eta = 0.25$ and $\eta = 0.5$.

3. Black phosphorus Pancharatnam-Berry phase metasurface

In 2021, we demonstrated electro-optic polarization conversion in electrostatically doped three-layer black phosphorus (Biswas, et.al. *Science*, 2021). Spatial variation in the polarized output across a metasurface can enable the generation of exotic forms of structured light, and we have designed an angle-tunable Pancharatnam-Berry phase metasurface comprised of electrostatically doped black phosphorus strips, allowing for independent control of the output polarization along each strip. By configuring the output polarization with geometrical rotation across the metasurface, it is possible to generate a Pancharatnam-Berry phase in reflection, causing a polarization beam splitting effect when linearly polarized light is incident, metasurface design is underway.

Awards and Honors:

- Clarivate Web of Science Highly Cited Researcher 2022 (Harry Atwater)
- MRS Graduate Student Gold Award, Spring MRS 2022 (Souvik Biswas)
- Von Hippel Award of the Materials Research Society, 2021 (Harry Atwater)
- Optica Fellow, 2021 (Harry Atwater)

Training and Professional Development

Melissa Li and Souvik Biswas - graduate students in Applied Physics.

Publications:

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Plasmon and Photon Excitations in Two-Dimensional and Layered Materials

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Program Scope

Study of light-matter interactions in layered and two-dimensional materials represents a method to both achieve extreme optical confinement, approaching the atomic scale, and also a tool for observing and exploring new materials phenomena. Layered narrow bandgap and zero bandgap materials such as black phosphorus, graphene and layered chalcogenides support unusual and intriguing quantum-confined electronic states in thin layers and topological surface electronic states. Our research project seeks to understand the nature of localized and propagating plasmons and phonon polaritons in black phosphorus, graphene and surface states of topological insulators as well quantum confinement effects on electronic structure, transport and light emission in these materials.

Recent Progress

Quantum-confined states and tunable dichroism in black phosphorus

The incorporation of electrically tunable materials into photonic structures enables dynamic, electrical control of light propagation at the nanoscale. Fewlayer black phosphorus is a promising material in this context due to its in-plane anisotropic, quantum well band structure, with a direct band gap that can be tuned from 0.3 to 2 eV with a number of layers and subbands that manifest as additional optical transitions across a wide range of energies. We performed an experimental investigation of three different, anisotropic electro-optic mechanisms that allow electrical control of the complex refractive index in few-layer black phosphorus from the mid-infrared to the visible: Pauli-blocking of intersubband optical transitions (the Burstein-Moss effect): the quantum-confined Stark effect; and the modification of quantum well selection rules by а



Figure 1. Anisotropic electro-optical effects in few-layer BP. (a) Schematic figure of infrared tunability devices. Few-layer BP is mechanically exfoliated on SiO2/Si and then capped Al2O3. A semitransparent top contact of Pd is used to apply a field (VG1) while the device floats and Ni/ Au contacts are used to gate (VG2) the contacted heterostructure. (b) Crystal structure of BP with armchair (AC) and zigzag (ZZ) axes. (c) Illustration of: the quantum-confined Stark effect and symmetry-breaking modification of quantum well selection rules. The quantum-confined Stark effect causes a redshifting of the intersubband transition energies. Modification of selection rules breaks the symmetry and orthogonality of the quantum well wave functions, allowing forbidden transitions to occur (e.g., from v1 to c2,). (d) Illustration of anisotropic Pauli-

blocking (Burstein–Moss effect) in BP. Intersubband transitions are blocked due to the filling of the conduction band. Along the ZZ axis, all optical transitions are disallowed regardless of carrier concentration. (e) Raman spectra with excitation laser polarized along AC and ZZ axes. The intensity ratio between the Ag^2 peak and the Ag^1 peak is used to identify crystal axes.

symmetrybreaking, applied electric field. These effects generate near-unity tuning of the BP oscillator strength for some material thicknesses and photon energies, along a single inplane crystal axis, transforming absorption from highly anisotropic to nearly isotropic. Lastly, the anisotropy of these electro-optical phenomena results in dynamic control of linear dichroism and birefringence, a promising concept for active control of the complex polarization state of light, or propagation direction of surface waves.

In order to probe and distinguish the electro-optical tuning mechanisms evident in fewlayer BP, we use a combination of gating schemes wherein the BP either floats electrically in an applied field or is contacted, as shown in Figure 1a. We note that the samples are exfoliated on an oxide surface and encapsulated in Al₂O₃; therefore, while strain effects are known to influence the band gap of 2D materials,¹⁻³ including few-layer BP, these are identical for all measurements. Polarization-dependent optical measurements are taken aligned to the crystal axes, in order to probe the



Figure 2. Electrically tunable linear dichroism: quantumconfined Stark and Burstein–Moss effects and forbidden transitions. (a) Optical image of a fabricated sample with two Au contact pads for direct electrical contact to the BP and a semitransparent Pd top contact between them, separated from the BP by a thin layer of Al2O3. (b) Zero-bias infrared extinction of 3.5 nm flake, polarized along the armchair (AC) axis. (c) Calculated index of refraction for 3.5 nm thick BP with a Fermi energy at the midgap. (d) Tunability of BP oscillator strength with a field applied to the floating device, for light polarized along the AC axis. (e) Corresponding tunability for light polarized along the zigzag (ZZ) axis. (f) Tunability of BP oscillator strength with gating of the contacted device, for light polarized along the AC axis. (g) Corresponding tunability for light polarized along the ZZ axis.

structural anisotropy shown in Figure 1b. This enables us to isolate the contribution of chargecarrier density effects, i.e., a Burstein–Moss shift, and external field effects, i.e., the quantumconfined Stark effect and control of forbidden transitions in the infrared, to the tunability of linear dichroism, qualitatively illustrated in Figure 1c,d.⁴⁻⁷ In the anisotropic Burstein–Moss (BM) shift, the optical band gap of the material is changed as a result of band- filling and the consequent Pauliblocking of intersubband transitions. As the carrier concentration of the sample is changed, the Fermi level moves into (out of) the conduction or valence band, resulting in a decrease (increase) of absorptivity due to the disallowing (allowing) of optical transitions. Because intersubband optical transitions are only allowed along the armchair axis of BP, this tunability occurs only for light polarized along this axis. In the quantum-confined Stark Effect, the presence of a strong electric field results in the leaking of electron and hole wave functions into the band gap as Airy functions, red-shifting the intersubband transitions energies.

To illustrate the mechanisms of tunable dichroism of BP in the mid-infrared, we measure tunability of transmittance using Fourier-transform infrared (FTIR) microscopy as a function of externally (VG1) or directly applied bias (VG2), presented for a 3.5 nm thick flake, as determined from atomic force microscopy, in Figure 2. Figure 2b presents the raw extinction of the flake along the armchair axis at zero bias, obtained by normalizing the armchair axis 271 extinction to that of the

optically inactive zigzag axis. A band edge of approximately 0.53 eV is measured, consistent with a thickness of 3.5 nm. A broad, weak shoulder feature is observed at approximately 0.75 eV. The corresponding calculated optical constants for the flake are presented in Figure 2c for comparison. A Kubo formula approach is used for this calculation.

Electronically-tunable perfect absorption in graphene

Graphene has been the subject of intensive research as a promising candidate for tunable amplitude and phase modulation of THz and midinfrared light. Despite these exciting predictions and attractive features of tunable graphene nanostructures, a major obstacle for realizing perfect absorption in graphene has been the low carrier mobility in processed graphene samples⁸ as compared with the high carrier mobilities achievable in pristine or passivated and unpatterned graphene sheets,(25,



theoretical works predicting unity



Figure 3. At left a schematic of the graphene nanoribbon structures coupled to noble metal plasmonic resonators; surface plasmons excited on the Au surface are funneled into the slit where the electromagnetic energy is strongly coupled to a single graphene ribbon, whose permittivity is tunable under gate control of the Fermi level, enable tunable perfect absorption, as illustrated at right in the infrared absorption spectra as a function of graphene Fermi level. The peak absorption at 1350 cm⁻¹ reaches 97%.

absorption. The low graphene carrier mobility gives rise to a high nonradiative damping rate, which tends to under-couple the resonant modes of graphene nanoresonator arrays.(32) Since large-area high-performance functional graphene structures cannot rely on the high carrier mobility of exfoliated graphene flakes, achieving this performance level with graphene synthesized by chemical vapor deposition—with its attendant lower carrier mobility—is important.

We have experimentally demonstrated electronically tunable perfect absorption in graphene through graphene plasmonic nanostructures that exhibit dramatically higher resonant absorption, made possible by tailored nanophotonic designs that leverage the atomic thinness of graphene and the extreme confinement of graphene plasmons. First, we utilize lower-permittivity substrates, which allow better wavevector matching between free-space photons and graphene plasmons, to improve radiative coupling to graphene plasmonic ribbons (GPRs). Second, we combine the GPRs with noble metal plasmonic metallic antennas as sub-wavelength-scale intermediaries ($\sim \lambda_0/10$, λ_0 : free-space wavelength) to further enhance radiative coupling to deep sub-wavelength-scale GPRs ($< \lambda_0/70$). Unlike other perfect absorbers solely relying on noble metal plasmonic effects, our structures create perfect absorption in the graphene itself by utilizing graphene plasmonic resonances, providing an approach for tunable strong light–matter interactions. Notably, tunable perfect absorption is achieved with graphene nanoresonators covering less than 10% of the surface area, whereas an unpatterned graphene sheet covering 100% of the surface area exhibits low single-pass absorption ($\sim 2.3\%$).

Future Plans

The decay dynamics of excited carriers in graphene have attracted wide attention, as the gapless Dirac electronic band structure opens up relaxation channels that are not allowed in conventional materials. We are investigating mid-infrared emission in graphene originating from a previously unobserved decay channel: hot plasmons generated from optically excited carriers. In early work, we find a plasmon spectral flux that exceeds the blackbody emission flux by several orders of magnitude, and the observed Fermi-level dependence apparently rules out a Planckian light emission mechanism. Calculations for our experimental conditions indicate that a state of carrier inversion and plasmon gain may exist on the sub-100fs time scale, and that stimulated plasmon emission dominates spontaneous plasmon emission on this timescale, while the population inversion is lost at longer times, where spontaneous plasmon emission dominates stimulated and spontaneous emission processes.

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Quantum metamaterials

Principal Investigator: David Awschalom – Argonne National Lab

Co-Principal Investigators: Joseph Heremans – Argonne National Lab Andrew Cleland – Argonne National Lab David Schuster – University of Chicago Brian Stephenson – Argonne National Lab Daniel Lopez – Argonne National Lab

Program Scope

The quantum metamaterials effort at Argonne National Lab has been active at extending the established toolbox of techniques while building up new material growth capabilities related to quantum systems. Herein we highlight some of this recent progress regarding hybrid quantum systems, including studying mechanically driven spins in silicon carbide (SiC) with surface acoustic waves [1] as well as magnon-mediated quantum control of NV centers in diamond on ferromagnetic yttrium-iron-garnet [2]. Additionally, through close collaborations with other groups at MSD and Argonne, we continue to develop strain-sensitive X-ray imaging techniques that allow us to understand both the spin-phonon interactions [1,3] and the local crystalline strain surrounding these quantum defects[4,5]. These experiments build on and advance our understanding of defect lattice environments. This insight is key for improving the creation efficiency and coherence times of quantum systems, both essential parameters for the advancement of the field as a whole.

To complement this, ongoing synthesis efforts are discussed. These include homo-epitaxial microwave assisted CVD diamond growth alongside highly crystallized sputtered AlN thin films. Diamond growth is performed in the context of developing delta-doped and co-localized electronic-nuclear spin systems. Whereas AlN film growth and nanofabrication is targeted at the study of various quantum and crystalline defects in SiC via acoustic driving to create hybrid quantum system. These growth capabilities are complemented by an array of characterization tools which serve to guide iterative growth optimizations. Among these we note XRD based studies using both table-top tools and the synchrotron beam lines for the study crystalline properties, SEM/TEM observations of growth dynamics and morphology, and XPS chemical investigations of the material interfaces. Such understanding is key in surpassing current limitation of quantum systems such as NbTiN/NbN superconducting devices which are extremely sensitive to things such as surface/interface oxidation and shifts of stoichiometry.

Finally, we will present some new advances in localizing defects and nuclear spins along with developing a quantum sensing platform based on a patterned polymer-brush-array technique. All of the presented results allow us to better tailor the material growth and defect characteristics to the needs of specific quantum applications.

Recent Progress

We have recently installed our diamond CVD tool in our lab (see Figure 1) and have hired a postdoctoral scholar (Nazar Delegan) who started in early November to lead the diamond growth effort. To date, we have grown more than 5 samples of diamond with our new tool, including high quality single-crystal diamond epilayer films. Additionally, each iterative deposition has been guided by an ever growing material characterization toolbox.



Figure 1 | Seki SDS6300 diamond microwave-assisted plasmaenhanced chemical vapor deposition (PE-CVD) tool at ANL.

We have improved the quality of our AlN sputtered films on SiC through use of a heated etch to improve the crystallinity. This is shown as a significant narrowing, by more than a factor of two, in the rocking curve width (see Figure 2) of the AlN (004) XRD peak. This is expected to directly translate into an improvement of the piezoelectric properties of the film and by extension in the spin-strain coupling with the SiC. In sum, these improvements to the piezoelectric film should benefit our hybrid quantum system effort looking at mechanically driven spins in SiC using surface acoustic waves [1].

Also, we have recently completed several manuscripts exploring the spin-phonon interactions [1] using x-ray imaging techniques to map out the local acoustic standing waves in SiC [3]. These efforts highlight the strength of combining multiple techniques to understand the spatial interaction between spins and phonons. Furthermore, intimate collaborations with the Galli group at the University of Chicago allowed us to foster a better understanding of the shear strain component as it pertains to the mechanical control of spins [1].

Finally, we have made several steps toward understanding the defect creation process in our commonly used host material systems. Using Bragg Coherent Diffraction Imaging, we were able to detail the annealing driven vacancy diffusion dynamics in both diamond [4] and SiC [5] nanoparticles. We have also begun using

a localized nano-implantation technique to study the defect creation dynamics in an effort to improve creation efficiency and minimize unnecessary damage caused by the implantation process. This work is being done in collaboration using a modified focused ion beam at Sandia National Lab. The intent is to use their technical capabilities to nano-implant pristine SiC with silicon as a way to localize divacancy defects down to < 100 nm spots. We are in the process of



studying the local strain imparted by the implantation process via nanoscale x-ray imaging (see Figure 3).



Figure 3 | Nanoimplanted silicon ions into 4H-SiC. A broad spatial photoluminescence scan of the nanoimplanted spots (left). A zoom-in photoluminescence of the high dosed implanted areas of an unannealed (center-top) and annealed (center-bottom) sample. Note the annealed sample requires less excitation power suggesting a significantly higher divacancy defect density. The strain sensitive x-ray imagined of individual implanted spots shows a distinct broadening of the local strain structure post anneal (right).

Future Plans

A few of our future plans related to synthesis, defect creation, and spin-phonon hybrid quantum systems are as follows -

We look to continue our growth of CVD diamond, including nitrogen delta-doping and small spin ensembles. Additionally, we intend to explore the use of isotopically purified precursors for the growth of diamond super-lattice structures and optically distinguishable 3D localized NV⁻ defect ensembles. The former presents interesting possibilities in light of phononic structures and photonspin interaction, whereas the latter allows for controlled electron-nuclear spin systems. The traditionally employed (100) growth of diamond will be complimented with the ability to grow (111) oriented diamond for the purpose of obtaining highly oriented NV⁻ defects. This would allow an additional axis of control for various NV⁻ defect driven quantum sensing applications. Finally, the incorporation of other defect systems using similar delta-doping techniques, such as rare-earth and transition-metal, are being considered for their interesting properties in the context of quantum communication.

Incorporating our ever improving AlN film growth capabilities with nano-fabrication capabilities at the CNM/UChicago, we intend to fabricate quantum hybrid system devices and high Q mechanical resonators. This will include growing patterned AlN films on SiC membranes for improved photonic confinement. Such structures will serve to optimize the spin-strain interaction in mechanically driven hybrid systems.

We will continue our collaborative work with various groups at the APS. Using X-ray microscopy techniques to better understand the role of matrix crystal strain and defects in the vicinity of our quantum defects. This work is serving as a baseline in the development of new xray imaging techniques intended to allow us to perform phase-control mapping of acoustically generated strain waves in SiC. This approach would allow for a better understanding of the spinphonon hybrid quantum systems we are exploring.

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Digital Synthesis: A pathway to novel states of condensed matter

Anand Bhattacharya, Dillon Fong, Samuel Jiang (Argonne National Laboratory) Self-identify keywords to describe your project: Molecular beam epitaxy, interfacial

superconductivity, interfacial magnetism, spin transport, topological

Research Scope

In our program, we seek to create, explore and understand novel states of condensed matter and new functionalities that emerge at interfaces between different materials. These include collective states like interfacial magnetism and superconductivity, and interfacial topological states that may have relevance for spintronics and topological superconductivity. We seek to realize these states in materials synthesized with atomic layer-by-layer control using molecular beam epitaxy and related techniques. Thus, a significant part of our research is devoted to understanding growth processes that lead to these interfacial states and to improve our synthesis approaches. In the research presented here, we will focus on the formation of electron gases at the surfaces/interfaces of two perovskite oxides SrTiO₃ and KTaO₃, both 'quantum paraelectrics'. In SrTiO₃ the interfacial electron gas is superconducting for all known orientations - the [001], [110] and [111], with similar T_c 's of approximately 0.2 - 0.3K. On the other hand, in KTaO₃, the superconductivity is highly orientation selective, with the [111] interface having a maximum T_c of 2.2 K, the [110] interface with maximum T_c of ~ 1 K, while the [001] interface does not superconduct [Liu et al., Science 2021]. We have developed a theoretical model that explains this contrast [Liu et al., Nat. *Comm.* 2023]. Despite the striking similarities between dielectric properties of SrTiO₃ and KTaO₃, the striking orientation selectivity in KTaO₃ raises questions about its origin – these include the different spin-orbit couplings, and chemical/structural origins of the electron gas formation. In recent work, using a combined in-situ x-ray and ARPES study of SrTiO₃ films during growth, we unveiled a novel mechanism for the origin of two-dimensional electron gas formation in [001] oriented SrTiO₃, namely the formation of a TiO₂ double layer at the surface [Yan et al., Adv. Mater. 2022]. In our presentation (poster) we will explore this in detail and, also present our work on understanding the origin of electron gases at KTaO₃ interfaces, with the goal of better understanding and control of the electron gas formation at interfaces of quantum paraelectrics.

Recent Progress

Orientation selective superconductivity in KTaO₃ interfaces and its origins: The mechanism for Cooper pairs to form in unconventional superconductors is often elusive because experimental signatures that connect to a specific pairing mechanism are rare. KTaO₃ is a quantum paraelectric and whose interfaces can become superconducting on doping with electrons [Liu et al., *Science* 2021]. We observe distinct dependences of the superconducting transition temperature T_c on carrier density n_{2D} for electron gases formed at KTaO₃ (111), (001) and (110) interfaces. For the (111) interface, a remarkable linear dependence of T_c on n_{2D} is observed over a range of nearly one order of magnitude. Further, our study of the dependence of superconductivity on gate electric

fields reveals the role of the interface in mediating superconductivity. We find that the extreme sensitivity of superconductivity to crystallographic orientation can be explained by pairing via inter-orbital interactions induced by an inversion-breaking transverse optical (TO1) phonon and quantum confinement. These TO1 phonons soften at low temperatures leading to a diverging dielectric constant and 'quantum paralectric' properties, and typically do not couple to electrons at the Fermi surface. The inter-orbital interaction makes this possible. The calculated dependence of T_c on n_{2D} using our proposed mechanism is also consistent with experimental findings. Our study may shed light on the pairing mechanism in other superconducting quantum paraelectrics and polar materials [Liu et al., Nat. Comm. 2023].



Fig. 1. The ratio of the resistance R_s/R_N vs. temperature measured for (a) KTO (111) samples (b) and KTO (001), (110) samples, with varying n_{2D} . The direction of the arrow indicates the increase of n_{2D} . **c**, **d** n_{2D} dependence of T_c for KTO (111) samples shown in (**a**) and KTO (001), (110) samples shown in (**b**), respectively.

Origin of the 2D Electron Gas at the SrTiO₃

surface: Bulk SrTiO₃ is a well-known band insulator and the most common substrate used in the field of complex oxide heterostructures. Its surface and interface with other oxides, however, have demonstrated a variety of remarkable behaviors distinct from those expected. In this work, using

a suite of *in situ* techniques to monitor both the atomic and electronic structures of the SrTiO₃ (001) surface prior to and during growth, the disappearance and re-appearance of a 2D electron gas (2DEG) is observed after the completion of each SrO and TiO₂ monolayer, respectively. The 2DEG is identified with the TiO₂ double layer present at the initial SrTiO₃ surface, which gives rise to a surface potential and mobile electrons due to vacancies within the TiO_{2-x} adlayer. Much like the electronic reconstruction discovered in other systems, two atomic planes are required, here supplied by the double layer. The combined in situ scattering/spectroscopy findings resolve a number of longstanding issues associated with complex oxide interfaces, facilitating the employment of defect engineering atomic-scale in oxide electronics [Yan et al., Adv. Mater. 2022].



Fig. 2. Combined ARPES band maps and x-ray crystal truncation rods of $SrTiO_3$ (001) surfaces with (a) TiO₂ and (b) SrO terminations.

Future Plans

Understanding the structural and chemical origins of the 2D electron gas at interfaces of KTaO3: Given our investigations SrTiO3 interfaces and our findings in interfacial 2DEGs in KTaO3, it is a logical progression to study the process of 2DEG formation at KTaO3 surfaces in

detail. In particular, we'd like to understand the following: (i) How diffusion processes for oxygen vacancies differ between KTaO₃ and SrTiO₃, and how does that influence electron gas formation (ii) Determine how the different orientations of KTaO₃ differ in the manner in which the electron gas forms. (iii) The degree to which inversion symmetry breaking near the interface leads to polar distortions at different interfaces, and determine its consequences for electronic structure.

With the impending upgrade of the APS to a more coherent source, it will be possible to investigate the dynamics of thin film growth processes, shining new light on the behavior of adatoms and 2D island nucleation during epitaxial growth.ⁱ We will conduct similar *in situ* X-ray photon correlation spectroscopy (XPCS) studies during the growth/reduction of different complex oxides including KTaO₃ and exploit the ability to transfer samples directly between the MBE system and a nearby angle-resolved photoemission system to measure the accompanying electronic structure.

Ongoing studies of interfacial superconductivity in KTaO₃: Our theoretical work (with Mike Norman) suggests several paths to tune superconductivity and probe its underlying mechanism. We have several ongoing/planned experiments to elucidate and perhaps also exploit the superconducting state found at KTaO₃ interfaces. These include: (i) Studies of the kinetic inductance of the superconducting electron gas at different interfaces of KTaO₃. (ii) Tunneling spectroscopy of the superconducting state in KTaO₃ 2DEGs in different orientations (iii) Creating novel electronic states in patterned 2DEGs and nano-wires made out of KTaO₃. (iv) THz spectroscopy of the two-dimensional interfacial states in KTaO₃ (with Haidan Wen). (v) Consequences of spin-momentum locking in KTaO₃ interfacial 2DEGs.

Reduction of Nd_{0.8}**Sr**_{0.2}**NiO**₃: The synthesis of epitaxial Sr-doped nickelates by pulsed laser deposition and the subsequent topotactic reduction procedure are the key processes essential to achieving superconductivity in nickelate heterostructures. Topotactic reduction, however, is a complex process involving breakdown of the hydride molecule, diffusion of the hydrogen throughout the oxide, and removal of particular ions from the octahedral framework of the perovskite to achieve the square-planar structure. Here, we will employ *in situ* synchrotron X-ray scattering to monitor the topotactic reduction process for Nd_{0.8}Sr_{0.2}NiO₃ films grown on SrTiO₃ (001) substrates.



Fig. 3. Schematic of the reduction reaction for nickelate heterostructures illustrating different paths for the transformation and the change in crystal symmetry.

Charge-spin conversion and topological superconductivity in thin films of A15 compounds: The A15 family of compounds such as Ta₃Sb and Ti₃Pt have been predicted to have giant intrinsic spin Hall conductivities because of the large spin Berry curvature of its electronic band structure, making them attractive for spintronic applications.ⁱⁱ Due to superconductivity, the bulk the A15 superconductors are also promising candidates realization topological for the of superconductivity and Majorana fermions.ⁱⁱⁱ We have synthesized thin films of A15 phase Ta₃Sb and Ti₃Pt by sputter deposition. This will enable us to quantify the spin-charge conversion efficiency via transport or ferromagnetic resonance measurements, and to probe the



Fig. X-ray diffraction pattern of a sputter-deposited Ta₃Sb thin film showing all the expected crystallographic peaks. Inset: Crystal structure of A15-type Ta₃Sb.

possible existence of a topological *p*-wave superconducting state in mesoscale structures.

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Singlet and Triplet Exciton Interaction and Dynamics in Molecular Crystals

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Keywords: Organic, Exciton, Triplet Transport, Spin entanglement, Rubrene

Research Scope

We study excitonic effects in molecular crystals such as rubrene and related materials. Areas of focus are the triplet-pair state that is an intermediary to the fission process, how it is formed, how long the spin-correlation persists, and the mechanisms of triplet exciton diffusion and transport. Current activities include (1) the use of pump&probe transient grating to investigate the rise of the triplet population in a low-perturbation limit characterized by low excitation density, low repetition rate, and low peak intensity; and (2) the investigation of geminate triplet-exciton fusion and the related quantum beats to assess the persistence of the spin-entanglement in the presence of extensive diffusion in the crystal lattice in both one and two dimensions.

Recent Progress

Our group suffered from a forced interruption of the planned activities due to difficulties with the hiring and training of graduate students and to the pandemic. These issues were resolved during 2022, and this recent progress is reported here.

The first topic on which we report here is our study of the evolution of the initially photoexcited singlet exciton population using a pump&probe transient grating setup. The higher sensitivity of diffraction from a grating when compared to conventional transient absorption experiments allows to perform experiments in a low-perturbation regime, which is characterized in our case by low-peak-intensity 1ps excitation pulses, and a low 1kHz repetition rate for the experiment, which guarantees that no significant photoexcitation remnant exists when a new excitation pulse interacts with the sample. The latter is particularly important in a material like rubrene, where



Fig. 1. Transient Absorption bands in rubrene. The shaded green areas of incrased absorption correspond to the increase absorption due to transitions from the triplet ground state to its first or second excited state (T1 ->T2 and T1->T3). The complementary areas of decreased absorption are assigned to singlet transitions.

triplet states have a lifetime of the order of 100 μ s: MHz repetition rates would lead to a "triplet exciton sea" in the crystal instead of the unperturbed crystal, and any measurement would reflect the presence of those excitons. In addition, the use of 1ps pulses lowers dramatically the probability of multiphoton excitation to higher states and guarantees the spectral purity of the excitation.

In order to clarify open questions in a recent publication [1], we extended our pump&probe transient grating setup to support the use of a near infrared probe that is sensitive to the T1 \rightarrow T2 transition between the ground state of a triplet exciton and its first excited state. The motivation for doing this can be seen in Fig.1, which shows the result of transient absorption spectroscopy taken right after photoexcitation, and 25 ps after photoexcitation. This data was collected in a thick sample to reveal the additional weaker absorption band belonging to the T1 \rightarrow T2 transition, located near 800 nm.

Back-to-back probing of the sample using both visible and near infrared probe pulses allows to detect the evolution of the photoinduced transient grating using two different probes under identical excitation conditions. These experiments are now revealing an unexpected richness in the transient grating response that hints at different species increasing in density after singlet fission. These new measurements



Fig. 2. Transient grating dynamics at 460 nm when detected by either a 460 nm probe or a 770 nm probe. In both cases there is a strong signal that arises from the formation of a new type of excitation but the two detection wavelengths uncover drastically different time-evolutions.

show that the slower apparent triplet-state signals reported in Ref. 1 do not indicate a slower fission rate, but is instead a new contribution that occurs in addition to singlet fission in a sub 10ps time scale.

Fig. 2 shows a the results of a transient grating dynamics measurement done at an excitation wavelength of 460 nm in rubrene and with two different detection wavelengths. The plots on the left and on the right are the same data, plotted on two time scales.

The plots in the top row are the typical time-dynamics observed when detecting at 460 nm [1]. The solid curve through the data points is obtained from a grating-diffraction model that takes into account different possible contributions to the time-dynamics: An immediate appearance of a signal that can be due to the initial singlet population, a fast fission below 10ps, and a later rise of an unknown species, with an exponential time constant of about 80 ps for these data. An instantaneous response at time 0 that has the shape of the excitation and detection pulses can be assigned to third-order optical nonlinearities.

The plots in the bottom row are the time-dynamics observed when detecting at 770 nm. The immediate appearance of a signal during the excitation pulse is also observed here, but this is then followed by a fast exponential build-up with an exponential time-constant of the order of 5ps (assigned to the onset of the triplet-population arising from exciton fission) and by a weaker, but still visible later rise with an exponential time-constant of about 20ps.

This data clearly reveals the as yet unreported existence of different processes occuring between 1 and 100 ps after photoexcitation of singlet excitons. A common characteristic of a signal with a rise-time in the sub-10ps range can be consistently assigned to the rise of triplet exciton density, and is consistent with earlier data [1,2]. But in addition to this, there appears to be an additional evolution of the triplet population that takes place after 10ps, up until about 100ps.

We are presently collecting data at other excitation and detection wavelengths in order to disentangle these different contributions. An hypothesis to explain the time-dynamics result in Fig. 2 is the possibility that the triplet-exciton pair created via fission initially forms a spatially correlated 'bound state', and that the strong absorption band at 2.4 eV in Fig. 1 belongs to this spatially correlated triplet-pair. It is then possible that individual triplet states that arise from spatial separation of the triplet-pair have a slightly different excitation energy and can only be detected when the detection wavelength is moved outside the 2.4 eV absorption band (see Fig. 1), which is the case when detecting at 460 nm, the wavelength at which the slower rise of the diffraction signal is most clearly seen [1].

The second topic on which we report here is the study of the fluorescence quantum-beats that are due to fusion of the entangled triplet-pair state. We expect that the dependence of the quantum-beat frequency from the magnetic field orientation in the crystal will provide indirect information on the wavefunction of the triplet excitons and on their transport, completing and complementing the transport studies performed in Ref. 3.

The direction of an applied magnetic field will lead to a modification of the energies of the basis states that build the spin-zero triplet-pair state created via exciton fission. In the high-field limit reached for fields larger than about 0.1 Tesla, only two high-field basis states contribute significantly to the spin-zero configuration of the triplet-pair. Their different energies will then lead to quantum-interference when the two excitons in the triplet pair meet and initiate a fusion event. Given the orientation of the molecules in the crystal it is then possible to calculate these basis state energies from molecular properties, and therefore predict the quantum beat frequency.

We have done this by taking the molecular EPR parameters of tetracene, and using them to calculate the expected high-field basis state energies for the different magnetic field orientations in the rubrene crystal structure. It is a peculiarity of the rubrene crystal structure that, when varying the magnetic field direction from the 'c' direction to the 'a' direction while keeping the magnetic field perpendicular to 'b', the state energies determined by the two different molecular orientations in the unit cell are identical for both molecules. The same is true when varving the magnetic field direction from the 'c' direction to the 'b' direction (the data obtained for these angular dependencies is shown in Fig. 3). However, this does not happen when varying the magnetic field direction from the 'a' direction to the 'b' direction.



Fig. 3. Observed quantum beat frequencies as a function of magnetic field direction in rubrene. The different data points belong to different measurements in different crystals. The blue solid curve was obtained using the EPR parameters of the tetracene backbone and its orientation in the rubrene crystal structure. The crystallographic direction of the main axes of orthorhombic rubrene are labeled on the top axis. The absence of data points in the region between the *a* and *b* axes is caused by the fact that the quantum beats disappear in that region of magnetic field orientation.

We are currently investigating the manner in which the quantum beats disappear when moving away from the 'b' or 'a' axis while keeping the magnetic field perpendicular to 'c'. This disappearance of the fluorescence quantum beats for magnetic fields in the ab-plane can be explained if the triplet

exciton wavefunction does not completely delocalize over the two molecular families. For the case when the triplet exciton wavefunction is mostly localized on one or the other molecular types in a unit cell, any possibility for one of the excitons in a triplet-pair to spend time on the other type of molecule would lead to a different evolution of its quantum mechanical spin state, which would then lead to a random dephasing of the two elements of the triplet pair, destroying the coherence that leads to quantum beats. What makes this effect very interesting is that we can related it to our recent studies of exciton transport: The two excitons in the triplet pair will initially be confined to only one type of molecule, undergoing a one-dimensional random walk [3]. This should keep the spin coherence in the pair unperturbed, but could lead to the simultaneous presence of two beat frequencies. Then, as soon as the excitons start moving in the second dimension, the coherence would be impacted in a random way, leading to the disappearance of the quantum interference effect. For the moment our measurements imply that the triplet wavefunctions are indeed mostly localized on one or the other molecule in rubrene (in contrast to tetracene where the contributions of both molecules have been shown to average out), and also imply that the transition from 1D to 2D diffusion in the triplet pair happens after a time of the order of nanoseconds, consistent with the observations in Ref. 3. We expect that further development of this type of measurement and analysis will lead to a better understanding of how the triplet-pair evolves in a molecular crystal.

Future Plans

We will continue the characterization of the transient-grating dynamics for different excitation and detection wavelengths at room temperature, and also continue the analysis of quantum beat frequencies. Experiments and analysis are expected to be completed over the course of the next few months with the final results published this year. After this, we intend to obtain more information from temperature dependent measurements.

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Publications

Put the list of publications in the recent 2-years SUPPORTED BY BES here. If more than 10 publications, list only the 10 most relevant.

1. Eric A. Wolf, Ivan Biaggio, "<u>Geminate exciton fusion fluorescence as a probe of triplet exciton</u> transport after singlet fission," Phys. Rev. B Letters 103 (20), L201201 (2021)

Opening New Frontiers of Epsilon-Near-Zero Optics

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Keywords: Epsilon-near-zero, nonlinear, transparent conducting oxides, transition metal nitrides

Research Scope

This project focuses on discovering novel platforms to enhance the generally weak interaction of light and matter by exploring novel interaction regimes. Specifically, we explore epsilon-near-zero (ENZ) materials whose real part of the dielectric permittivity approaches zero, taking a holistic approach to understanding and controlling ENZ properties in transparent conducting oxides (TCOs) and transition metal nitrides (TMNs). We study the enhancement of nonlinear optics in ENZ regime and preform optical characterization of ENZ materials focusing on ultrafast and extreme modulation of optical parameters. We also study the control of various emission processes in the presence of homogeneous and structured ENZ media. Our major results can be broadly categorized into two divisions i) investigation of material properties for ENZ applications and ii) the dynamic control and tunability of light using ENZ.

Recent Progress

A signature advantage of ENZ materials is the enhanced optical nonlinearities. First, we explored the material platforms for ENZ applications and studied the ultrafast dynamics of these materials. Secondly, we utilized these findings to design experiments which provides new platforms for nonlinear optics and also pave the way forward towards new physics.

Investigating and Controlling of Material Properties for ENZ Applications

We investigated the effect of thickness on the ENZ point of TCO and TMN thin films. We found that for TCOs, the film thickness strongly affects the crystallinity, primarily through varying grain sizes influencing the free carrier concentration and the total scattering losses. We utilized this mechanism to control both the ENZ point and the losses at that point by varying the thickness. Using this effect, we have showed static tunability in the operating frequency of a Berreman absorber and reported its optical modulation properties [1]. We also expanded to new wavelength regimes, specifically in the technologically important infrared regime, where we obtained extraordinarily large optical modulation by using undoped zinc oxide (ZnO) and Yttrium doped

cadmium oxide (CdO) films [2,3]. We demonstrated tuning of the ENZ point in CdO by changing the dopant density to cover most of the telecom and the infrared frequencies.



Figure 15 a) Thickness dependence of real-part of the dielectric permittivity showing the control of ENZ point via thickness.[1] b) effect of yttrium doping concentrations (no doped -ND, low-doping - LD, medium doping - MD, and high doping – HD) on ENZ point.[3] c) and d) show ultrafast carrier response via reflection meaurements in TiN (c) and ZrN (d) measured on a streak camera. [4] e) and f) demonstrate the control of carrier dynamics enabled by combining fast and slow responses TCOs and TMNs. [5]

Another important aspect of ENZ materials is the investigation of the carrier dynamics. The strong modulation in the ENZ regime enables a powerful tool to investigate transient charge dynamics. We uncovered ultrafast carrier dynamics in titanium nitride (TiN) and zirconium nitride (ZrN) [4]. We have uncovered the two-step relaxation dynamics illustrating separate electron-scattering and phonon-scattering mechanisms. The uncovered understanding of transient dynamics inspired the combination of fast and slow relaxation mechanisms of TCO and TMN films in a metasurface to obtain a dynamic device with tunable operation speed [5].

Dynamic Control and Tunability of Light Using ENZ

Our work on understanding and controlling ENZ properties expanded the capability to enhance known nonlinear processes and explore new phenomena in ENZ materials. We investigated ENZ enhanced wave mixing processes by generating visible photons from a near-zero-index film demonstrating highly tunable visible frequencies from near infrared pump pulses [6]. We have also applied the enhanced harmonic generation in an ultra-thin ENZ-based frequency-resolved optical gating (FROG) scheme [7]. The innovative scheme integrates both second and third harmonics – enabled by ENZ enhancement – into a new FROG that outperforms the commercial ones in terms of bandwidth, sensitivity and cost. Additionally, the nonlinearity occurs in a thin film, thus relaxing design constraints. We extended our investigation to include coupling between emitters and ENZ film. We employed an effective-ENZ lattice resonance to demonstrate strong long-range interactions between emitters [8]. This method can lead a way forward to observe superfluorescence and entanglement between quantum emitters.



Figure 16 a) Third harmonic FROG trace generated from thin aluminum doped ZnO film. b) Reconstruction of ultrafast pulse duration from third harmonic from trace in (a). c) experimental schematic for measuring time-refraction. d) Pump-probe data of time-refraction of probe pulse (1.2 micron wavelength) from a single-cycle modulator showing ultrafast frequency modulation.

Finally, strong and ultrafast light-matter interactions in ENZ materials offers a unique way to realize time-varying optical materials. We began initial investigations into the blossoming area of photonics in time-varying media. We have studied the enhancement of time refraction in an ENZ film [9], and are currently pursuing the observation time reflection (which has not been shown in optical range yet) using an ENZ material [10].

Future Plans

Our future plans branch out from the work of both funded efforts in three interconnected directions. First, we will combine our recent efforts with controlling and tuning ENZ properties of transparent conducting oxides (ZnO and CdO) and transition metal nitrides (TiN) with nanofabrication of metasurfaces and metamaterials to explore the extreme limit nonlinear optics of ENZ materials. Second, we plan to build upon our work on optically modulated ENZ materials to examine the temporal insulator-metal interfaces that are unique to ENZ materials. Finally, we will explore the localization of the spin and orbital degrees of freedom of light in disordered ENZ media.

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Fundamental Studies on Heat Conduction in Polymers of Varying Crystallinity and under Extreme Dynamic Deformations

Svetlana V. Boriskina

Polymers, heat transfer, thermal conductivity, configurational entropy, dynamic tunability

Research Scope

This project aims to gain a fundamental understanding of heat conduction mechanism in polymer materials and structures (fibers) of similar chemical composition but varying crystallinity level and configurational state. Prior experimental measurements on semicrystalline polyethylene fibers and films have shown that their thermal conductivity values can be varied in a wide range (across several orders of magnitude) by varying the resin molecular weight and fabrication process parameters. While the mechanisms underlying the high thermal conductivity of highly crystalline and highly aligned polymers have been studied to a great detail recently, the mechanisms hindering the thermal conductivity in amorphous polymers are far less understood.

The low thermal conductivity of amorphous polymers (0.1-0.5 W/mK) is typically ascribed to their high configurational entropy. Yet, a much wider thermal conductivity range can be achieved in amorphous dielectrics and metals. For example, amorphous silicon has a thermal conductivity around 1.5 W/mK, while many amorphous ceramics/glasses have thermal conductivity from 1-10 W/mK. Amorphous metal alloys have thermal conductivity in range 5-10 W/mK, exhibiting a much higher upper bond of thermal conductivity than polymers. Furthermore, the covalent bonds in polymer chains have a bond energy of 100-1000 kJ/mol (345 kJ/mol for C-C bond), which is on par with that of usual metallic bonds in metals (50-900 kJ/mol) and coordinate covalent bonds in dielectric materials (100-1000 kJ/mol). It is intriguing why amorphous polymers exhibit such a narrow range of thermal conductivity distribution relative to other amorphous materials.

We are combining molecular dynamics (MD) simulations and experiments to gain fundamental insights into mechanisms of heat conduction in amorphous and semi-crystalline polymers. We are also exploring the opportunities to dynamically tune the configurational entropy and thermal conductivity values of these materials by extreme mechanical deformations (including stretching and twisting) as well as temperature variations. Finally, we explore applications in passive radiative cooling technologies where the moderate thermal conductivity values achievable in melt-spun semi-crystalline polyethylene (PE) fibers can provide almost the same functionality as much more thermally conductive yet much more expensive gel-spun ultra-high molecular weight polyethylene (UHMWPE) fibers. We achieve our research goals via a combination of polymer fabrication, structural and mechanical characterization, MD and heat transfer modeling techniques, as well as thermal conductivity measurements.

Recent Progress

1. Normal mode localization and its effect on heat transport in amorphous polymers. Polymers consist of individual chains with repeating units and strong intra-chain covalent bonds, and amorphous arrangements among chains with weak inter-chain van der Waals, and for some polymers also electrostatic interactions. This strong heterogeneity in bond strength gives rise to special features in the constituent phonon modes, which have not been studied in detail before. By analyzing the normal modes in several amorphous polymers, we found a great degree of mode localization (over 90%), as measured by both participation ratio and mode spatial extent. Such a high degree of localization was never reported in any other materials, while the highest fraction of localized modes in literature is 10% in amorphous silicon dioxide. The cumulative density of states versus mode

participation ratio is shown in Fig. 1a for three representative amorphous polymers. The vertical line indicates the threshold of localization.



Figure 1. (a) Cumulative density of states versus normal modes participation ratio in amorphous polymers from lattice dynamics. The dashed vertical line indicates threshold of localized modes. (b) Normalized cumulative thermal conductivity (TC) versus participation ratio from Green Kubo Mode Analysis.

While the phonon spectral contribution to thermal conductivity is important an characteristic for crystalline materials, the phonon picture fails in amorphous systems without translational symmetry¹. For decades, thermal transport in amorphous materials has been modeled under Allen Feldman (AF) picture², where thev separated vibrational modes as propagons, diffusions, and locons.

Under AF picture, locons have zero contribution to thermal transport. Our analysis shows, however, that for amorphous polymers, over 90% of normal modes are locons. We used the recently developed Green Kubo Mode Analysis (GKMA) to study different modal contributions to thermal conductivity³ (Fig. 1b). Our main conclusions include: *(i) Strongly localized mode can still be very active in thermal transport in polymers. (ii) Localized modes on average have smaller contributions to transport. (iii) Localized modes accumulate to have a dominant contribution (over 80%) to thermal transport because of their large population.* This explains why amorphous polymers have low thermal conductivities and stimulates us to study how the localized modes can be modified to modify thermal transport in amorphous and semi-crystalline polymers.



2. Dynamic modulation of structural and thermal transport properties in elastic amorphous polymers. Through а combination of experiments MD and simulations, we study the effects of dynamic reversible modification of polymer chain the configuration and thermal transport properties of semi-crystalline PE

Figure 2. (a) WAXS spectra of the elastic olefin block co-polymer fiber under increasing degree of the uniaxial strain deformation. (b) 2D WAXS diffraction patterns revealing the extreme polymer chain alignment with the increasing uniaxial strain. (c) FTIR spectra of fibers under uniaxial stretching.

materials and amorphous olefin block co-polymers. We have engineered fibers from these materials that exhibit excellent elastic properties (withstanding uniaxial stress deformations up to 1000%), and have observed experimentally the strain-induced reversible changes in their structure and the vibrational modes spectra. These include: *(i) a decrease in the orthorhombic crystalline phase accompanied by a slight increase in the monoclinic crystalline phase and the simultaneous dramatic increase in the amorphous polymer chains alignment* revealed via the wide-angle X-ray spectroscopy (Fig. 2a,b); and *(ii) elimination of some of the vibrational modes from the polymer infrared spectra* revealed via the FTIR spectroscopy (Fig. 2c). We are conducting MD studies of these effects with the aim to understand how these structural changes affect the normal modes within the fiber material, and the different modes contributions to the thermal conductivity.


Figure 3. (a) Model predictions of the differential skin temperature covered by a textile as the function of its across-the-plane thermal conductivity. (b) Measured along-the-fiber thermal conductivity of several melt-spun PE yarns with varying material crystallinity.

Semi-crystalline fibers 3. PE engineering for applications in passively cooling textiles. Personal thermoregulation passively mediated by textiles increases the level of comfort, improves productivity in the workplace, and can help to achieve significant energy savings and emissions reduction. Recently explored passive cooling engineering strategies focused on improving the textile infrared transparency⁴, which often compromises the material tactile comfort, strength and costs. We showed experimentally and

confirmed via modeling that knitted fabrics composed of multi-filament PE yarns with moderate thermal conductivity values in the range 0.6-0.9 W/mK fabricated by a conventional melt-spin process can reduce skin temperature via the mechanism of heat removal via thermal conduction. Our experiments show that textiles knitted from our fibers reduced the textile-clad skin temperature by a few degrees relative to conventional textiles. We also developed a model to calculate the expected temperature of the skin covered by a textile as a function of the textile effective across-the-plane thermal conductivity. The model predictions plotted in Fig. 3a reveal that the increase of the textile effective thermal conductivity by an order of magnitude, from 7.5 $\frac{W \cdot mm}{m^2 C^o}$ to 75 $\frac{W \cdot mm}{m^2 C^o}$, is expected to result in a significant (about 7C°) reduction in the expected skin temperature. Conductivities of conventional textiles fall within this range (e.g., $\sim 50 \frac{W \cdot mm}{m^2 C^0}$ for cotton), while the effective conductivity of our knitted PE textile is shown as a star. We fabricated several types of multi-filament PE yarns with a varying level of crystallinity and measured their along-the-yarn thermal conductivities (Fig. 3b). Y3 yarn has been used to fabricate the knitted PE textile in Fig. 3a. Although thermal conductivity values up to 20 $\frac{W}{mK}$ can be achieved in the gel-spun UHMWPE fibers⁵, our data show that the skin cooling effect saturates at the through-the-textile effective conductivity values above $\sim 100 \frac{W \cdot mm}{m^2 C^o}$, achievable with yarns featuring along-the-fiber thermal conductivity on the order of $\sim 1 \frac{W}{m K}$ (compare Figs. 3a,b). These – still high by the textile fiber standards – thermal conductivities can be achieved via conventional melt-spinning fiber technologies used for mass production of textile-grade yarns worldwide.

Future Plans

Our ongoing and future studies are focused on further quantitative understanding on the mechanism of energy transport between locons. Our current models show that (i) more than half of the locons are nested onto one single chain, and (ii) the locons involving more than two chains contribute more to thermal conductivity. This leads us to the conclusion that engineering strategies need to be developed to control the bridge locons, i.e., the bridge modes that connect vibrations from different chains. We will also continue studying the effect of the large-scale reversible deformations (including stretching, twisting and their combinations) on the structural and thermal transport properties of amorphous polymers.

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A Nonlinear Approach to Weyl Transport

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Self-identify keywords to describe your project: Weyl Semimetals, Nonlinear, Photocurrent, Raman, Transport

Research Scope

The project explores the nonlinear and inelastic optical responses of topological semimetals (TSM), towards understanding their dynamics and unleashing their potential for plasmonics, nonreciprocal photothermoelectrics, high-speed interconnects, efficient nonlinear optoelectronic elements, and magneto-resistive sensors. Topological semimetals possess an array of novel transport and nonlinear responses, including ultrahigh mobilities, chiral anomalies, extreme magneto-resistance, and nonlinear responses. These properties' origins remain controversial, such as whether the nontrivial topology is responsible for ultrahigh mobility and enormous nonlinearities. In this work the PI is using his unique combination of expertise in optical spectroscopy and device fabrication to uncover the mechanisms governing the dynamic and topological properties of Semimetals. This will require deciphering the intertwined roles of the band dispersion, symmetry, phonons, and quantum geometry. In particular, one must controllably tune one of these components and observe the effects on various physical responses. It is also highly desirable to expand nonlinear techniques to provide more detailed information about the quantum geometry from particular momentum regions of the band structure. To this end, the PI is developing new means to probe the nonlinear responses originating from specific regions of momentum space using current-induced nonlinear responses. The scattering and role of phonons will be disentangled through Raman experiments, performed on well-chosen materials that tune either the Fermi level or phonon spectra.

Recent Progress

The advances in Raman scattering and nonlinear photocurrents have contributed to several works. Specifically, our group has uncovered new terms in Raman scattering in topological magnets, optimized the fabrication of novel 2D heterostructures, and provided unambiguous evidence for the role of phonons in enhancing transport in topological semimetals. Lastly, we reported the discovery of the Axial Higgs Mode in a topological semimetal. This new quantum excitation is the first multi-component amplitude mode, signaling a new broken symmetry state. In addition, it results from the

intertwined strong electron-phonon coupling and unique quantum geometry of rare earth tritellurides. This was achieved through careful analysis of the symmetry response of charge density wave in Raman (see Figure).

Future Plans

The group is currently finishing our initial thirdorder nonlinear photocurrent measurements. Once the technique is optimized, we will begin applying it to various topological semimetals. In addition, we have completed a study of the topological semimetal family (Ta,Nb)(Ge,Si)₂. Here the





Raman has revealed a surprising competition between the anharmonic scattering and the electronphonon coupling. Upon minimizing the anharmonic scattering, we find the emergence of superconductivity. We are working to understand the origin of these results that could pave the way to new means of unleashing superconductivity in topological systems.

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Observation of Vector Spin Seebeck Effect and Spin Swapping Effect in Non-Collinear Antiferromagnets C. L. Chien The Johns Hopkins University

Keywords: pure spin current, quantum materials, and topological triplet superconductors

Research Scope

We report the observation of vector spin Seebeck effect in non-collinear antiferromagnetic insulator LuFeO₃, where pure spin current can be thermally injected in the out-of-plane (longitudinal) as well as in the in-plane (transverse) directions, as opposed to only longitudinal injection for ferromagnetic insulators with aligned moments. The mechanism of the newly observed transverse spin Seebeck effect is consistent with the spin swapping effect predicted by Lifshits and Dyakanov in 2009.

Recent Progress

Injection and detection of pure spin current has been well-established in heavy-metal (HM)/ferromagnet (FM) heterostructures [1], where the HM layer detects the pure spin current injected from the FM using spin Seebeck effect (SSE), spin pumping (SP) and other techniques, according to the inverse spin Hall effect (ISHE) described in

$$E_{ISHE} = r \operatorname{Q}_{SH} \boldsymbol{j}_{s} \times \boldsymbol{s},$$

(1)

where j_s is the pure spin current density, s the spin index set by the magnetization of the FM, r the resistivity and Q_{SH} the spin Hall angle of the HM that measures the spin/charge conversion efficiency. In SSE, the thermal gradient ∇T dictates the spin injection direction, which may be normal or parallel to the HM/FM interface as in longitudinal or transverse SSE respectively. Numerous experiments in HM/FMs have shown that there is only longitudinal SSE but no transverse SSE. For example, in W/YIG [2], where YIG = Y₃Fe₅O₁₂, with $\nabla_z T$ in the out-of-plane z direction (*Fig. 1a*), s in the inplane y direction, one measures a large ISHE voltage V_x but $V_y = 0$ according to Eq. (1). In contrast, with an in-plane thermal gradient (*Fig. 1b*), there is no ISHE voltage for any direction of s. The exclusive longitudinal

SSE been wellhas established in FMs (e.g., YIG) with aligned moments, where the large magnetization M can be aligned to other directions magnetic bv а field exceeding the anisotropy field. In antiferromagnets (AFs) with no magnetization $(\mathbf{M} = 0)$ (e.g., Cr_2O_3 and MnF_2) there is no SSE unless under a large magnetic field, which induces a



Fig. 1. (a) Longitudinal and (b) transverse spin Seebeck effect in W/YIG heterostructures. [Xu et al., Phys. Rev. Lett. **129**. 117202 (2022)].

small M that facilitates longitudinal SSE.

In non-collinear AFs, as we recently demonstrated in LuFeO₃, one observes vector SSE [2], where the temperature gradient and spin injection can be directed along any direction, in-plane as well as out-of-plane, and realize the ISHE voltage in all directions. LuFeO3 has an orthorhombic structure with lattice constants of $a \approx 5.35$ Å, $b \approx 5.61$ Å and $c \approx 7.67$ Å Each Fe³⁺ ion in an [3]. octahedral cage of six O²⁻ ions carries a 5 μ_B magnetic moment and Lu³⁺ is nonmagnetic. The strong AF exchange interaction gives rise to the AF ordering, whereas the Dzyaloshinskii-Moriya interaction (DMI) together with the single ion anisotropy give rise to the non-collinear AF spin the structure, where Fe



Fig. 2. Spin Seeebeck effect in the longitudinal geometry (a) V_x and (b) V_y under $\nabla_z T$ and the transverse geometry (c) V_x under $\nabla_y T$ and (d) V_y under $\nabla_x T$. [Xu et al., Phys. Rev. Lett. **129**. 117202 (2022)].

moments on the two AF sublattices are nearly antiparallel along the *a* axis but with a small tilt angle of about 0.8° towards the *c* axis. With the *x*, *y*, and *z* axes along the crystal axes of *a*, *b*, and *c* respectively, LuFeO₃ exhibits a small and non-collinear magnetization of $M = M_x i + M_y j + M_z k$, with the values of $M_z \gg M_y \gtrsim M_x$, and $M_z = 0.053 \mu_B$ /Fe at room temperature. Furthermore, only H_z , or the field component along the *c* axis, induces switching with a switching field of only 150 Oe. Unlike those in FMs, the small *M* in LuFeO₃ cannot be directed to other directions by an external magnetic field.

The vector SSE in W/LuFeO₃ are shown in *Fig. 2*. Since only H_z can alter the non-collinear magnetization, we use H_z in all the measurements. The longitudinal SSE results are shown in *Fig. 2a*, where the ISHE voltage switches sharply at 150 Oe. In additional to the expected ISHE voltage in V_x , we have also observed a voltage V_y as shown in *Fig. 2b*. We note in the longitudinal SSE in W/YIG under $\nabla_z T$ as shown in *Fig. 1a*, one observes maximal V_x but $V_y = 0$.

Most distinctively, under an in-plane thermal gradient, where no transverse SSE has previously been observed in FM insulators as shown in *Fig. 1b*, we observe a large transverse ISHE voltages in W/LuFeO₃ with both in-plane injection directions of $\nabla_x T$ and $\nabla_y T$ as shown in *Fig. 2c* and *Fig. 2d*, respectively, with more than an order of magnitude larger than those of the longitudinal SSE. These different ISHE voltages are related to the specific components of the magnetization as described in Eq. (1). In longitudinal SSE under $\nabla_z T$, the ISHE V_x and V_y scales with M_y and M_x respectively, whereas in transverse SSE under $\nabla_x T$ and $\nabla_y T$, both V_y and V_x respectively scale with M_z . In the vector SSE in W/LuFeO₃ with the components $M_z \gg M_y \gtrsim M_x$, the transverse SSE voltages are much larger than those of the longitudinal SSE, fulfilling the vector relation of Eq. (1) in all three directions.

In the transverse SSE results shown in *Fig. 2c* and *Fig. 2d*, a spin current injected in the inplane direction has been detected in the out-of-plane direction in the HM metal layer. Specifically, as shown in *Fig. 2c*, a spin current injected in the *y*-direction with spin index in the *z*-direction has been detected as a spin current in the *z*-direction with spin index in the *y*-direction. A similar situation occurs in *Fig. 2d*. This is the spin swapping effect first predicted by Lifshits and Dyakanov in 2009, where the spin current direction and spin index direction interchanged [4]. This intriguing effect is absent in collinear FM systems but realized in non-collinear AFs [2, 5].

In summary, we have observed vector spin Seebeck effect and spin swapping effect in non-collinear antiferromagnets of W/LuFeO₃ heterostructures with results altogether different from those in collinear ferromagnets (e.g., W/YIG).

Future Plans

We plan to investigate other non-collinear moments systems to explore the characteristics of the vector spin Seebeck effect and the spin swapping effect. The spin current injected by spin waves (i.e., magnons) and the magnetization are expected to exhibit different temperature dependences, which remain to be established in W/LuFeO₃. With low magnetization and low switching fields, non-collinear antiferromagnets may be explored as new materials for spintronic phenomena and applications.

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Spin-Mediated Heat Conduction and Thermoelectric Effects in Novel Materials

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Program Scope

This program involves experimental transport studies of spin-mediated heat transport and thermoelectric effects in novel materials (oxide conductors, magnetic insulators). Recent work focuses on transport studies of the extreme low-carrier density ground state of the superconductor $Li_{0.9}Mo_6O_{17}$ (LiPB) and spin-thermoelectric studies (spin Seebeck, spin-injection) in interfaces of superconducting Nb films with bulk single crystals of the insulating helimagnet, Cu₂OSeO₃.

Recent Progress

Superconductivity at Carrier Density $n \approx 10^{17}$ cm⁻³ in quasi-one-dimensional $Li_{0.9}Mo_6O_{17}$ [submitted to Phys. Rev. Lett.]

This project, comprising a comprehensive analysis of data accumulated over several years under current and prior contract, has progressed in the past year. The work incorporates low-T ($T \ge 0.4$ K) magnetotransport data (Hall, magnetoresistance, Seebeck and Nernst) within the most conducting *bc*-plane (field along *a*) for both superconducting (SC) and non-superconducting (non-SC) LiPB crystals of this quasi-one-dimensional (q1D) compound. Prior work shows Luttinger liquid character at $T \ge 100$ K; photoemission and band structure calculations indicate two q1D, nearly degenerate electron bands crossing the Fermi energy, derived from d_{xy} orbital overlap along the zig-zag Mo-O chains (crystallographic *b* axis).¹

Our principal findings are extremely low carrier densities ($n \approx 10^{17} \text{ cm}^{-3}$) throughout the range $T \leq 100 \text{ K}$ [Fig. 1 (a)] and a rich multi-carrier physics that our analyses have revealed to imply an unusual low-energy electronic structure. The mobile carrier densities are among the lowest known for any superconductor^{2,3} placing the superconductivity of LiPB in a regime at the border between BCS and Bose-Einstein condensation.

LiPB's resistivity is metallic at high *T*, exhibits a minimum at 15 K $\leq T_{min} \leq$ 30 K and rises below T_{min} to the superconducting transition at $T_c \approx 2$ K. The mechanisms for the upturn and superconductivity remain a mystery in spite of substantial experimental efforts over decades. The superconducting state is three dimensional with highly anisotropic upper-critical fields (H_{c2}) consistent with its normal-state electrical anisotropy.⁴ For field applied along the q1D chains, H_{c2}

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substantially exceeds the Pauli paramagnetic limit, motivating the proposal that LiPB is a triplet superconductor.⁴

A key to our recent advances in revealing the complexities of the superconducting ground state are measurements on multiple crystals with electrical and heat currents applied along (*b*-axis) and transverse to (*c*axis) the q1D chains in both SC and non-SC crystals, and successful self-consistent fitting of the field-dependent Hall and magnetoresistance data sets to an anisotropic, two-band Drude model that includes densities for electrons and holes, n_h , n_e , and four mobilities (two each along each direction), with field dependencies dictated by the effective mobilities, $\mu_h =$ and $\mu_e = \sqrt{\mu_{eb}\mu_{ec}}$. The $\sqrt{\mu_{hb}\mu_{hc}}$ densities and mobilities from analyses on both sets of specimens (in the fieldsuppressed normal state at $T < T_c$) are shown in Fig. 3 (a)-(c).

A comparison of the SC and non-SC specimen carrier densities at $T \leq 10$ K [Fig. 1 (a)] gives insight into the lowenergy electronic structure and absence of superconductivity in the latter. The SC densities increase modestly with decreasing T, becoming constant at $T \leq 1$ K where $n_h \approx n_e \sim 2.4 \times 10^{17}$ cm³. This extremely low density of carriers is corroborated by linear-in-T Seebeck and Nernst coefficients that impute Fermi temperatures, $T_F \approx 18 - 20$ K.

In contrast, non-SC crystals have carrier densities three orders of magnitude lower at $T \sim 1 \text{ K}$ ($\cong 1 - 3 \times 10^{14} \text{ cm}^3$), with $n \sim n_0 e^{-\varepsilon/k_BT}$ at $T \gtrsim 2 \text{ K}$ [inset, Fig. 1(a)] and averaged values $\varepsilon/k_BT \cong 8.3 \text{ K}$ (0.7 meV), $n_0 \sim 10^{17} \text{ cm}^3$. Thus, all but a small



Fig. 1 Carrier densities (a) and mobilities for (b) SC and (c) non-SC specimens determined by simultaneous fitting to the anisotropic two-band model. Different symbols represent the two crystals for which $J \parallel b$ and $J \parallel c$. Solid and dashed curves are guides except in (b) where solid curves are $\langle \mu \rangle = \int \mu (E) [-\partial f / \partial E] dE$ computed using the energy-dependent mobilities in (f). (d) Fermi surface from Ref. 1 -- note the greatly expanded scale along k_b . (e) Energy band scheme inferred for non-SC and SC crystals. (f) Model energy-dependent mobilities (see text) for SC crystals (upper panel -- q1D bands, lower panel -- minority bands).

residual density of mobile carriers reside in low-mobility states at ε below the q1D band edge – this implies that E_F is positioned near the bottom of the q1D bands [Fig. 1 (e)].

Transport at $T \gtrsim T_c$ in SC crystals and at all T in non-SC crystals is dominated by the mobilities μ_{eb} and μ_{hc} [Fig. 1 (b), (c)], corresponding to in-chain electrons and interchain holes – these are attributed to carriers moving in the q1D d_{xy} bands. The electron character along the chains is expected from the strongly dispersing bands along k_b . The interchain hole-like character, though less obvious, is compatible with the detailed near- E_F electronic structure¹ which includes rather unique k_c dispersions caused by hybridization through long-range indirect hopping to the gapped xz and yz valence and conduction bands. These interactions are responsible for the small Fermi surface (FS) warping [appearing as ``fingers" in the sheets near $k_c = \pi/2c$, $3\pi/2c$ and most prominent for the inner (red) sheet, Fig. 3 (d)]. The states in the finger regions are hole-like, $\partial^2 E/\partial k_c^2 < 0$ – their predominance for interchain transport indicates that contributions from electron-like regions of the FS closer to the Brillouin zone center ($k_c = 0, 2\pi/c$) and boundary ($k_c = \pi/c$) are suppressed, perhaps owing to their better nesting and strong scattering associated with incipient density-wave order.

Striking differences in the mobility T dependencies and magnitudes at $T \leq 10$ K also distinguish SC and non-SC specimens. The "minority" mobilities μ_{hb} and μ_{ec} (in-chain holes, interchain electrons) may hold a key to superconductivity. In SC samples the minority (band) mobilities increase (decrease) strongly with decreasing T such that at the lowest T along each direction the mobilities are comparable in magnitude, $\mu_{hb}/\mu_{eb} \sim 0.5$, $\mu_{ec}/\mu_{hc} \sim 0.3$ – the superconducting ground state is characterized by ambipolar conduction in both directions. These same mobility ratios are 3-4 orders of magnitude smaller for non-SC samples.

Regardless of the origin of the minority carriers (e.g., FS modifications from density-wave order, defects, correlation effects, etc.), their itinerancy in SC samples suggests that the relevant states have moved up in energy relative to those of non-SC samples so as to overlap with the q1D bands [Fig. 3 (e)]. These states appear to be distinct from those of the q1D bands given their very different *T* dependencies and partial Seebeck coefficients (determined using the fitting parameters from Fig. 3 as input to fit the field-dependent Seebeck data – not shown here) having opposite sign to those of the band carriers and values for $|dS/dT|_{T\to 0}$ that are 2.5 times higher. A narrow and sharp density of states peak just below E_F is implied. We propose that the minority states resonantly scatter the q1D band states with which they may weakly hybridize, similar to resonant levels (virtual bound states) in the conduction or valence bands of narrow-gap semiconductors or semimetals. A simple model for resonant scattering having step-like energy-dependent mobilities [Fig. 1 (f)] convolved with the Fermi function derivative fits the SC mobility *T* dependencies well [solid curves in Fig. 1 (b)].

To put things in context, LiPB's low carrier density is comparable to those of SrTiO₃ ($T_c \approx 0.86$ K at $n = 5.5 \times 10^{17}$ cm⁻³) [Ref. 2] and pure Bi ($T_c \approx 0.53$ mK at $n = 3 \times 10^{17}$ cm⁻³) [Ref. 3], and thus its much higher T_c is remarkable. The interelectron distance at T_c , $d_{ee} \approx n^{-\frac{1}{3}} \approx 22 nm$, is comparable to or smaller than the relevant superconducting coherence lengths⁴ $\xi_b \sim 30$ nm and $\xi_c \sim 10$ nm, i.e. Cooper pairs do not substantially overlap. Equivalently, the ratio of critical temperature to effective Fermi temperature, $T_c/T_F \gtrsim 0.1$. Both assessments place LiPB's parameters near the border between BCS superconductivity and Bose-Einstein condensation. What role the resonant levels and associated ambipolar conduction play in the mechanism for superconductivity remain to be established.

Spin-Seebeck and Spin injection studies using Niobium/Cu₂OSeO₃ interfaces

[in progress]

Building on work under prior contract for the insulating helimagnet Cu₂OSeO₃ [Phys. Rev. B **101**, 100407, *Rapid Communications* (2020); Phys. Rev. B **99**, 020403, *Rapid Communications* (2019); Phys. Rev. B **95**, 224407 (2017) (Editor's Suggestion)], we have recently succeeded in fabricating superconducting 10-nm-thick Niobium films grown on the (111) polished face of a Cu₂OSeO₃ crystal.

Interfaces between ferromagnets and superconductors have attracted renewed interest in spintronics, given substantially extended spin lifetimes in superconductors and possible generation of spin-

polarized supercurrents at interfaces. Proposals have also been put forward for generating topological superconductors using non-collinear FM-SC heterostructures.¹ Only recently have FM insulatorsuperconductor interfaces been investigated within the spin pumping context.

My program is uniquely positioned to contribute to this topical area by leveraging our prior work on noncollinear Cu₂OSeO₃ which has three low-field spin phases, all of them accessible at fields well below the upper critical field of Nb. As shown in Fig. 2, we have successfully grown 10nm-thick superconducting Nb (onset $T_c \approx 4.7$ K) on the polished (111) surface of Cu₂OSeO₃. Notably the superconductivity exhibits thermal hysteresis, attributable to the influence of Cu₂OSeO₃ magnetism. The measurements depicted in Fig. 2 are for a large (111) surface (a few mm scale). Our next goal is to deposit Nb on the free end of a small crystal beneath a chip heater (our usual thermal conductivity/spin Seebeck set-up) to begin conducting thermal spin injection experiments.

Future Plans

• Tunneling measurements in the normal and superconducting states of LiPB using thin-film Pb/bulk LiPB crystal junctions.



Fig. 2 (a) R(T) for 10-nm thick Nb deposited on (111) Cu₂OSeO₃ (initial cooling, B=0). (b) R(T) in the helical (B=0), conical (B=0.05 T) and fully polarized (B=0.08 T) spin phases near the superconducting transition, demonstrating thermal hysteresis.

• Thermal spin-Seebeck/spin injection studies of Niobium/Cu₂OSeO₃ interfaces

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Characterization of Functional Nanomachines

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Research Scope: This program is focused on exploring and developing nanostructures (termed "nanomachines") that utilize their mechanical degrees of freedom to convert energy and information from one form to another. Central goals include controlling nanomachine behavior down to atomic length scales, understanding how dissipation affects nanomachine activity, and performing energy transduction processes with quantum limited control. The program is focused on two broad thrusts: (1) fabrication and characterization of *molecular scale* nanomachines, and (2) *phase coherent* control of nanomachines. Controlling the behavior of nanomachines down to the atomic scale requires the development of new techniques for assembling molecular nanostructures and for incorporating them into operational devices. At the smallest length scales the placement of even a single atom can change nanomachine function, and so new methods for creating *atomically-precise* nanostructures must be explored. Phase coherent control of nanomachines is necessary for performing effective energy and information conversion processes. We utilize atomically-thin materials to create new nanostructures that exhibit mechanical, electromagnetic, and quantum phase coherence, and which allow different quantum degrees of freedom to be flexibly coupled. Phononic crystal and metamaterial concepts are exploited to control energy transfer processes and to enhance resonator performance in new size and frequency regimes. This program has seven co-investigators whose expertise span physics, chemistry, and electrical engineering. The experimental tools utilized within our collaboration range from synthetic chemistry, electron microscopy, and scanned probe techniques (Fischer, Zettl, and Crommie), to optical spectroscopy, silicon-based NEMS, and quantum characterization (Wang and Sipahigil). Cohen and Louie provide theoretical support through the use of *ab initio* density functional techniques and molecular dynamics calculations.

Recent Progress:

Here we highlight our activities in the thrust area that is focused on **Imaging Molecular Actuation** in Nanodevices. We will highlight three separate projects within this thrust: (1) *Reversible fielddriven phase transitions in 2D molecular materials*, (2) *Tunable ergodicity of molecular adsorbates in a moiré potentia*l, and (3) *Use of "off-zero modes" to tune electronic and magnetic structure in bottom-up-fabricated nanographene*.

(1) Reversible field-driven phase transitions in 2D molecular materials: Solid-liquid phase transitions are useful for mechanical actuation, but effective implementation requires atomically-resolved microscopy to understand the dynamics of such transitions at the nanoscale. We have developed a new technique for controlling the melting and freezing of 2D molecular layers at the surface of a graphene field-effect transistor (FET). This enables unprecedented imaging of phase transition dynamics via atomically-resolved scanning tunneling microscopy (STM).



Fig. 1: (a)-(d) STM images show the melting of self-assembled chains of F_4TCNQ molecules (solid phase) into isolated molecules (liquid phase) as gate voltage (V_G) is increased from -30V to 30V. (e)-(h) The reverse phase transition (liquid to solid) is observed at the same spot with molecules coalescing from liquid phase into self-assembled chains as V_G is decreased from 6V to -30V.

This was achieved by depositing F_4TCNQ molecules onto clean graphene FETs that have back-gate and source-drain electrodes operable at T = 4.5K in an ultrahigh vacuum STM. We find that lowering the Fermi energy (E_F) of the FET via electrostatic gating causes molecular F_4TCNQ adsorbates to freeze into a 2D solid, while raising E_F causes the solid to melt into a 2D liquid phase (Fig. 1). Scanning tunneling spectroscopy (STS) measurements reveal that molecules in the solid phase are charge-neutral while molecules in the liquid phase are negatively charged. By applying short pulses of source-drain current to transiently heat the device, we are able to observe the nonequilibrium dynamics of molecules undergoing both melting and freezing processes. We have developed an analytical theoretical framework that explains the equilibrium energetics of this first-order solidliquid phase transition as a function of gate voltage (including the mixed phase regime), and we have also performed Monte Carlo simulations that capture its nonequilibrium melting dynamics.

(2) Tunable ergodicity of molecular adsorbates in a moiré potential: Nanomachines operating at the atomic scale must often harness the stochastic motion of microscopic particles to facilitate nanomechanical actuation. Understanding the diffusive properties of particles in nanomachine environments is thus important for developing new nanomachine systems. Many different mechanisms of particle diffusion exist, and these can be classified according to whether or not they follow ergodic behavior. We have explored the diffusion of small organic molecules at the surface of a graphene moiré superlattice and we find that this diffusive landscape leads to a transition from ergodic to non-ergodic behavior at low temperature.

Ergodicity is a key assumption in equilibrium statistical mechanics and typically means that a physical system will relax to its ensemble average configuration given enough time. While this occurs rapidly for well-ordered systems, heterogeneity in a system can significantly extend the time required, in which case ergodicity can be broken at shorter timescales. Such transient non-ergodic behavior is difficult to determine experimentally using canonical statistics. We have explored this type of behavior by controlling the heterogeneity of a molecular diffusive landscape through deposition of molecules onto moiré superlattices generated by graphene/BN heterostructures (Fig. 2). This allowed us to probe how molecule-substrate interactions modify molecular surface diffusion. Using video scanning tunneling microscopy and an analysis framework based on deep learning combined with canonical statistical tests, we have discovered that moiré systems exhibit anomalous non-ergodic

molecular diffusion at low temperature, as mediated by the moiré superlattice potential. Computational modeling of molecular surface diffusion on moiré superlattices confirms that the relaxation time of our observed molecular diffusion is comparable to the observation time scale of our video STM experiment. This study reveals that anomalous non-ergodic diffusion emerges due to the spatial energy heterogeneity introduced by a moiré superlattice and demonstrates the utility of moiré landscape engineering for tuning anomalous molecular diffusion.

(3) Use of "off-zero modes" to tune electronic and magnetic structure bottom-up-fabricated in nanographene: The ability to engineer the electronic and magnetic structure of atomically-precise molecular nanostructures is critical for the design and synthesis of molecular nanomachines. One way to accomplish this is to introduce low-energy states into nanographenes (NGs) through the design of sublattice imbalance in the carbon honeycomb lattice. When atoms on the A sublattice outnumber those on the B sublattice, the extra states associated with this surplus emerge as zero-modes localized on the A sublattice: a result known as Lieb's theorem. Even when the sublattices are matched, local imbalances can still trigger the formation of zero-modes per Ovchinnikov's rule or due to topological frustration.



Fig. 2: Top: STM image of F4TCNQ molecules (yellow) on graphene/BN moiré superlattice. **Bottom:** Sketch shows molecule diffusing from one moiré site to another.

In each case the zero-energy character of these molecular states implies that they have magnetic moments, since at charge neutrality they are singly occupied; however, notable exceptions exist, such as the end states of 7-AGNRs (i.e., armchair graphene nanoribbons seven atoms wide) at the surface of gold, which are known to be vacant due to *p*-doping by the surface. When two zero-modes lie in close proximity they may also couple through hybridization and/or exchange interactions.

We have demonstrated a new strategy for creating localized states in NG that we call "off-zero modes" that are energetically offset compared to their zero-mode counterparts. Off-zero modes provide new basis elements for generating designer quantum states in NGs. Synthesis of off-zero modes is facilitated by the intrinsic electron-accepting character of 5-membered cyclopentadienyl rings. By fusing cyclopentadienyl rings to the zigzag ends of 7-AGNRs, we convert zero-modes to off-zero modes and thus prevent electron transfer to the underlying gold that would leave these states unoccupied (Fig. 3a,b). We have exploited this new ability to facilitate a systematic study of the coupling strength between two off-zero modes in 7-AGNR oligomers as a function of their intramolecular distance while supported by a Au(111) substrate (Fig. 3c-f). We find that short 7-AGNRs, or oligoanthenes, with 3 or 4 repeating anthracene units are nonmagnetic and exhibit a closed-shell ground state resulting from the hybridization of off-zero modes at their ends. Longer 7-AGNRs have open-shell character and display Kondo resonances on Au(111), signifying weak exchange-coupling between their singly-occupied off-zero modes.

Future Plans:

Our plans for the future in this molecular nanomachine thrust area are to develop new experimental tools and molecular structures to provide additional nanomechanical control over nanomachine systems. This will involve the development of new device configurations, new excitation (especially modalities opticallyinduced), and new abilities to excite the internal mechanical degrees of freedom of molecular nanomachine systems. Here we describe our plans for these directions in more detail:

(i) <u>Achieving greater control over</u> <u>current-induced actuation</u>: We intend to fully characterize how flowing current interacts with nanoscale scatterers and leads to mechanical actuation (i.e., electromigration). We will determine the relative



Fig. 3: Sketches show 7-AGNR structures with off-zero modes at their ends for (a) 3 interior spacer units and (b) 5 interior spacer units. (c) STS spectrum shows wide hybridization gap (blue line) due to the strong overlap of off-zero modes in a short GNR (closed-shell ground state). (d) STS spectrum for a longer GNR shows the Kondo effect due to the magnetic moment of an off-zero mode end-state (open-shell ground state). (e) dI/dV maps show HOMO / LUMO states taken at the hybridization gap edges for the closed-shell ground state. (f) dI/dV map shows the SOMO state for the magnetic open-shell ground state. (Scale bars are 3Å).

magnitudes of the electromigration "direct" force (i.e., E-field-induced) and "wind" force (i.e., current-induced) and will characterize how they are related to the atomic-scale structure of molecular scatterers (i.e., the molecular structure/function relationship). We will also implement new electrode geometries in our devices that allow us to flexibly control the *direction* of current flow in 2D (presently we only have two current electrodes and are thus limited to uniaxial current flow). This will allow us, in principle, to dynamically change the *direction* of electromigration particles, thus opening many new avenues of nanomachine control.

(ii) <u>Optical control of molecular actuation</u>: We will further integrate optical actuation into our molecular nanomachine device set-up. We are particularly interested in exploring the idea of utilizing optically-induced shift-currents to control the motion of molecular objects. If successful this will enable an extraordinary new level of nanomechanical control, since shift currents can be dynamically tuned by simply rotating the polarization of light, thus enabling flexible dynamical control of molecular motion. Implementing this idea will involve developing new hybrid devices with 2D semiconducting substrates instead of the semi-metallic graphene substrates that we currently use.

(iii) <u>Actuating molecular internal degrees of freedom</u>: A long-standing challenge is to flexibly and dynamically control the internal mechanical degrees of freedom of molecular nanostructures for nanomachine applications. This can be done, in principle, through gate-induced charging and/or optical absorption. We will explore both of these mechanisms by developing new semiconducting substrates whose chemical potential can be shifted through a wider range of energies than graphene, and that will not quench the optical absorption of supported nanostructures (a problem for graphene). We will complement this with new molecular components designed to take advantage of known molecular isomerization modalities involving charge-induced and exciton-induced mechanical actuation.

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Atomic Dynamics in Metallic and Other Liquids and Glasses

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Self-identify keywords to describe your project: Liquid and glass, atomic dynamics, neutron and x-ray scattering, correlation function in space and time, the glass transition

Research Scope

The science of liquid and glass is much less developed than that of crystalline materials, even though liquid and glass are as important as crystalline materials in energy-related applications and in daily life. The main origin of this slow progress is the non-periodicity of their structures, which eluded the application of modern condensed-matter theories, many of which presume lattice periodicity. The overarching goal of this program is to establish a fundamental understanding of atomistic mechanisms which control the structural and dynamic properties of liquid and glass through combination of tightly coupled experiment, simulation and theory. To achieve this overarching goal this project focuses on the following three specific aims: (1) advance the science of bulk metallic glasses to improve mechanical properties, (2) develop better understanding of a basic unanswered question on the nature of liquid and glass and the origin of the glass transition, and (3) extend the study of local dynamics to various functional liquids relevant to the DOE mission. Owing to recent advances in experimental tools and computational power, we now have an excellent prospect of achieving substantial progress. In particular, we examine the mechanism of rapid increase in viscosity of liquid upon cooling, using a new approach with inelastic neutron and x-ray scattering combined with simulation and theory. The outcome of this proposed work will guide us to the development of glasses and liquids with superior properties, and ultimately contribute to the DOE mission through the development of the physics of dynamic aperiodic matter, such as liquids and glasses.

Recent Progress

1. Ductility and structure of metallic glasses

Metallic glasses are promising as structural materials because of their high mechanical strength. However, their limited ductility presents a major hurdle in their application, whereas the microscopic origin of their ductility and lack thereof is not well understood. We found that the structural provides response to stress useful information, even though the structure itself does not. We determined the anisotropy in the atomic structure of metallic glasses under stress by highenergy x-ray diffraction [P7]. The pair distribution function (PDF), g(r), which depicts the distribution of atom-atom distances, becomes anisotropic under stress [1]. If the deformation is uniform (affine)



Figure 1. Metallic glasses with large non-affine strain ratio $(\Delta \varepsilon_R / \varepsilon_{\infty})$ are ductile with large plastic strain, whereas those with smaller ratio are brittle with no plasticity [P7].

the second order anisotropic PDF is proportional to the derivative of the isotropic PDF. But the data show that the strain in the nearest neighbor atomic shell is non-affine, suggesting that the near neighbor atoms become rearranged under stress [1]. We found that the extent of atomic

rearrangement is related to ductility as shown in Fig. 1 [P7]. This work shines new light on the atomistic mechanism of plastic deformation in metallic glasses. It also provides a non-destructive method of predicting ductility (BES Highlight).

2. Atomic dynamics in molten salt

Dynamic atom-atom correlations can be expressed by the Van Hove function (VHF), which is the PDF in space and time. Recently we developed a method to determine the VHF by inelastic x-ray and neutron scattering [P3], and applied it to molten salts, a class of materials important to nuclear reactor application as coolant and fuel [P9]. Real-space analyses of local dynamics through the VHF by inelastic neutron scattering, shown in Fig. 2, reveal apparent differences in the correlated motion of ions with same versus opposite charge in magnesium chloride molten salt, painting a more complex picture of dynamic behavior than previously understood. Critical knowledge



obtained through this study also serves as a benchmark for development of accurate atomistic simulation models, significantly enhancing our ability to predict the atomic-scale dynamics of condensed matter in extreme environments.

3. Origin of the structure in liquid and glass

The origin of the atomic structure in liquids and glasses has been a subject in debate for a long time. The conventional approach to elucidating the structure of liquid and glass is to start with an atom and its near neighbors forming a cluster with the short-range order (SRO), and to keep adding atoms on the cluster, a bottom-up approach [2]. Now, the PDF of metallic and other simple liquids and glasses shows a strong medium-range order (MRO) which is seen as exponentially decaying oscillations in the PDF extending to many atomic distances, as shown in Fig. 3, which shows the exponential decay of |G(r)|, where $G(r) = 4\pi r \rho [g(r) - 1]$. In the bottom-up approach the MRO is a direct consequence of the SRO. However, we found that they show distinct behaviors in temperature dependence. The MRO freezes at the glass transition, but the SRO does not [P4]. To explain this distinction, we proposed a dual scheme which includes the top-down as well as the bottom-up approaches [P8]. In the top-down approach we start with a high-density gas and introduce interactions among atoms. This is best done in reciprocal (q) space, but the strongly repulsive part of the potential presents a problem. However, the strongly repulsive part plays no role in reality because no pair of atoms come so close to each other. Thus, w Figure 4. The pseudopotential for the Lennard- rm a pseudopotential. The pseudopotential has a mini Jones potential for argon in q space [P8]. on of



the first peak in the structure function, S(q), q = 2.0 Å⁻¹, as shown in Fig. 4. This minimum promotes the density wave instability. However, the density wave state has a poor SRO. Thus, the attempt to minimize energy in q space (top-down approach) and the attempt to minimize energy in real space (bottom-up approach) are in conflict, and the compromise results in the MRO characterized by the exponentially decaying density waves [P8]. This dual scheme explains various properties of liquids and glasses, including the temperature dependence of its structure [P5].

Future Plans

1. Atomic dynamics in covalent and ionic liquids

So far, our study focused on metallic liquids and glasses, which are relatively simple liquid and glass because of non-directional metallic bonds. We now extend our study to more complex covalent and ionic liquids. It is known that the MRO plays a prominent role in these glasses, but the physical mechanisms are poorly understood. We will determine the VHF for various liquids by inelastic x-ray/neutron scattering experiment and classical as well as ab initio molecular dynamics (AIMD) simulation. Our on-going study of liquid selenium (Se) shows significant changes in the structure and dynamics with temperature, as seen by inelastic neutron scattering and by AIMD. In liquid Se atoms form random chains with dissociating covalent bonds, which control viscosity near the glass transition temperature. As temperature increases the effect of covalency decreases and gradually the effect of close packing becomes dominant. We will extend the study to Se-Ge alloys where the floppy transition occurs around 22%Ge, and Ge-Sb-Te liquids used for phase-change memory application.

2. Origin of the glass transition

The viscosity of a glass-forming liquid changes more than 15 orders of magnitude down to the glass transition where a liquid freezes into a glass. The origin of such a drastic change has been a mystery for a long time, even though many theories have been proposed [3]. Our new theory on the MRO based on the density waves [P8] has a potential to advance this field significantly. We already related the MRO to viscosity [4], liquid fragility [P2], through the examination of experimental and simulation data. We also explained its temperature dependence, the Curie-Weiss law [P5], which justifies our theory of the glass transition temperature in terms of local density fluctuation [5]. Our recent work related the MRO also to ductility of metallic glasses. Longer MRO coherence length promotes ductility. Our goal is to develop a comprehensive theory to explain the mechanical properties of liquid and glass in terms of the MRO. We will relate the MRO to the activation energy of viscosity as a function of temperature and demonstrate that the increase in the MRO leads to the

glass transition. At present mechanical deformation in liquid and glass is explained in terms of structural defects, such as dynamical heterogeneity, free-volume and shear transformation zones. Our view is that defect may start the deformation process, but the final outcome is determined by the resistance by the MRO.

3. Electronic correlation in space and time

The method of the VHF can also be applied to study dynamic correlations among electrons. We carried out a preliminary study of electronic VHF of beryllium metal and graphite with the medium-resolution inelastic x-ray scattering at the Advanced Photon Source (APS) of Argonne National Lab. The results show that the same-time (t = 0) part shows the exchange/correlation hole, which disappears quickly with time. Also, the interference due to atomic scattering can be seen. For graphite the band effect, the dispersion gaps, are observed. Our plan is to apply this method to strongly correlated electron systems to study correlated electron dynamics directly.

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Coherent Terahertz Synthesis through Plasmon-Coupled Surface States

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Keywords: Surface states, plasmonics, Fermi energy pinning, semiconductor heterostructure,

wavelength conversion

Research Scope

The scope of this research program is to conduct fundamental physical studies on interaction of optical waves with plasmonic photoconductive nanostructures for high power terahertz wave generation. Toward this goal, we have continued our investigation on physical characteristics of plasmon-coupled surface states for wavelength conversion from optical to terahertz regime and coherent terahertz synthesis. Surface states are naturally formed when a semiconductor lattice is terminated on the surface, pinning the Fermi energy level at the surface of the semiconductor to the energy level at which the surface state density peaks. The alteration of the electric potential profile at the semiconductor surface enables bending the semiconductor band structure and inducing a localized built-in electric field that can be used for optical-to-terahertz wavelength conversion when coupling optically-generated carrier plasmons to the surface states. Under the support of this DOE program, we have investigated the alteration of the electric potential profile at the surface of InAs and utilized the unprecedented functionalities of plasmon-coupled surface states in InAs to demonstrate passive wavelength conversion of nanojoule optical pulses at a 1550 nm center wavelength to terahertz regime with record-high efficiencies that exceed nonlinear optical methods by 4-orders of magnitude [1]. We have also extended our studies to III-V semiconductor heterostructures, which provide more physical flexibility in the alteration of the electric potential profile not only at the semiconductor surface, but also within the bulk semiconductor. This flexibility in the alteration of the electric potential profile has enabled a significant enhancement in the optical-to-terahertz conversion efficiency.

Recent Progress

Figure 1 shows the band diagram of the investigated semiconductor heterostructure where the Fermi, conduction band minimum, and valence band maximum energy levels are marked as E_F , E_c , and E_v , respectively. The presence of the InAs surface states and the graded InGaAs bulk compositions enables the alteration of the electric potential profile not only at the surface, but also within the bulk semiconductor. Surface plasmon waves are optically excited through a metallic nanoantenna array and coupled to the semiconductor regions with the induced built-in electric field caused by band-bending. The photo-generated electrons drift toward the nanoantenna array and induce a current along the nanoantennas, which contains mixing product of different optical frequency components, generating radiation at the beat frequencies of the incident photons. To examine the impact of the Indium composition gradient on the carrier transport, Fig. 2 shows the energy band diagrams and conduction band (CB) quasi-electric field profiles of graded InGaAs structures with different starting compositions at the InGaAs/GaAs interface. As clearly shown in



Fig. 1. Band diagram of the investigated semiconductor heterostructure where the Fermi, conduction band minimum, and valence band maximum energy levels are marked as E_F , E_c , and E_v , respectively. The semiconductor heterostructure consists of a 500-nm-thick, 1.4×10^{19} cm⁻³ Be-doped InGaAs layer grown on a semi-insulating GaAs substrate. The InGaAs layer has a linearly graded Indium composition varying from 60% at the InGaAs/GaAs interface to 100% at the surface. The presence of the InAs surface states and the graded InGaAs bulk compositions enables the alteration of the electric potential profile not only at the surface, but also within the bulk semiconductor. Surface plasmon waves are optically excited through a metallic nanoantenna array and coupled to the semiconductor regions with the induced built-in electric field caused by band-bending. The photo-generated electron drift within the graded InGaAs layer toward the nanoantenna array is illustrated. In order to excite surface plasmon waves at ~1550 nm wavelength range, the nanoantennas are designed in the form of gratings with a 440 nm periodicity, 80 nm gap, and 80 nm metal height, covered by a 240-nm-thick Si₃N₄ anti-reflection coating.

Fig. 2, the p+ graded InGaAs structure has a non-zero CB quasi-electric field, which depends on the starting Indium composition at the InGaAs/GaAs interface, while the valance band (VB) quasi-electric field is almost zero except for a ~20 nm depth near the surface. For the starting Indium composition of 60%, the CB quasi-electric field is ~ 6 kV/cm throughout nearly the entire epitaxial structure, which leads to a steady-state drift velocity of ~ 1.5×10^7 cm/s Higher composition gradients could [2]. potentially lead to stronger built-in quasielectric fields, but the material quality could be severely degraded by the additional dislocation defects caused by the larger strain in the lattice [3]. Therefore, the starting Indium composition of 60% is chosen for the epitaxial growth to significantly enhance optical-to-terahertz wavelength conversion through a coherent terahertz synthesis process [4]. Figure 3 shows demonstration of coherent terahertz the synthesis spanning 2.8 octaves by coupling dispersion controlled microresonator modes to the plasmonic nanoantenna array [5].



Fig. 2. Energy band diagram and CB quasi-electric field of the graded InGaAs semiconductor structure for different starting Indium compositions (x_0) .



Fig. 3. Coherent terahertz synthesis spanning 2.8 octaves by coupling dispersion controlled microresonator modes to passive plasmonic nanoantenna arrays. Coherent optical-to-terahertz wavelength conversion is achieved via plasmon-coupled InAs surface states.

Specifically, we demonstrated a tunable optical parametric oscillator by exciting the plasmon-coupled surface states with a nonlinear microresonator that provides both broadly tunable single-frequency and multi-frequency oscillators in the terahertz regime [6]. Benefiting from multi-segmented cavity mode dispersion control and thermally-controlled cavity-mode-pulling in the microresonator, we observe broadly-tunable optical parametric sidebands at different azimuthal cavity modes via cavityenhanced $\Box^{(3)}$ nonlinear process, along with the competition between mode-crossing Turing and Faraday instabilities. Subsequently, the phase-locked parametric oscillation is down-converted from near-infrared optical frequencies to terahertz regime with the plasmonic nanoantenna array through plasmon-coupled surface states. Coherent terahertz radiation spanning 2.8-octaves is achieved from 330 GHz to 2.3 THz, with a cavity-mode-limited frequency tuning step of \approx 20 GHz and \approx 10 MHz intracavity mode continuous frequency tuning range at each step. By properly controlling the microresonator intracavity optical power and pump-resonance detuning, multi-frequency terahertz oscillators are also generated by beating the pump laser and the generated localized sub-comb lines. Additionally, with active feedback stabilization of the microresonator pump power and pump wavelength, sub-100 Hz linewidth of the terahertz wave, along with 10⁻¹⁵ residual frequency instabilities, are observed.

Future Plans

The presented wavelength conversion scheme via plasmon-coupled surface states can be used for optical wavelength conversion to different parts of the electromagnetic spectrum ranging from microwave to far-infrared regimes in both pulsed and continuous wave operation. We plan to explore

enhancing the wavelength conversion efficiency by investigating alternative semiconductors with a larger number of surface states above the conduction band, introducing higher p-type doping levels, and incorporating larger gradient compositions to introduce a steeper band-bending at the semiconductor surface and, therefore, would further enhance the built-in electric field. In addition, by growing the semiconductor active layer on a distributed Bragg reflector and an appropriate choice of nanoantenna geometry, most of the excited surface plasmons would be trapped in the semiconductor active layer and, therefore, a much stronger spatial overlap between the built-in electric field and photoabsorption profiles can be achieved.

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Electronic Materials Program

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Research Scope

The stimulation and ultimately control of excitons and phonons in nanoscale electronic materials under real-world operating conditions are critically important to the realization of solutions that address our energy needs now and into the future. The Electronic Materials Program (EMAT) pursues the understanding and manipulation of these quasiparticles through external fields and new nanostructured semiconducting materials. EMAT advances the state-of-the-art knowledge of i) photoscience in low-dimensional materials at room temperature and ii) thermal science of engineered semiconductors. We elucidate the mechanisms underlying photoluminescence quantum yield, phonon transport, light-matter interactions, and other fundamental processes enabling us to push the performance limits of materials relevant to energy applications. Through a combination of materials theory, advanced spectromicroscopies, and materials synthesis, EMAT will perform fundamental studies on the role of defects and strain fields on carrier recombination, exciton dynamics, and phonon

transport. We develop materials in which structural as well as electronic phases are designed to achieve control of radiation and thermal transport beyond what is currently available.

Recent Progress

Photophysics of 2D materials.

EMAT research has made substantial contributions to the understanding of photophysics in 2D materials. Previously, we had established a complete model of nonradiative recombination pathways in TMDC monolayers and identified the crucial role of background free charge in creating trions. Further, we had shown that electrostatic or chemical counterdoping suppresses background charge hence and the trion-based recombination channel, allowing the PL QY of TMDC monolayer to be near-unity even with their highly density of native defects. Still, the PLQY in monolayer transition metal dichalcogenides declines at high emission intensities because the excitons undergo nonradiative annihilation, raising the question of whether this is an intrinsic limit in this material. From topological arguments a 2D system will have at least one logarithmically-divergent critical point (van Hove singularity, vHs) in its joint density of final states (JDOS). In many TMDCs, the vHs energy



Fig. 1. In unstrained MoS₂ monolayers, electrostatic doping via backgating reduces background charge and trion formation, producing unity QY at low generation rates (top). When uniaxial strain is applied, the high QY persists to very high generation rates (bottom). Adapted from *Science* **2021** DOI: 10.1126/science.abi9193

appears to be resonant with twice the exciton binding energy, providing a high DOS for the final states of exciton-exciton annihilation (EEA). However, application of small mechanical strains (~0.5%) detunes the resonance and suppresses the non-radiative channel (**Fig. 1**). The model appears to be general to many TMDCs, as near-unity PL QY at high exciton densities was seen in strained monolayers of exfoliated MoS₂, WS₂, and WSe₂, as well as centimeter-scale WS₂ monolayers grown by chemical vapor deposition.¹



Fig. 2. Photoluminescence spectra of BP layer (20 nm) as function of strain along the zigzag (*y*) direction showing the wide range of bandgap tuning. Adapted from *Nature* **2021**, DOI: 10.1038/s41586-021-03701-1.

Extreme bandgap tuning in black phosphorus.

EMAT has discovered means to apply very large strains to low-dimensional semiconductors. By transferring mechanically exfoliated of black phosphorus (BP) onto polymer substrates, it is possible to generate compressive strains by cooling from elevated temperatures or tensile stain by bending the substrate. Owing to the effective transfer of mechanical strain and extraordinary sensitivity of the bandgap to strain, we have achieved tuning of the BP band gap from 0.22 to 0.53 eV (Fig. 2), covering a large fraction of the mid-IR spectral range and allowing demonstration of BP-based light-emitting diodes and photodetectors. This work opens up the possibilities of extending even deeper into the IR by further increasing the amount of compressive strain through substrate engineering and by using the thickness-mediated transition from excitonic to free carrier behavior to explore

new physical phenomena.²

Giant isotope effect in silicon EMAT has made substantial progress in understanding the thermal behavior of low dimensional materials. Isotopic enrichment of Si in its majority isotope ²⁸Si is known to increase thermal conductivity, but the enhancement is only 10-15% at room temperature. Further, it would be expected that reduced size would lead eventually to boundary scattering being dominant, further reducing the enhancement. Surprisingly, the opposite is true; we have discovered a 2.5 times higher thermal conductivity at room temperature of isotope enriched ²⁸Si nanowires compared to natural Si nanowires with the same diameter, surface roughness and doping (**Fig. 3**). Using a first-principles phonon dispersion model, this surprising giant isotope effect is attributed to a mutual enhancement of isotope scattering and surface scattering of phonons in ^{nat}Si



Fig. 3. In bulk Si, there is only a small room temperature isotope effect for thermal conductivity. However, the isotope effect is large in nanowires. Adapted from *Phys. Rev. Lett.* **2022**, DOI: 0.1103/PhysRevLett.128.085901.

nanowires, correlated via transmission of phonons to the native amorphous SiO₂ shell.³



Fig. 4. a) TARC schematic showing patterned deposition of W_xV_{1-x}O₂ with insulator to metal transition (b) Metallic state has high emissivity in the IR, causing radiative cooling because the insulating state, with its low emissivity, leads to heat retention. Adapted from Science 2021. DOI: 10.1126/science.abf7136

theory

The theory enables calculation of the free energy barrier for nucleation, the amorphous-Te/crystalline Te interfacial free energy, and the change in free energy upon transforming Te from the amorphous to the crystalline phase. The theory provides a detailed understanding of the temperature dependence of the nucleation rate, and even enabled development of a theory for nucleation in finite domains. Armed with these insights, we developed a low-temperature processing route to obtain crystalline Te films with large grain size (up to 6 µm) and preferred out-ofplane orientation ((100) plane parallel to the surface on various substrates including glass and plastic.⁵ By using thermal evaporation at cryogenic temperatures we fabricated high-performance wafer-scale p-type field-effect transistors with an effective hole mobility of $\sim 35 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, on/off current ratio of $\sim 10^4$ and subthreshold swing of 108 mV dec⁻¹ on an 8-nmthick film.

Electronic materials with temperature adaptive radiative properties

Building on the framework of comprehensive control on thermal properties in low dimensional materials, EMAT has created lithographically patterned structures that use the metal-insulator transition in W-doped VO₂ to switch between strong and weak emissivity in the IR while retaining high solar reflectance (Fig. 4).⁴ As implemented in the temperature adaptive radiative coating (TARC) concept, smart roofs based on this concept are capable of dynamic radiative cooling for self-adaptive applications across different climate zones.

Nucleation and growth of Te thin films.

Thermally evaporated Te has an intriguing but poorly understood crystallization behavior, displaying an amorphous to crystalline phase transition at temperatures as low as 0 °C. we showed that the kinetics and dynamics of the crystallization of thermally evaporated Te films can be visualized and modeled using classical nucleation





Fig. 5. a) processing schematic and (b) overview of crystallization mechanism (c) FET structure showing (d) on/off current ratio of $\sim 10^4$ for a 8 nm Te film. Adapted from Adv. Mater. 2021 DOI: 10.1002/adma.202100860 Nanotech. 2020. DOI: and Nature 10.1038/s41565-019-0585-9

Future Plans

Photoscience and emergent strain-induced phenomena in low dimensional systems

EMAT intends to gain a comprehensive understanding of lossy non-radiative processes in lowdimensional electronic materials and develop means to mitigate them. We are focusing on the effects of strain, background carrier concentration and dielectric environment with an emphasis on material performance at room temperature. So far, our experimental work has focused on 2D monolayers only. However, our established photophysics should be applicable to all excitonic systems, including semiconductor quantum dots (QDs), carbon nanotubes, and organic molecules. Therefore, a fundamental question arises: are neutral excitons inherently bright in all excitonic semiconductors, regardless of defects? This motivates our investigation of the critical role of background change in dictating material brightness. Experimental motifs to be used include electrostatic doping of QD ensembles (i.e., thin films), monitoring of the recombination mechanism in black phosphorus as a function of thickness from bulk (free carrier like) to monolayer (exitonic), and quantification of the joint density of states (JDOS) which mediates exciton-exciton annihilation in these systems. We are also investigating emergent strain behaviors which arise from the relaxation of strained 2D materials. *Thermal behavior of 2D materials.*

Here, we are advancing the understanding of materials physics related to thermal properties of electronic materials. Specifically, we are developing and exploring new electronic materials with dynamic and spectrally selective absorption including VO₂ as a model system and also exploiting BP's tunable bandgap, measuring thermal conduction in Moiré- and wrinkle- engineered 2D materials, and aiming to understand thermal transport across phononically mismatched materials and interfaces

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Super-Ionic Clusters - Structure, Stability, and Energy Applications

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Keywords: super atoms, ionic clusters, structure, stability, energy materials

Research Scope

The objective of the project is to provide a fundamental understanding of the structureproperty relationships of a novel class of superatomic clusters mimicking the chemistry of atoms and to explore their potential for promoting unusual reactions as well as serving as building blocks of new energy and magnetic materials. Working closely with experimental groups, the goal is not only to validate our theoretical predictions but also to guide experimentalists in the focused discovery of new materials.

The project exploits the unique size- and composition-specific properties of clusters and explores their potential as building blocks of functional materials. Using first-principles theory, our approach is an atom-by-atom rational design of a new class of superatomic clusters such as superalkalis and superhalogens that not only mimic the chemistry of alkali and halogen atoms, respectively, but also are suitable for forming supersalts with unusual properties. Our project involves three interrelated thematic areas: (1) Ligand assisted rational design of highly reactive clusters based on closo-boranes and Co-chalcogenide clusters. (2) Cluster-based magnetic materials: Following our recent joint experimental and theoretical work that UAu₆ cluster is magnetic even though neither U nor Au is magnetic, we explore if a material composed of two non-magnetic and metallic elements can form a magnetic semiconductor. (3) Super-ions as building blocks of energy materials: Given that electrolytes in metal-ion batteries are salts composed of metal cations and halogen anions, we study a wide range of superhalogens as the building blocks of electrolytes in Li-, Na-, and K-ion batteries and their interaction with the electrode surfaces. Similarly, halogens in thermoelectric materials such as Re₆Se₈I₂ are replaced by superhalogens to see if the new cluster degrees of freedom can enhance the figure of merit, ZT, value due to the inherent rich phonon dynamics. Use of superatomic clusters as building blocks opens new opportunities for the design and synthesis of novel materials

Recent Progress

Our work during this period covered a broad range of topics dealing with a fundamental understanding of structure-property relationships of clusters and low-dimensional materials with a focus on unusual reactions, catalysis, energy materials for storage and conversion, and magnetism. These include how properties of clusters evolve with size and composition, how they change when ligated or supported on substrates, and how knowledge gained from clusters in the gas phase can be used to design materials ranging from electrolytes and electrodes in Li and Na-ion batteries to ferroelectric, piezoelectric, and thermoelectric materials. Our work provided new atomic-level insight into properties of nanomaterials and guided experimental research [1-2].

We developed multiply charged clusters that can promote unconventional chemistry, superhalogens and superalkalis. We showed that gas-phase di- and tri-anions with record-high stability and compactness can be achieved by utilizing a series of stable mono-anions with linear configurations as ligands. Our systematic study of the effect of cluster size and terminal ligands showed that the interaction between the cluster and the noble gas atoms becomes stronger with increasing cluster size and the electron affinity of the terminal ligands. This led to a counter-intuitive finding -- removing multiple terminal ligands can enable electrophilic centers to bind multiple noble gas atoms simultaneously, without compromising their binding strength. We also demonstrated that

these super-electrophilic clusters can make Zn achieve an oxidation state of +3 that has eluded researchers for decades. We have significantly expanded the list of superhalogens and provided a new path for their design and synthesis. We showed that superhalogens can be created by doping metal atoms in *closo*-borane (B₁₂H₁₂) which is stable as a dianion, leading to a new class of superhalogens. termed metallo-boranes. Motivated by recent experimental advances in endohedral cage clusters, we demonstrated a rational design principle for creating a new class of such superhalogens. We studied 54 different clusters and showed that these clusters possess electron affinities as high as 8.5 eV. We also showed that recently synthesized [Si₉{Si (tBu)₂H}₃] and [Si₉{Si (TMS)₃}₃] Zintl clusters not only behave like halogens but also when functionalized with suitable ligands exhibit superhalogen characteristics. These endohedral superhalogens as well as Zintl clusters have the potential to serve as new electrolytes in Li-ion batteries. Working in close collaboration with experimentalists [3], we demonstrated an unusual property of Au, brought about by the relativistic effects. We showed that Au can behave like a halogen in small clusters. We further found that, unlike UF₆, UAu₆ exhibits strong Au-Au interactions, resulting in different structures. That two nonmagnetic elements in the cluster can become magnetic and opens possibilities for designing magnetic nanowires composed of nonmagnetic elements.

We have designed and developed a new class of materials with unique properties, using clusters, instead of atoms, as the building blocks. We showed that clusters as building blocks can lead to novel ferroelectric materials. We found that ionic crystals can develop polarity by changing their building blocks from elemental ions to superalkali and superhalogen cluster-ions. Due to the non-spherical geometries of these cluster ions, corresponding supersalts can form anisotropic polar structures with ionic bonding, yet covalent-like directionality, akin to sp³ hybridized systems. A series of stable ferroelectric/ferro elastic supersalts were developed, with ultra-low switching barrier, endurance to large reversible strain, and a rare triferroic coupling of ferroelectricity, ferro elasticity, and antiferromagnetism with controllable spin directions. We also showed that dimerization of SbCl4 superhalogen can yield a polar cluster. When assembled, these clusters can form a super-crystal that is thermodynamically stable, with a combination of mixed valence and lone pair electrons leading to electric polarizations along all directions. This generates a type of unconventional multimode ferroelectricity containing three different modes of ferroelectricity with distinct magnitudes and Curie temperatures.

We have continued our study of 2D materials, particularly focusing on the electronic, magnetic, catalytic, and optical properties that can arise if clusters are used as building blocks, with applications as piezoelectric and thermoelectric materials [4]. We discovered two competing lowenergy phases in the layered VI₃ ferromagnetic semiconductor, where the metal-insulator transition is driven by strong electronic correlation, and the orbital symmetry breaking is robust against geometrical distortions. We also showed that controlling magnetism of two-dimensional multiferroics by an external electric field can provide special opportunities for both fundamental research and future development of low-cost electronic nanodevices. In another study, we demonstrated the unique triferroic couplings in recently synthesized CrI₂ monolayer. Such coupling can be applied to other 2D and their Janus monolayers, enabling electrical manipulation of spintronics for efficient nonvolatile random-access memories. We contributed to the fundamental understanding of the spillover mechanism in catalysis by showing that BH_3 , a secondary catalyst, can be produced by symmetrically splitting its stable precursor, B₂H₆, on doped metal-free surfaces such as graphene and h-BN as well as on MOF5. We further examined the potential of a new series of two-dimensional boron chalcogenides, B_2X_3 (X = S, Se, Te) as photocatalysts for water splitting. A bilayer van der Waals heterostructure consisting of B₂Te₃/B₂Se₃ is found to have the greatest potential for two-step photoexcitation for water splitting reaction. Conversion of waste heat into usable energy requires development of thermoelectric materials with high efficiency in a wide temperature range. We
showed that the thermoelectric performance of the p-type single-layer $Sb_2Si_2Te_6$ has a record high average ZT of ~1.93. We also studied the recently synthesized superatomic $Re_6Se_8I_2$ monolayer and found that the large mass and anharmonic Re-I bond introduce strong phonon scattering and result in low lattice thermal conductivity, while the strong and harmonic Re-Se network ensures a high TE power factor. Due to the low thermal conductivity and high TE power factor, this material exhibits a record high ZT values among all the cluster-based thermoelectric materials reported so far.

We have made a number of new discoveries in advanced materials for solid state Li-, Na-, and K batteries. We found that yttrium halide-based materials are promising solid-state electrolytes for Na-ion batteries, with high ionic conductivities and stable interfaces. We showed that the recently proposed topological semi-metallic carbon, HZGM-42, has high energy density, good rate capability, and excellent cycling stability, and can serve as a universal anode material for both Li/Na batteries. We also proposed a new anode material, germanium carbide, g-GeC, for Li/Na batteries, with both benefits of the high stability of graphene and the strong interaction between Li/Na and germanene. Based on theoretical-experimental combined studies, we found that the antiperovskite K₃OI and its derivative $K_{2,9}Ba_{0.05}OI$ are promising K-ion solid-state electrolyte. We also developed a strategy for modifying the structure of solid-state electrolytes to reduce the cation diffusion activation energy. leading to two heavily W-doped sodium thioantimonate electrolytes exhibiting record low activation energies among all the known Na solid electrolytes [5]. We have successfully designed halogen-free electrolytes based on modified boranes, $YB_{n-1}H_n^-$ (Y = C, Si; n = 5-14) anions, and their respective alkali metal salts. We have developed new design strategies and uncovered new ion diffusion mechanisms that can support superior ionic conductivities in cluster-based solid-state electrolytes. The new ion diffusions are characterized as correlated ion-ion and ion-cluster dynamics beyond the well-known paddle-wheel effect. Our work in 2022 led to 18 publications in high-impact journals.

Future Plans

Our future projects include: (1) Ligand assisted rational design of highly reactive clusters and their interaction with chemically inert species: This study will involve state-of-the-art theoretical calculations to design and realize stable, yet highly reactive agents capable of activating molecules like H₂, CO₂, and N₂ by using a new class of super-electrophilic anions based on *closo*-borate structures $B_{12}L_{11}$ (L = H, F, CN) and atomically-precise core- and ligand-tailored chalcogenide clusters, Co_6S_8 (PEt₃)₆. (2) Single-atom vs. superatom catalysis and cluster-based magnetic materials: We will study the advantages of single superatom catalysis versus single atom catalysis by focusing on Au and its superhalogen analog ($B_{12}L_{11}$, L = H, F, CN) as well as Li and its superalkali analog Li₃O deposited on metal-oxide surfaces such as TiO₂, Fe₂O₃, and MgO. We will examine if two otherwise metallic and nonmagnetic elements can form a magnetic semiconductor by focusing on UAu₆ as the building block. Similar studies will be carried out by tailoring the core and ligands of $Co_6S_8(PEt_3)_6$ and study their magnetic properties. (3) Superiors as building blocks of energy materials: Given that electrolytes in metal batteries and thermoelectric materials are nonmetallic and composed of cations and anions, we will study a wide range of superhalogens as building blocks of energy materials. We will focus on the design of solid-state electrolytes based on perovskites and argyrodites for K-ion batteries using clusters as building blocks and study their stability against electrodes. We will also study thermoelectric materials such as Re₆Se₈I₂ whose properties will be tailored by replacing halogens by superhalogens.

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DNA-Controlled Dye Aggregation – A Path to Create Quantum Entanglement

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Keywords: Quantum entanglement, DNA-templated dye aggregates, molecular exciton delocalization, exciton-exciton interactions, excitonic coherence

Program Scope

Our overarching research goal is to study how fundamental properties of molecular exciton delocalization and coherence can be controlled to enable quantum entanglement. Our research is motivated by the hypothesis that exciton delocalization and exciton-exciton interactions can be tuned through the controlled arrangement of dyes into aggregates of dyes using deoxyribonucleic acid (DNA) templating to create and control exciton quantum entanglement that is at the center of the DOE's quantum information science (QIS) initiative.

Our technical approach involves experiment, theory development, and computational modeling. These approaches are accomplished in an integrated and complementary manner across our now five research teams. Our primary molecular dye material systems of interest include squaraine (SQ) and squaraine:rotaxane (SR) dyes assembled into dye aggregates via the DNA self-assembly process by which a variety of DNA scaffolded architectures can be used to assemble dye aggregates. Dyes are functionalized to assess their structure-property relationships, the aggregates characterized via steady-state and transient ultrafast spectroscopy techniques, dye orientation precision assessed by single molecule microscopy approaches, and aggregate properties modeled through our in-house Kühn-Renger-May (KRM)¹ Model Simulation Tool. The tool uses spectral data to determine the spatial orientation and proximity of dyes within an aggregate.

Our work to date—in Phases I and II of our Department of Energy, Basic Energy Sciences (BES), Established Program to Stimulate Competitive Research (EPSCoR) grant—has identified specific functionalized dyes that have large J (excitonic hopping parameter), based on the transition dipole moment (μ) of each dye, whose aggregates created by those dyes exhibit strong exciton delocalization. Theoretical work has been performed on the less studied, yet fundamentally crucial for creating many-particle entangled states, K (exciton-exciton interaction energy), to identify dyes exhibiting large Ks induced by the difference static dipole moment (Δd). Experiments to measure K in dye aggregates have been initiated and an approach has been identified by which entangled exciton states can be created using J and K.

Recent Progress

We are now in Year 2 of Phase II of our BES, EPSCoR grant. During Phase II, 17 journal articles have been published/accepted to date (grant total: 20) and an additional paper is currently in review. Several articles have been featured in three special journal issues, including *Journal of Physical Chemistry* (JCP) *A*'s "Physical Chemistry of Quantum Information Science"², *JCPA*'s "Celebrating 25 Years of 2D IR Spectroscopy"³, and *Molecules*' "Excitonics in Molecular Aggregates"⁴. In addition, to date, 7 invention disclosures are associated with our EPSCoR funded research, either as conceptual advances or reduction to practice.

In the past two years in particular, we have developed new capabilities due to our grant funding. These include: (1) multistep organic synthesis, which gave us access to custom-designed synthetic dyes; (2) custom-built Stark spectroscopy and custom-built femtosecond (fs) coherence spectroscopy (FCS), which enable direct measurements of Δd , exciton hopping frequency (ω_h), and dephasing lifetime ($\underline{\tau}_d$; function of the population lifetime, τ_p); (3) in parallel, via a Department of the Navy Office of Naval Research grant, we have implemented custom-built fs one quantum two-dimensional electronic spectroscopy (1Q 2D ES) and 77 and 4 K cryogenic capabilities, both of which greatly facilitate measurement of ω_h and τ_d and possibly even K; (4) custom-built fluorescence lifetime imaging microscopy (FLIM) that enables single-molecule fluorescence lifetime measurements with

picosecond time resolution and dye orientation characterization; and (5) an automated simulation pipeline on five new computing servers to reduce simulation times.

We have shown several ways to enhance the Coulombic coupling, or the exciton hopping parameter, $J_{m,n}$, in SQ aggregates templated by DNA Holiday Junctions (HJ). First, we demonstrated that the proximity of thyminemodifiers (Ts) tethering the dyes to the HJ core via single flexible linkers influenced the intermolecular distance and, hence, $J_{m,n}$, in the dimers. The proximity of Ts (i.e., dye attachment sites in the HJ) was evaluated using thymine photocrosslinking reaction. Ts were found to be closer when positioned on the partially complementary strands of the HJ (i.e., adjacent dimer) than on the noncomplementary strands (i.e., transverse dimer). The proximity of Ts correlated with J_{m,n} (Fig. 1a).[Basu et al. 2022] examined the effect Second, we of hydrophobicity, sterics and electronic asymmetry on $J_{m,n}$. In collaboration with SETA BioMedicals Inc., we realized novel SQ and SR dyes with altered hydrophobicity, sterics, and asymmetry. We demonstrated that more hydrophobic SQs afforded, in general, larger $J_{m,n}$ (Fig. 1b) [Mass et al. 2022]. A steric effect of the rotaxane ring was shown to be a common means to achieve elusive oblique packing in SR dimers,



Fig. 1 Approaches to enhance Coulombic coupling in squaraine aggregates templated by HJ. (a) photocrosslinking efficiency evaluated the proximity of thymine-modifiers and its correlation with Jm,n. (b) SQ aggregates with hydrophobic substituents exhibit large Jm,n [Mass et al. 2022a]. (c) SR dimers consistently form oblique aggregates with near-equal intensity absorption bands [Barclay et al. 2022a].

whereas rotaxane fluorination promoted denser packing and larger $J_{m,n}$ (Fig. 1c) [Barclay *et al.* 2022a]. In addition, to exhibiting large $J_{m,n}$, asymmetric SQ monomers were found to have appreciable Δd , though small τ_p as shown by computational screening and spectroscopic measurements.²

Recent progress on computation and simulation and on modeling two-exciton states has been made in three computational areas: (1) machine learning (ML)-driven density functional theory (DFT) and time-dependent (TD)DFT, (2) quantum-mechanical models and simulations relative to 2Transient-absorption spectroscopy (TA), and (3) theory that demonstrates a key element in producing entangled two-exciton states. Specific to (1), we comprehensively explored the μ , Δd , and angle θ between μ and Δd of various dye monomers using ML-driven DFT and TD-DFT calculations. [Ketteridge et al. 2023, Biaggne et al. 2022] We found that substituent (i.e., functional group) effect is correlated with the empirical Hammett constant σ_p , which demonstrates its electron donating or electron withdrawing strength. Attaching substituents along the long axis of the dye could increase μ while placement off the long axis is shown to increase Δd and reduce θ . We further applied molecular dynamics (MD) to simulate the dye dimers attached to DNA HJs.[Barcenas et al. 2023] The MD results, validated by experimental measurements, suggested that the adjacent dimer promotes stronger $J_{m,n}$ and less dye–DNA interaction than the transverse dimer. The dyes with specific substituents could facilitate a closer degree of aggregate packing via hydrophobic effects, leading to a stronger $J_{m,n}$. Additionally, relative to (2), TA has a well-understood interpretation arising from quantum-mechanical models and simulations. Surprisingly, no tractable models or simulations existing for the technique of transient circular-dichroism spectroscopy (TCD). In this contribution, we developed a model of TCD appropriate for molecular aggregates that simulates TCD spectra for arbitrary few-molecule aggregates. [Arpin and Turner 2022] We have now undertaken the daunting task of constructing a TCD spectrometer based on insights learned during the model development process. Finally, specific to (3), we theoretically demonstrated a key element devised in producing entangled two-exciton states [Yurke et al. 2023]. This key element employs the Δd interaction between two excitons residing on separate exciton transmission lines to induce a phase shift. This element enables the implementation of an aggregate that functions as a Hadamard-CNOT gate. This gate transforms a two-exciton product state into a maximally entangled state.

Our progress to understand and mitigate heterogeneity in DNA-templated dye aggregates has been demonstrated by controlling the orientation of single dyes, rigid dyes, and dyes tethered to DNA.

As controlled positions and orientations of dye aggregates are key to establish homogeneous excitonic devices useful for detecting quantum entanglement, we demonstrated two strategies for controlling the orientation of single dyes by tuning the surrounding molecular environment (Fig. 2).[Cervantes-Salguero *et al.* 2022] The first strategy relies on "sandwiching" the dye between DNA bases (dye intercalation), whereas the second strategy relies on stretching the dye via its two tethers by adding unpaired bases in between. The reduced dispersion provided by both



Fig. 2 Dye orientation control. Left panel: Spherical coordinates (θ and ϕ). Middle and right panel: Intercalation and stretching strategy for controlling the θ and ϕ coordinates in a DNA duplex. [Cervantes-Salguero *et al.* 2022]

strategies sets the stage for developing excitonic devices with mitigated heterogeneity, the degree of which can be characterized by our established methodology that correlates single-molecule experiments and theory. Additionally, we assembled our first aggregates of rigid dyes, specifically perylene dyes, using DNA. The dimer aggregates exhibited optical properties consistent with excitonic interactions and H- and J-type aggregate behavior (Fig. 3). Although the goal was to observe singlet exciton states decay into spin-entangled triplet pair states, charge transfer was observed likely due to the highly polar aqueous environment.⁴

We have made substantial progress on constructing custom-built advanced femtosecond (fs) spectroscopy systems that enable measuring key parameters critical for detecting quantum entanglement in molecular aggregates. We have recently finished constructing a custom-built femtosecond coherence spectroscopy (FCS) system incorporating a broadband sub-10 fs noncollinear optical parametric analyzer (NOPA) to measure quantum beats.[Barclay *et al.* 2022b] We used FCS coherence spectroscopy to measure quantum beats in the monomer dye molecules. As monomers, these quantum beats are purely vibrational and serve as a control experiment for upcoming measurements on molecular aggregates whose quantum beats arise from vibrations as well as coupled electronic states. Unfortunately, FCS is susceptible to line broadening from structural heterogeneity;

however, our newly designed and custom-built femtosecond, one quantum two-dimensional electronic spectroscopy (2DES) system, incorporating a broadband sub-10 fs noncollinear optical parametric analyzer (NOPA), that overcomes broadening due to structural heterogeneity. Specifically, we examined spectra of a cyanine dye to probe local conformations in three samples of DNA structures.³ The measurements—paired with MD simulations—revealed signatures of static disorder in only the double-stranded DNA sample. This supports the conclusion of Asanuma *et al.* that doublestranded DNA can act as a 'soft crystal'.⁵

Future Plans

Given our promising initial results to date, we now hypothesize that dye aggregates with long fluorescence lifetimes, high fluorescence yield (Φ_F) , large ω_h , and long τ_d , will enable the detection of excitonic entanglement. Our ability to mitigate mechanisms detrimental to fluorescence lifetimes (excited state quenching and structural



Fig. 3 DNA Holliday junctions (left) are used to template dimers of rigid perylene dyes (upper right), which are observed via steady state absorption and fluorescence emission (lower right) to pack as H- and J-aggregates and undergo charge transfer.⁴

heterogeneity), maintain large J and K, and demonstrate large ω_h and long τ_d are crucial success metrics. Our goal for Phase III is to: (1) define design rules for creating and controlling entanglement and (2) demonstrate methodologies that enable detection of entanglement.

At the same time, given our jurisdiction as a DOE EPSCoR state, we will continue to leverage DOE BES EPSCoR and other funding sources to build our capacity in dye synthesis, DNA construct design, ultrafast laser spectroscopy and single molecule microscopy instrumentation and techniques, and Frenkel exciton theory development as it relates to excitonic entanglement.

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Unique optical excitations in topological insulators

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Keywords: Molecular beam epitaxy, topological materials, plasmonics, terahertz

Research Scope

The overall goal of this project is to have a complete understanding of and control over Dirac plasmon polaritons in topological insulators (TIs). TIs are materials that exhibit a bulk bandgap crossed by surface states with linear dispersion and spin-momentum locking. Electrons occupying these surface states are two-dimensional, massless, and have reduced scattering since their spin is locked to their momentum. Dirac plasmons made from these electrons are predicted to inherit these properties. In addition to the interesting properties of the plasmons, the plasmons can be used as a probe to better understand the properties of the TI. The goal of this program is to explore the properties of Dirac plasmon polaritons in TIs, understand how these plasmons couple both to each other and to other excitations in the system, investigate plasmons in TI nanoparticles, and discover how this coupling in both single-layer and multi-layer systems modifies the photonic band structure of the TI system.

Recent Progress

TI synthesis

Before we can explore plasmon modes in TIs, we first must be able to synthesize high quality films. heterostructures, and nanoparticles. The highlights from the past two years include developing techniques to grow ultra-thin Bi₂Se₃ films using molecular beam epitaxy (MBE), understanding which factors impact MBE growth of TIs, and growing self-assembled TI nanostructures through conventional epitaxy and droplet epitaxy. Ultra-thin films of Bi2Se3 are of interest because they allow us to probe the properties of the material as it transitions from the TI state to either a trivial insulator or a quantum anomalous Hall (QAH) state. Unfortunately, growing continuous and flat films of Bi₂Se₃ with thicknesses less than ~10 nm is challenging. We found that we could



obtain flat, coalesced films only when the c-plane sapphire substrate had been pre-treated. The pretreatment consisted of depositing a 5 nm film of Bi_2Se_3 followed by desorbing that film through a thermal treatment. We infer that this treatment is changing the chemistry of the sapphire substrate by passivating dangling bonds and/or by replacing some of the oxygen atoms in the substrate with selenium atoms. Films deposited on the pre-treated substrate showed much lower roughness than films grown on pristine substrates. In addition, we found that the lowest surface roughness was obtained when the first few layers were deposited at a relatively low temperature and the final layers were grown at a higher temperature (a two-step growth method). Finally, we determined that a lower growth temperature and a higher growth rate for the first step led to the smoothest films, contrary to what is observed in conventional materials. We attribute all of these observations to the poor wetting of Bi on sapphire. By changing the surface chemistry and by lowering the adatom mobility, we are able to control the nucleation of films, leading smooth ultra-thin films.

We also explored the growth of thicker Bi₂Se₃ films on both passivated (sapphire) and unpassivated (GaAs) substrates. Because of the difference in surface passivation, we observe very different growth dynamics for Bi₂Se₃ thin films. Growth on self-passivated sapphire can be done over a wide substrate temperature growth window, and the film quality is relatively insensitive to substrate pre-treatment. A two-step growth strategy in which the majority of the Bi₂Se₃ layer is deposited near the thermal decomposition point was found to generate films with the best electronic performance: a 20% decrease in carrier density and 60% increase in mobility at room temperature compared to the direct growth method. This is primarily caused by the increased adatom mobility at the high substrate temperature. In this case, the low-temperature deposition acts as a wetting layer to enable the hightemperature deposition. In contrast, growth on GaAs substrates shows a significant dependence on the substrate pre-treatment and temperature. The unpassivated surface dangling bonds result in growth of both the (0001) and (1015) orientations. The anisotropy of the 2×4 reconstructed GaAs surface leads to anisotropic bismuth adatom mobility, which eventually leads to favored in-plane epitaxy along the GaAs [011] axis. Direct growth generates films with carrier concentrations and mobility similar to films on sapphire, while adding a BIS buffer layer cuts the carrier density in half and increases the mobility by 60%. This is a significant result since the growth of vdW films on technologically important semiconductor substrates is crucial for the future integration of these materials.

Finally, we also explored the growth of TI nanostructures, which are predicted to host surface topological plasmons.[1,2] We found that we could grow self-assembled Bi₂Se₃ nanopillars when growing the material on a BiInSe₃ seed layer on GaAs substrates at very high temperatures and with high selenium overpressures. We attribute the formation of these nanocolumns to a reconstruction of the selenium atom dangling bonds that reduces the chance for Bi incorporation at the edges of a domain along with the high Bi adatom mobility at these high substrate temperatures. We also synthesized Bi₂Se₃ nanoparticles using droplet epitaxy. We could control the size and density of the nanoparticles by controlling the growth conditions.

DPPs in Tis

As describe above, we have explored out-of-plane coupling in TI thin films and heterostructures. However, to fully understand DPPs in TIs and how to control them, we must also explore in-plane coupling. To that end, we measured DPP modes in TI ribbon arrays as a function of ribbon spacing. We found that the ribbons do indeed couple to each other, as shown in Figure 2(a) in which we can clearly see a shift in the plasmon peak as a function of ribbon width. In Figure 2(b), we can see that the extracted DPP modes positions can be fitted by an exponential decay curve. For stripes of width 2.5 mm, we find that the coupling becomes negligible with the separation between ribbons is larger than 4.5 mm or 2.8x the





stripe width. Both the shape of the curve and the particulars of the fitting match well with a dipole-

dipole coupling model, as has been observed for plasmons excited on metal nanoparticles and on graphene disks. This result lays the groundwork for creating THz metasurfaces based on DPPs in TIs. In our previous work, we demonstrated out-of-plane coupling between DPPs in TI layers separated by band insulators. In that work, we explored coupling among four TI surface states on two TI layers. However, if we are able to couple DPPs in many TI layers, we may be able to create a Dirac hyperbolic metamaterial. Such a structure would have a hyperbolic photonic density of states in the THz and could be used for a variety of applications including superresolution imaging. We therefore decided to synthesize, fabricate, and measure such a structure comprising 5 periods of BI/TI with a BI cap. This structure will host ten TI surface states, leading to the possibility of many coupled DPP modes and, hopefully, a Dirac hyperbolic metamaterial. After growing this structure using molecular beam epitaxy, we fabricated it into stripe arrays with different stripe widths. Changing the stripe width changes the wavevector of the DPP mode since these modes are standing wave resonances. Extinction curves for these samples using transverse magnetic polarized light are shown in Figure 3(a) as open, colored symbols. To extract the DPP mode frequencies, we fit the data with a Fano fitting model that incorporates the a and b phonons in the Bi_2Se_3 and the In_2Se_3 , the epsilon near zero modes in the structure, and the DPP modes. Those curves are shown as solid black lines. We get a good agreement between the experimental data and the modeling. The solid purple, blue, and pink symbols in Figure 3(a) are the extracted DPP mode frequencies. We refer to these modes as volume plasmon polaritons or VPPs in analogy with conventional hyperbolic metamaterials.



Figure 19 (a) Extinction curves (colored symbols) and Fano fitting (black lines) for the TM extinction spectra of the 5L-50nm HMM grown on silicon. The data are multiplied by 3 and offset for better visualization. The VPP mode frequencies are marked with symbols. The dashed lines are a guide to the eye. (b) Transfer matrix modeling of the 5L-50nm Bi₂Se₃-BIS HMM shown in grayscale. Data points are the corresponding DPP mode frequencies.

In Figure 3(b), we plot the dispersion relationships for all the modes as solid symbols. The grayscale plot is a transfer matrix model of the structure. We see good agreement between the two, indicating that our modeling is an accurate representation of our structure. From the modeling, we can see that we are exciting 2-3 DPP or VPP modes in the structure, depending on the particular wavevector and frequency. These modes have mode indices of ~150-500, indicating an extremely high confinement of light in this structure. The benefit of this structure is that it can easily be tuned by adjusting the TI or BI layer thickness and the total number of layers in the structure. In addition to our far-field measurements, we also used scattering-type scanning near-field optical microscopy to measure and image TI plasmons in real space. We found that the DPP modes had good confinement and reasonably long decay times, but somewhat short propagation distances. This is caused by the relatively small group velocity, which results in long relatively propagation lengths but short real-space propagation lengths.

Future Plans

We plan to finish our characterization of the plasmonic properties of TI nanoparticles with the ultimate goal of observing surface topological plasmon modes. We will also explore how the plasmons in TI thin films change as the film undergoes the transition from a topological to a trivial insulator either by changing the thickness of the film or by changing its composition. Finally, we plan to exploit our in-plan coupling measurements to design TI metasurfaces for the THz.

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Orienting Strained Interfaces Designed to Direct Energy Flow

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Keywords: Pulsed laser deposition, Epitaxial thin films, Vertical heteroepitaxial nanostructures, Ion conduction, Strain

Research Scope

Achieving fast ion transport at reduced temperatures is a key requirement to develop advanced oxide-based energy applications. This research program aims to develop a new paradigm for oxide heterostructures with an exceptionally large number of strained interfaces that are designed to direct energy flow by controlling the orientation of interfaces for fast ion transport along the interfaces, and to explore the key role of interfacial strain in oxygen ion migration. On the synthesis side, pulsed laser deposition (PLD) of oxide multilayer films and vertical heteroepitaxial nanostructures (VHNs) plays an important role. In combination with electrochemical impedance spectroscopy (EIS) and electrical conductivity relaxation (ECR), real-time temperature-dependent high-resolution X-ray diffraction (HRXRD) is utilized to understand the effect of interfacial strain on oxygen ion migration. The central challenge of this program is to create, understand, utilize self-assembled vertical heteroepitaxial nanostructures with the goal of obtaining and understanding fast ion transport properties by modulating interfacial strain. The specific objectives of this research program are: (1) to synthesize multilayer thin films and vertical heteroepitaxial nanostructures with fluorite Gd-doped CeO_2 (GDC) and bixbyite RE₂O₃ (RE = Y and Sm), (2) to evaluate the interfacial strain states under various temperature and ambient conditions, (3) to understand the effect of interfacial strain on ionic conductivity of the proposed nanostructures, (4) to understand the three-dimensional atomic structure of the proposed material design and interface phenomena at the atomic scale. The success of this program will provide a foundation of essential data and understanding for fast ionic conducting

materials design. Beyond understanding the interfacial phenomena on the strain-enhanced ion transport properties, this research will also help facilitate the implementation of oxide heterostructures for practical applications.

Recent Progress

GDC-RE₂O₃ lateral multilayer films

Prior to the synthesis of multilayer thin films, the growth of singlelayer films is required to optimize growth conditions for each layer. XRD θ -2 θ scans confirmed that GDC and RE₂O₃ (RE = Sm and Y) singlelayer films were epitaxially deposited on single crystal Al₂O₃ with a (111) orientation. Based on the optimized growth conditions of single layers, epitaxial GDC-RE₂O₃ (RE = Sm and Y) multilayers were deposited on Al₂O₃. The strain of GDC was modulated by altering the thickness of GDC in the multilayers. The strain percentage increased as the thickness decreased, where GDC with the thickness of 5nm on Sm₂O₃ (tensile $\varepsilon = 1.2\%$) and Y₂O₃ (compressive $\varepsilon = -1.9\%$) reached the maximum theoretical strain percentage. To measure the ionic conductivity of the multilayers, the in-plane dc measurements were performed in the temperature range from 450 to 700 °C. The dc measurements were also performed upon varying the oxygen partial pressure $p(O_2)$ in the $10^{-3} - 1$ atm range to confirm that the conductivity of the films is dominated by an ionic contribution within our test range



Figure 1. Ionic conductivity of (a) GDC-RE₂O₃ (RE = Sm and Y) multilayers and (b) $[(GDC)_1|(Sm_2O_3)_1]_n$ superlattice films. [1]. As shown in Figure 1a, an increase in the ionic conductivity by tensile strain in the GDC-Sm₂O₃ films was observed. As the GDC thickness decreased, ionic conductivity increased as the tensile strain increased. In contrast, a decrease in ionic conductivity was observed for compressive strained GDC- Y_2O_3 films. Generally, tensile strain is known to create more oxygen vacancies compared to compressive strain [2]. Using *in-situ* HRXRD, we confirmed that more oxygen vacancies were formed in the tensile strained GDC-Sm₂O₃. Raman spectroscopy measurements also revealed that the peak of the tensile strained GDC-Sm₂O₃ films shifted to the lower Raman energy compared to compressive strained GDC-Y₂O₃ films, indicating increased oxygen vacancy concentration in GDC [3].

To study the interface effect on the ionic conductivity, superlattice films of $[(GDC)_1|(Sm_2O_3)_1]_n$ (n = 1, 3, and 20) where n is the number of GDC-Sm₂O₃ bilayers were prepared. The thickness of the GDC layer was fixed at 5nm to maintain the same tensile strain amount ($\varepsilon = 1.2\%$) in the superlattice films while controlling the number of layers. Interestingly, there was no discernable difference in the ionic conductivity by increasing the number of interfaces from 1 to 20 (Fig. 1b). This result implies the increased instability of interfaces due to the geometric contraints of lateral thin films [4]. Therefore, new design concepts which enable a large number of interfaces while maintaining the strain state regardless of the thickness of films are required.

Vertical heteroepitaxial nanostructures (VHNs) with GDC-RE2O3

We used different compositions and frequencies of GDC-RE₂O₃ (RE = Sm and Y) as 50:50, 30:70, 70:30, and 1, 3Hz for the deposition to control the structure and strain amount of the VHNs. Prior to the synthesis of VHNs, the growth of single-layer films was required to optimize growth conditions for each layer on the STO substrate. XRD θ -2 θ scans confirmed that GDC and RE₂O₃ (RE = Sm and Y) single-layer films were all epitaxially deposited on single crystal STO with a (001) orientation. Based on the optimized growth conditions of single layers, the GDC-RE₂O₃ (RE Table 1. Strain percentageextracted from reciprocal spacemaps (RSM).

	1Hz	3Hz	
GDC:Sm2O3 70:30	0.28 %	0.56 %	
GDC:Sm2O3 50:50	0.30 %	0.73 %	
GDC:Sm2O3 30:70	0.88 %	0.89 %	
GDC:Y2O3 70:30	-0.67 %	-	
GDC:Y2O3 50:50	-1.05 %		
GDC:Y2O3 30:70	-1.94 %	-	
GDC:Sm2O3 50:50 GDC:Sm2O3 30:70 GDC:Y2O3 70:30 GDC:Y2O3 50:50 GDC:Y2O3 30:70	0.30 % 0.88 % -0.67 % -1.05 % -1.94 %	0.73 % 0.89 % - - -	

= Sm and Y) VHNs were grown on STO using different compositions and frequencies to control the strain amount, as shown in Table 1. The strain percentages were extracted based on X-ray reciprocal space maps (RSMs) around the (103) peak of STO substrate for the VHNs.

Scanning electron microscopy (SEM) was used to evaluate the morphology information, such as film thickness and surface topography of the VHNs with GDC-RE₂O₃ (RE = Sm and Y). The micron-scale thickness of GDC-RE₂O₃ (RE = Sm and Y) VHNs was confirmed with the cross-section SEM images. The top view SEM image of GDC-Sm₂O₃ 50:50 1Hz VHNs (Fig. 2a) showed a nanomaze structure, where Sm₂O₃ nanocolumns were embedded in the GDC matrix. As the frequency increased to 3Hz (Fig. 2b), the width of the Sm₂O₃ nanocolumns reduced. As the Sm₂O₃ ratio decreased (Fig. 2c), GDC-Sm₂O₃ 70:30 VHNs maintained the nanomaze structure while the density of Sm₂O₃ nanocolumns decreased compared to GDC-Sm₂O₃ 50:50 VHNs. Interestingly, as the Sm₂O₃ ratio increased (Fig. 2d), the surface topology of the GDC-Sm₂O₃ 30:70 VHNs changed to one found in the matrix-pillar configuration, indicating that GDC nanocolumns were embedded in the Sm₂O₃ matrix.



Figure 2. The top view SEM images of (a) GDC-Sm₂O₃ 50:50 1Hz, (b) GDC-Sm₂O₃ 50:50 3Hz, (c) GDC-Sm₂O₃ 70:30 1Hz, and (d) GDC-Sm₂O₃ 30:70 3Hz VAHs.

EIS was employed to access the ionic conductivity of the GDC-RE₂O₃ (RE = Sm and Y) VHNs. The Nyquist plot of the GDC-RE₂O₃ (RE = Sm and Y) VHNs showed a high-frequency arc reflecting ion transport through the film and a low-frequency range reflecting the electrode characteristics. An equivalent circuit of two (RQ) parallel circuits in series was used to fit the impedance data. Figure 3

shows the temperature-dependent ionic conductivity of the GDC- RE_2O_3 (RE = Sm and Y) VHNs extracted from the EIS measurements. GDC-Sm₂O₃ 70:30 1Hz and GDC-Sm₂O₃ 50:50 1Hz VHNs showed similar ionic conductivity compared to the GDC single layer. However, an increase in the ionic conductivity was observed in the GDC-Sm₂O₃ 30:70 1Hz VHNs owing to the increased tensile strain. As the deposition frequency increased, the ionic conductivity increased compared to the 1Hz VHNs, where GDC-Sm₂O₃ 30:70 3Hz VHNs exhibited the highest ionic conductivity among our samples. The decrease in the activation energy as the tensile strain increases supports that the strain dominates the ionic conduction. In the case of the compressive strained GDC-Y₂O₃ 1Hz VHNs, a decrease in the ionic conductivity was observed. As the GDC ratio decreased, the ionic conductivity decreased as the compressive strain increased.



To examine the change of oxygen vacancy concentration of the GDC-RE₂O₃ (RE = Sm and Y) VHNs, *in-situ* HTXRD was performed. The unit cell volume of the tensile strained GDC-Sm₂O₃ VHNs was larger than that of the compressive strained GDC-Y₂O₃ VHNs, indicating an increase in the concentration of oxygen vacancies. However, despite the similar strain percentage between GDC-Sm₂O₃ 30:70 1Hz and 3Hz VAHs (Table 1), GDC-Sm₂O₃ 30:70 3Hz VHNs exhibited much higher ionic conductivity, which could not be fully explained with the concentration of oxygen vacancies. It was therefore hypothesized that the increase in the density of vertically strained interfaces along with the increased oxygen vacancies can lead to the highest ionic conductivity for the GDC-Sm₂O₃ 30:70 3Hz VAHs. Further studies are needed to elucidate the exact mechanism on this observation.

Future Plans

The next plan of this project is to explore the structure of GDC-RE₂O₃ (RE = Sm and Y) VHNs in more detail by using transmission electron microscopy (TEM) and APT. Cross-sectional TEM images will be used to obtain the column shapes and width of our VHNs. It is expected that increasing the deposition frequency in the VHNs will increase the number of interfaces and decrease the column width, which leads to increased strain. APT will be performed to study the 3D structural configuration of the GDC-RE₂O₃ (RE = Sm and Y) VHNs. Using APT with our samples, the chemical composition analysis will define the GDC and Re₂O₃ (RE = Sm and Y) part in the VHNs. Moreover, areas of maximum oxygen isotopes (¹⁸O) concentration will provide a direct display of a preferential local oxygen diffusion pathway, which we expect to be the GDC nanocolumns.

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Quantum Coherence of Moiré Excitons in Transition Metal Dichalcogenide Twisted Homobilayers

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Key words: quantum dynamics, excitons, atomically thin layers, moiré superlattices

Research Scope

Moiré superlattices are formed when two atomically thin van der Waals (vdW) layers are vertically stacked together. In moiré superlattices formed by transition metal dichalcogenide (TMD) monolayers, optical properties are dominated by excitons. Similar to TMD monolayers, exciton binding energy in moiré superlattices is exceptionally large ($\geq 200 \text{ meV}$), making these quasiparticles stable at room temperature and relevant for various optoelectronic devices. This program aims to understand new optical excitations and resonances in atomically thin semiconductors and moiré superlattices. We apply a wide range of optical spectroscopy techniques, most uniquely, two-dimensional electronic coherent spectroscopy (2DECS) to understand new optical resonances and their quantum dynamics in atomically thin layers and twisted bilayers.

Our specific goals in this funding period include:

- Investigating basic properties of moiré excitons in WSe₂ and MoSe₂ twisted homobilayers including modified optical selection rules and the emergence of flat bands;
- Probing unique quantum dynamics of moiré excitons in ThBLs that originate from phononassisted valley scattering, momentum space band rotations, and the moiré potential;

Recent Progress

In the past year, we have made great progress in fabricating devices in which electron and hole doping density and an electric field can be independently tuned. Using such devices, we made two major scientific discoveries.

In the first project, we investigate the formation of new quasiparticles, namely attractive and repulsive polarons, in doped MoSe₂ and WSe₂ monolayers. Fermi-polarons are mobile impurities (e.g., excitons) that are coherently dressed by density fluctuations (particle-hole excitations) of a surrounding Fermi sea. There are two interesting, yet drastically different regimes of the Fermi polaron problem: (i) the attractive polaron branch, connected to pairing phenomena spanning the crossover from BCS superfluidity to the Bose-Einstein condensation of molecules; and (ii) the repulsive branch, which underlies the physics responsible for Stoner's itinerant ferromagnetism. Doped semiconductor monolayers represent a playground for studying Fermi polarons in two-dimensional systems, where many questions and debates regarding their nature persist.

A variety of exciton resonances (neutral or charged states, biexcitons, spatial and momentum-space indirect excitons) have been identified and investigated in TMDC monolayers. The trion, a three-body bound state consisting of an exciton bound to an extra electron or hole, has been used widely in the literature to describe an optical resonance appearing at an energy ~ 20-30 meV below the neutral excitons. However, the trion picture is only valid and equivalent to the polaron picture at low doping density. As doping increases, a continuous energy shift suggests that the three-body bound state picture is insufficient. Instead, attractive and repulsive polarons (APs and RPs) form as illustrated in Fig. 1a and manifested in reflectivity spectra of doped MoSe₂ monolayer. A critical question remains: does polaron theory predict different properties of APs and RPs? Quantum decoherence associated

with APs and RPs, for example, has never been investigated experimentally. Thus, a comparison between experiments and theory has not been possible so far.

We study the emergence and evolution of APs and RPs in a MoSe₂ monolayer as the electron doping density increases. Using two-dimensional coherent electronic spectroscopy 2DCES, we follow the changes in resonant energy, oscillator strength, and quantum decoherence of the AP and RP branches. We perform one-quantum rephasing measurements as a function of the doping density. The amplitude of the photon echo signal as a correlation between absorption and emission frequencies is shown in Fig. ??. The elongation along the diagonal direction indicated by the dashed line is determined by the inhomogeneous linewidth while the full-width half maximum (FWHM) along the cross diagonal direction indicated by two arrows reveals the homogeneous linewidth. We carefully analyze the energy shifts and quantum decoherence rates of APs and RPs extracted from 2D spectra. The homogeneous linewidth of the RP rapidly increases with electron doping density. In contrast, the decoherence rate of APs remains largely constant until the doping density exceeds a critical density. In the range of gate voltages that correspond to a modest doping density, a continuous red shift of the AP resonance is observed, suggesting the coherent dressing of the quasiparticle can lower its energy. The red shift of the APs against doping level is often overlooked or left unexplained in previous studies.

Remarkably, most of the key experimental observations (doping-dependent energy, oscillator strength, and quantum decoherence rate) can be well captured by a microscopic theory based on the simple Chevy ansatz of Fermi polarons. The excess electrons have two main effects: exciton renormalization and polaronic dressing. The former modifies the resonance frequency and oscillator strength of excitons but does not lead to polaron formation or two separate branches. These excitons interact with excess electrons and the polaronic dressing splits them into AP and RP branches. Polaronic physics is solely responsible for the relative behavior of the two branches (i.e., the relative frequency, broadening, and oscillator strength).

The comparisons between experimental observations and predictions from the Fermi-polaron theory are summarized in Figs??. A hallmark of the Fermi-polaron theory in 2D is a linear increase of the energy splitting between APs and RPs as a function of Fermi energy: $\Delta E_{RP-AP} = \epsilon_T + 3/2\epsilon_F$, where ϵ_T is the trion binding energy and the factor 3/2 originates from the inverse reduced exciton-electron mass $2/3 m_e$ in TMD. The experimentally extracted energy splitting matches the prediction remarkably well (Fig. ??d) including the slope of the linear dependence.

We further analyze the relative oscillator strength transfer between the APs (f_{AP}) and RPs (f_{RP}) as a function of the Fermi level. The oscillator strength of both APs and RPs is evaluated by integrating the amplitude over the area around the resonances in the 2DCES spectra. An excellent agreement is found between our measurements and the prediction of the polaron theory in Fig.

Another key prediction of the Fermi-polaron theory is that the AP linewidth is almost doping independent, which agrees well with the experimental observation up to $\epsilon_F = 15$ meV. This behavior cannot be captured within the trion picture, which instead predicts that the AP linewidth increases approximately linearly with ϵ_F . However, the polaron theory substantially underestimates the observed RP broadening as doping density increases. The observed RP linewidth is very well fitted by adding an extra quadratic term to the linear dependence on ϵ_F predicted by the polaron theory (blue solid line in Fig. ??). This discrepancy suggests the existence of a qualitatively new contribution to RP decay. The quadratic dependence of the additional broadening hints at the involvement of electron-electron interactions. In particular, the additional RP decay can originate from nonradiative transitions from the RP to the AP.

Examples of accurate theory for strongly interacting many-body systems are rare. In this work, we demonstrate how the Fermi polaron theory can be used to describe the quantum dynamics of an imbalanced quantum mixture of excitons and an electron gas in a MoSe₂ monolayer. While Fermi

polarons in the cold atom systems and 2D semiconductors share similar properties, e.g., the linear RP-AP energy splitting and stable quantum dynamics of APs as a function of Fermi level, there are also important differences. The quantum dephasing rate of RPs increases quadratically with the doping density in TMDC monolayers in contrast to the linear dependence found in cold atom systems. The additional broadening is intricately connected with the rich and complicated interplay of two valleys that is present not only in MoSe₂ but also in all TMDC monolayer semiconductors. Our study demonstrates another fruitful playground to study the Fermi polaron problem complementary to cold atoms where this problem has been investigated intensely in recent years.

Future Plans

We plan to extend quantum dynamics studies in TMD monolayers to natural and twisted bilayers in the next 1.5 years. As linear reflectivity spectra on a twisted MoSe₂ homo-bilayer have shown, moiré potential leads to rich internal structures in excitons and trions in our preliminary studies. Quantum dynamics measurements on these unusual moiré excitons are anticipated to lead to exciting discoveries.

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Ultrafast Electron Imaging of Photocarrier and Ion Transport in Energy Materials

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Self-identify keywords to describe your project: ultrafast electron microscopy, photocarrier dynamics, ion migration, perovskites, boron arsenide

Research Scope

The main objectives of this reporting period are to further develop the scanning ultrafast electron microscopy (SUEM) technique, including establishing the theoretical foundation to quantitatively understand its image contrast mechanisms, and to apply SUEM to study photophysical processes in technologically important energy materials. With the combined high spatial and temporal resolutions of SUEM, we aim to (1) directly visualize the photo-induced carrier transport processes and (2) quantitatively understand the light-matter interaction processes in a range of energy materials, including semiconducting polymers, emerging semiconductors and photovoltaic materials.

Recent Progress

1. Fundamental Understanding of the SUEM Contrast Mechanisms. Despite early demonstrative SUEM works, there is currently no clear understanding of the physical mechanisms responsible for the contrast observed in SUEM images. This is a major obstacle towards developing SUEM into a quantitative imaging platform. SUEM contrast images reflect the change in the number of emitted secondary electrons (SE yield, or SEY) from each location on the sample surface as a result of photoexcitation [1]. Thus, the key to understanding SUEM contrast mechanisms is to examine how the SE generation, transport, and emission processes are affected by photoexcitation. Currently, several SUEM contrast mechanisms have been proposed, including bulk photocarrier effects and surface effects [1]. Despite these theoretical proposals, no understanding of relative contributions of these factors were established. To tackle this challenge, we have conducted systematic experimental and theoretical studies to fundamentally establish the foundation to understand the SUEM image contrast mechanism, as summarized in Fig. 1. Experimentally, we carefully characterized the change in SEY as a function of the modulation frequency of the optical excitation beam [Fig. 1(a)]. From the frequency dependence of the SEY, we concluded that the SPV effect plays a major role in the SUEM contrast in doped semiconductors. Theoretically, we combined Monte Carlo simulation of highenergy electron transport and time-dependent density functional theory (TDDFT) to quantify the impact of photoexcitation on the SEY [2], as shown in Fig. 1(b) and (c). Our simulation suggests that the thermalized photocarriers contribute negligibly to the SUEM contrast, while both the SPV and the hot photocarrier distribution immediately after photoexctation can significantly affect the SEY and, thus, contribute to the observed SUEM contrast. In collaboration with the Sandia National Laboratory, we further showed that the SPV effect can play a major role even in the SUEM images of a buried interface. This series of studies have established a framework to quantitatively examine previous SUEM results and laid the foundation for the future development of SUEM as a quantitative imaging tool.



Figure 1. Fundamental Studies of SUEM Contrast Mechanisms. (a) A schematic showing the experiment to quantify the frequency response of secondary electron (SE) emission as a result of modulated photoexcitation. P-type and n-type silicon displayed different contrasts due to the SPV effect, as shown in the insets. Results of our combined Monte Carlo/TDDFT simulation are shown in: (b) Change in the secondary electron yield (SEY) as a function of the effective temperature of photoexcited hot carriers with different primary electron energies; (c) Change in the SEY as a function of the SPV voltage and the primary electron energy.

2. SUEM Imaging of Strain-induced Electronic Structure Modulation in a Semiconducting Polymer. We applied SUEM to image the photo-induced elastic response in a semiconducting polymer (P3HT) and we correlated this photo-response to the strong modulation of its electronic structure due to photo-induced strain [3] (Figure 2). The goal of this work is to image the photoexcited charged species in organic conductors that can differ from those in inorganic materials. We also aim to demonstrate the capability of SUEM to characterize a wide range of materials including organic ones. Two main physical mechanisms in semiconducting polymers are investigated in this work: the

strong photon-lattice coupling that leads to a large photo-induced strain and the impact of the strain on the electronic properties of the semiconducting polymer. Using SUEM, we observed characteristic ring-shaped contrast in P3HT that we attributed to strain-induced modulation of its electronic structure. This study demonstrates the capability of SUEM to characterize organic materials and also provides new insight into the interaction between elastic strain and electronic properties of semiconducting polymers.



Figure 2. Time-resolved SUEM Images of Photoexcited Semiconducting Polymer P3HT. (a) shows the characteristic ``ring-shaped" contrast feature in semiconducting polymers that is attributed to photo-induced transient strain. (b) shows the rise time of the SUEM contrast. The relatively slow rise time (300 ps) indicates that the observed contrast is of photoinduced elasticity nature. (c) shows a schematic of the photo-induced strain profile that generates the observed ring-shaped contrast in SUEM images.

3. Time-resolved Imaging of Persistent Hot Photocarrier Diffusion in Cubic Boron Arsenide.

We used SUEM to characterize other emerging materials with unusual photocarrier dynamics [4]. For example, we measured the photoinduced hot carrier diffusion in single crystals of boron arsenide (Figure 3), a III-V semiconductor that has attracted a lot of attention recently due to its ultrahigh thermal conductivity, which has been attributed to a large frequency gap between acoustic and optical phonon branches that limits the phonon scattering channels. We hypothesized that the same feature would to a significant phonon bottleneck effect that restricts the cooling of photoexcited hot carriers: when the hot photocarriers transfer their energy to optical phonons, these optical phonons cannot efficiently cool down due to their isolation from the acoustic branches. Due to the small size of available boron arsenide single



Figure 3. Persistent hot carrier diffusion in cubic boron arsenide imaged by SUEM. (a) shows the schematic of the SUEM experiment and (b) shows a normal SEM image of the boron arsenide single crystal that we studied. (c) shows the SUEM contrast images showing the initial fast superdiffusion of photocarriers in boron arsenide after photoexcitation. (d) shows how the radius of the photocarrier distribution evolves with the delay time, indicating clearly two regimes: a fast superdiffusion regime and a normal slow diffusion regime.

crystals, it is challenging to characterize charge transport using conventional methods. With SUEM, we are able to directly visualize the initial fast diffusion process of the photo-excited hot carriers and extract the hot carrier transport time. The unusually long hot carrier lifetime (greater than 200 ps) signals that cubic boron arsenide can be a promising candidate material for hot-carrier based photovoltaic, photosensing and photocatalytic applications.

4. Probing Photo-induced Ion Migration in Organic-Inorganic Hybrid Perovskites.

We also applied SUEM to probe in situ photo-induced ion migration in organic-inorganic hybrid

halide perovskites (Figure 4). These perovskites are highly promising photovoltaic materials due to their high power conversion efficiency but suffer from material instability, partly due to its low ion migration barrier. SUEM is uniquely suitable to quantify photo-induced ion migration effect in these hybrid perovskites. We observed long-range and significant migration of the halide ions under illumination, as well as short-range migration of other ions [5]. We correlated the ion migration to the local change of cathodoluminescence from the perovskites that can have profound influence on the performance of solar cells based on these materials.



Figure 4. Imaging photo-induced ion migration in halide perovskites. (a) shows the evolution of the secondary electron image contrast as a function of optical exposure time, correlated to the ion distribution profiles measured by X-ray energy dispersive spectroscopy, demonstrating long-ranged photo-induced ion migration. (b) shows a quantitative analysis of the ion distribution profile as a function of exposure time, from which the ion diffusivity can be extracted as shown in (c).

Future Plans

In the next reporting period, we aim to continue developing the one-of-a-kind SUEM at UCSB and to apply it to resolve the photoexcited dynamics of electrons and phonons in emerging quantum and energy materials with simultaneously high spatial and temporal resolutions. Detailed plans include: (1) Develop time-resolved electron backscattering diffraction mode (EBSD) in SUEM to probe photo-induced surface lattice dynamics. (2) Probe photoexcitation of electrons and phonons in modulation-doped 2D heterostructures. Particularly, we will apply SUEM to directly image the charge transfer process between 2D semiconductors and a charge acceptor layer (α -RuCl3) to understand the microscopic mechanism of the achieved modulation doping. (3) Image spatial-temporal transport of photocarriers in organic-inorganic hybrid perovskites.

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Control of light-matter interactions in hybrid structured environments with novel nanomaterials of different dimensionalities

(Project # DE-SC0010697)

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Research Scope

The rich photophysics of novel semiconductors like transition metal dichalcogenides (TMDs), lead halide perovskites (LHPs) as well as nanocrystal quantum dots (NQDs) can be gainfully exploited in integrated photonic structures alongside conventional semiconducting and dielectric materials. Realization of the prospects of such hybrid structures crucially depends on the ability to fabricate these "designer" assemblies while preserving and enhancing the optoelectronic properties of individual components. We study emission properties of these materials at both bulk and single particles levels to elucidate their intrinsic photophysical properties in order to minimize energy losses and facilitate their judicious integration *via* control of energy/charge flows and photon-exciton interconversions.

Recent Progress

Photon emission from semiconductor nanocrystals at telecom wavelengths in various photonic environments. In collaboration with Dr. Hollingsworth at LANL, we studied PbS/CdS core/shell NQDs as functional single-photon emitters for room temperature, solid-state operation in the telecom O and S bands. Two shell-growth methods (cation exchange and successive ionic layer adsorption and reaction (SILAR)) were employed to prepare PbS-core/CdS-shell NQD hetero-structures with shells of 2–16 monolayers. NQDs were bright and stable to resolve PL spectra representing both bands from single nanocrystals using standard detection methods, and for a NQD emitting in the O-



Figure 1 (a) TEM image and shell structure of PbS/CdS NQD. (b,c) PL spectra and photon antibunching of an individual PbS/CdS NQD. (d) Sketch of the wavelength-size, metal-dielectric bullseye antenna structure. Inset: individual NQD placement by dip-pen technique. (e) Directionality of the emission from CdSe/CdS NQD placed in the bullseye nanoantennae. (f) a schematic representation of Fe_3O_4 thin film coated with spacer layer and PbS/CdS deposited on the surface. (g) The normalized absorption spectrum of Fe_3O_4 suspended in TCE (blue dashed line) and emission spectrum of NIR-PbS/CdS QDs (solid red line). (h) Fluorescence decays of QDs on a 2.5 nm GSS layer (red) and coupled to Fe_3O_4 NC thin film separated by 2.5 nm GSS layer (blue) (i) Calculated Purcell factor (ratio of total decay rates) for an array of Fe_3O_4 NCs between two disks as shown in the inset with different spacers GSS (red), GSST (blue), and Al₂O₃ (gray).

band a second-order correlation function showed strong photon antibunching, important steps toward demonstrating the utility of lead chalcogenide QDs as single-photon emitters (SPEs), Figure 1(a-c). We demonstrated that shell engineering and the use of lower laser-excitation powers can afford significantly suppressed blinking and photobleaching. Using dip-pen deposition technology, we presented a method for directly locating single free-standing NQD SPE with high spatial accuracy at the center of highly directional bullseve metal-dielectric nanoantennas, Figure 1(d,e). Taken together, this approach results in a record-high collection efficiency of 85% of the single photons into a low NA= 0.5, setting the stage for efficient coupling between on-chip, room temperature nanoantenna-emitter devices and a fiber or a remote free-space node without the need for additional optics.¹ Next, we developed spinel metal oxide (Fe₃O₄ sp-MO) semiconducting plasmonic nanocrystals. We established the synthetic conditions for tuning sp-MO NC size, composition and doping characteristics, resulting in wide tunability of electronic behavior and plasmonic response over 450 nm. In particular, with diameter-dependent variations in free-electron concentration across the Fe₃O₄NC series, we introduce a strong NC size dependency onto the optical response. We observe plasmonics-enhanced decay rates from telecom-emitting QDs that reveal Purcell enhancement factors for simple plasmonic-spacer-emitter sandwich structures up to 51-fold, Figure 1 (f-i) which are comparable to values achieved only for emitters in the visible range coupled to conventional noble metal NCs.4

High biexciton emission yield and efficient lasing using quantum shell nanocrystals.

In collaboration with Prof. Zamkov at Bowling Green State University, we explored emission properties of CdS/CdSe/CdS (core/shell/shell) quantum shells (QSs - spherical quantum wells). We demonstrated that Auger recombination is strongly suppressed in QSs, where a relaxed confinement of charges leads to diminished exciton-exciton interactions. We employed single photon counting and photon correlation spectroscopy (photon antibunching) to show that two-dimensional QSs reach high values biexciton emission yield (QY^{BX}).⁹ The Auger suppression was found most prominent in QSs with the largest shell diameter, with average QY^{BX} values reaching QY^{BX} of ~ 82 % for large-core QSs ($D_{core} = 8.2 \text{ nm}$) with individual particles exhibiting QY^{BX} of up to 100%, **Figure 2 (a-d)**. A combination of ultralong (>15 ns) biexciton (BX) emission lifetimes and strong exciton-exciton



Figure 2. (a) Expanded view of a blinking trace, with discrete X; X⁻; and X⁺ intensity levels. (b) Extracted lifetimes from color-coded intensity levels in (b). (c) Gated antibunching traces at different gate values TG with evolution of the middle peak due to BX emission. (d) Statistics of $g^2(0)=QY^{BX}$ values vs. QSs core size. (e) PL as a function of excitation fluence for large core QSs. Inset: Integrated PL intensity vs. fluence, revealing ASE threshold. (f) Variable stripe length setup to measure optical gain. (g) Integrated PL (regular exciton PL subtracted) recorded using variable stripe length configuration (h) Narrow lasing lines for QSs in nanopillar resonators.

repulsion in these QS samples allowed demonstrating low-threshold amplified spontaneous emission (ASE), large modal gain ($g \sim 500 \text{ cm}^{-1}$), and microcavity lasing featuring sharp emission modes at the BX and MX transitions, **Figure 2(e-h)**.^{5,6}

Engineering dopants and defects in TMD monolayers. Metal organic chemical vapor deposition (MOCVD) is used to grow uniform Re-doped MoS₂ monolayers on sapphire substrates. By tuning Re dopant precursor flow during MOCVD synthesis, Re concentration can be controlled from >5 at.% to 500ppm as confirmed by combination of X-ray photoelectron spectroscopy (XPS) and laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS). Re is chosen as Mo-site dopant as it forms shallower donor levels relative to other dopants (e.g. Mn, Fe) in 2D TMDCs. Z-STEM images reveal that Re dopants aid in reducing the sulfur vacancy density from $\approx 3 \cdot 10^{13}$ cm⁻² in pristine samples to $5 \cdot 10^{12}$ cm⁻² in Re-MoS₂. Z-STEM also evidences that Re dopants preferably incorporate at the domain edges of growing MoS₂ films. Density functional theory (DFT) modeling of the MoS₂ growth front shows that the inclusion of Re at the grain edge during synthesis leads to a notable rise in the formation energy of sulfur vacancies. Low-temperature (77 K) PL measurements presents direct evidence for quenching of defect-related emission in Re-MoS₂. At 77K, the PL spectra of pristing MoS₂ is dominated by a broad defect-related peak (X_D) centered at ≈ 1.65 eV originating from sulfur vacancies in the lattice. With the inclusion of even dilute levels of Re dopants (0.05 at.%), X_D emission is greatly suppressed. At 1.0 at.% doping level, X_D is completely quenched and the PL spectra at 77 K only features emission from free excitons. When further increasing Re concentration above 1 at.%, Re-MoS₂ films exhibit a broad emission peak at ≈ 1.75 eV which closely matches the calculated energy of Re-related defect states in MoS₂ and the indirect bandgap of ReS₂. This emission may be attributed to Re dopant aggregation in highly doped films.³ Back-gated field effect transistors (BGFETs) of MoS₂ with and without Re evidences that Re-doping improves transistor performance. BGFETs of dilute-doped Re-MoS₂ films (0.1 at.%) exhibit a maximum I_{DS} of $\approx 61.5 \mu A/\mu m$, nearly $10 \times$ higher than pristine MoS₂ ($\approx 7.6 \ \mu A/\mu m$). The enhancement in drive current may be attributed to the reduction in MoS₂ lattice defects. Average field effect mobility values of 0.1 at.% Re-MoS₂ devices also show moderate improvements from 4.1 cm²/Vs to 8.8 cm²/Vs when compared to the pristine counterpart. Notably, V_{TH} values extracted from drain current (I_{DS}) versus drain voltage (V_{DS}) curves do not significantly shift with Re doping evidencing low dopant activation in monolayer devices. In this reporting period we have begun growing few-layer (2-4L) MoS₂ films to reduce dopant ionization energy and further boost transistor performance. We have developed a novel multistep MOCVD process which enables a layer-by-layer growth and tight control of layer number over large areas. Future studies will focus on benchmarking carrier transport properties in few-layer films through both device fabrication and non-destructive optical characterization methods.

Future Plans – The project is discontinued after this reporting period.

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Response of Gallium Oxide to Pressure, Temperature, and Alloying

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Keywords: Gallium oxide, Photoluminescence, Raman, Defects

Research Scope

Improving the efficiency of power devices such as solar-cell inverters is a major component of energy conservation. The physical behavior of materials used in these devices and the link between defects and performance are important considerations for improving reliability [1]. Monoclinic β -Ga₂O₃ is an excellent candidate for next-generation power electronics due to its ultra-wide bandgap of 4.5-4.8 eV, which results in a high breakdown field estimated at 8 MV/cm. Pushing the bandgap higher by alloying with Al could yield even higher breakdown fields. β -Ga₂O₃ also benefits from being relatively cheap to produce and easy to grow in single crystals.

This project investigates the physical behavior of β -Ga₂O₃ and (Al_xGa_{1-x})₂O₃ alloys in response to hydrostatic pressure, nonhydrostatic stress, and temperature. Specific physical properties to be investigated include band structure, vibrational spectra, and defect levels. The results of this fundamental work will improve device modeling by providing quantitative insight into how β -Ga₂O₃ behaves under different physical conditions. The research is aligned with the DOE Physical Behavior of Materials program, which supports basic research on the behavior of materials in response to external stimuli.

Recent Progress

<u>Persistent photodarkening</u>: Semi-insulating β -Ga₂O₃ substrates, essential for many power devices, can be produced by doping with acceptors such as Fe, Mg, and Zn. A Cu-doped crystal was grown at WSU to determine if Cu could also serve as a viable acceptor dopant. Unexpectedly, the β -Ga₂O₃:Cu samples showed *persistent photodarkening*. First-principles calculations indicate that a Cu-Ho pair is responsible. When a photon is absorbed by this defect, the Cu oxidation state goes from Cu²⁺ to Cu³⁺, which absorbs visible light due to an internal transition. O–H modes are also observed following illumination.

As shown in Fig. 1, upon photoexcitation, hydrogen leaves the oxygen vacancy and forms a metastable O–H bond. The defect becomes a copper-vacancy pair (Cu- $V_{\rm O}$). The copper in this pair has the Cu³⁺ state, which is responsible for the visible darkening. The liberated electron is captured by an iridium donor, changing its oxidation from Ir⁴⁺ to Ir³⁺. The effect can be erased by annealing in air at 300-400°C.



<u>Photoluminescence of chromium impurities:</u> Alloying β -Ga₂O₃ with Al₂O₃ to create (Al_xGa_{1-x})₂O₃ enables ultra-wide bandgap material suitable for applications deep into the ultraviolet. In this work, photoluminescence (PL) spectra of Cr³⁺ were investigated in monoclinic single crystal β -Ga₂O₃, and 10 mol.% Al₂O₃ alloyed with β -Ga₂O₃, denoted β -(Al_{0.1}Ga_{0.9})₂O₃ or AGO. Temperaturedependent PL properties were studied for Cr³⁺ in AGO and β -Ga₂O₃ from 295 K to 16 K. For both materials at room temperature, the red-line emission doublet *R*₁ and *R*₂ occurs at 696 nm (1.78 eV) and 690 nm (1.80 eV), respectively, along with a broad emission band at 709 nm (1.75 eV). The

linewidths for AGO are larger for all temperatures due to alloy broadening. For both materials, the *R*-lines blue-shift with decreasing temperature.

The (lowest energy) R_1 line is dominant at low temperatures due to the thermal population of the levels. For temperatures above ~50 K, however, the ratio of R_2 to R_1 peak areas is dominated by nonradiative combination. Dotted lines in Fig. 2 represent the thermal population, which does not fit the data for higher temperatures. To correctly model the results, we invoked nonradiative recombination, which is thermally activated. This effect also plays an important role in intrinsic PL processes, discussed next.

Self-trapped holes and phonon interactions at extreme temperatures: Due to its large crystal distortion, the holes in β -Ga₂O₃ are highly localized at the oxygen 2*p* orbitals and as a result the holes become immobile. This is a deterrent to achieving *p*-type β -Ga₂O₃ and inhibits free electron-hole pair recombination [2]. Instead,



Fig. 2. PL intensity ratio (R_2/R_1) versus temperature for β -Ga₂O₃ and AGO. Dotted lines represent the thermal population Arrhenius fit only. Solid lines include nonradiative recombination.

these self-trapped holes (STH) create a radiative center below the bandgap energy (~3 eV) with relatively strong luminescence at room temperature that could be used in optical applications.

This part of the research focuses on the temperature response of the STH at 77 – 622 K, which provides vital knowledge for the thermal management of devices operating at extreme temperatures. Figure 3 shows highly resolved PL spectra of a β -Ga₂O₃ film as function of temperature, at a wide energy range that spans the near-UV (~2.85 eV) up to the deep-UV (~5 eV). The main peak at ~3.5 eV is assigned to the STE. The PL intensity of the STE is strongly temperature dependent, implying that nonradiative mechanisms compete with the PL. The activation energy $E_a = 71.4$ meV for this process was determined by fitting the data with the model calculation:

$$I(T) = \frac{I_o}{\left(1 + A * \exp\left(\frac{E_a}{k_B T}\right)\right)}$$
(1)

One plausible mechanism that can explain the strong PL quenching is a nonradiative process that involves phonons. The rationale for considering this mechanism is that β -Ga₂O₃ has a very strong phonon coupling due its large crystal distortion. In the following section, we present results from Raman spectroscopy, which enable us to quantify the phonon properties.





spectra as a function of temperature. The $A_g(10)$ and the $A_g(8)$ modes which are due to the stretch and bending of the Ga₁O₄ site [3], and which is also the crystallographic location of the STH, exhibit reduction in intensity as a function of increasing temperature. In contrast to that behavior, the group of $A_g(5)$, $A_g(6)$ and $B_g(4)$ shows an intensity increase with temperature, implying phonon creation.

We propose the following mechanism to correlate the luminescence characteristic of the STH to that of the phonons [4]. Figure 5 shows a configurational coordinate diagram for the ground state of the bulk and the STH excited state. Due to the strong lattice distortion their minimum points are displaced, and a crossover point *C* is formed. At moderate temperatures, the STH luminesces (point *O* to *B*). When the STH is thermally excited with E_a , from point *O* to *C* via interaction with $A_g(10)$ and $A_g(8)$ phonons, it transitions to point *C*. Then nonradiative relaxation takes place to point *B* via phonon creation [$A_g(5)$, $A_g(6)$, and $B_g(4)$].

Future Plans

Manuscripts describing the pressure response of Cr^{3+} PL and STHs at high temperatures are under preparation and will be submitted in 1-2 months. In addition to phonon interactions, other routes to nonradiative process can coexist such as interactions with impurities and native defects. This in principle should manifest itself by having more than one activation energy, and future work will address this issue.





Fig. 5. Configuration coordinate diagram of a nonradiative process via phonon interactions.

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Extraordinary Responsive Magnetic Rare Earth Materials

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Rare earth materials; Magneto-structural transitions; Theory of 4*f*-element compounds; Spin phenomena; Magneto-functional materials

Program Scope

Extraordinary responsiveness of certain magnetic rare-earth compounds to external thermodynamical stimuli, such as temperature (T), pressure (p), and magnetic field (H), covers a range of intriguing physical behaviors and functionalities rooted in strongly coupled crystal and magnetic lattices. Relevant examples of the remarkable basic and functional properties are: giant magnetocaloric, magnetoresistive, and magnetostrictive effects; spontaneous thermoelectricity; training and acoustic effects; magnetic deflagration; large magnetic anisotropy; exchange bias; and phase-separated glass-like states. Theory-guided design of novel magnetically responsive 4f materials will transformatively change our lives when basic understanding of energy-relevant physics is sufficiently developed. Thus, this research program focuses on the fundamentals of 4f-element interactions at varying energy, spatial, and time scales, on predictive knowledge of the physics and chemistry of 4f-element compounds, and on manipulating the functionality of 4f-electron systems by tuning their electronic, atomic, and microscopic structures.

Our *overarching aspiration* is to transform the field of responsive magnetic rare-earth compounds into predictive science with the *principal objective* of understanding and controlling 4f materials at the electronic, atomic, and microscopic scales, leading to predictions of chemistry, structure and properties, hence, a priori design of materials with desired functionalities. Our main hypothesis is that fundamentally novel magnetoresponsive behaviors can be revealed and manipulated by tailoring 4f-Np,d-4f electronic interactions in rare-earth intermetallic compounds. By identifying and manupulating a number of diverse lanthanide-based model systems, this FWP seeks answers to the following fundamental questions: a) What underlying electronic and magnetic features give rise to magnetostructural (or magnetoelastic) transitions in some compounds but not in the others? b) Can we design and predict intimately coupled lattice and electronic (spin and orbital) phenomena, loss and gain of inversion symmetry, and crystalline and magnetic anisotropies in our interpretation of phase stability and properties? c) How to use this knowledge to create and manipulate nonequilibrium magnetic and structural states in metallic materials? d) What are the key interactions necessary to predict/model responses of a crystal lattice to both strong, e.g., temperature and pressure, and weak, e.g., magnetic field, external stimuli? e) What are the key intrinsic and extrinsic factors necessary for tailoring intriguing magnetic properties for functionalities, such as exchange-bias, magnetic memory, and magnetic anisotropy in rare earth intermetallics? f) How do the intra- and interlayer interactions, interfacial and surface effects, and mesoscale features such as grain morphology modify responsive properties of rare earth intermetallic compounds in their lowdimensional form? g) Can we manipulate magnon fluctuations across discontinuous magnetic phase transitions in rare earth intermetallics to control generation of spin current and associated spin-Seebeck effects?

Recent Progress

By combining our experimental and theoretical expertises, we revealed and explained the origins of several novel physical phenomena in rare earth intermetallic compounds where magnetism is governed by 4f electrons. A few of our recent achievements are highlighted below:

Origins of magnetic memory and strong exchange bias in magnetically compensated mixed-lanthanide intermetallics: Antiparallel magnetic moments alignments of of crystallographically equivalent Pr and Gd in the Pr_{1-x}Gd_xScGe system, directly probed with Xray magnetic circular dichroism, XMCD (Fig. 1), produce *nearly ideal magnetic compensation*, unusual magnetic memory, and strong exchange bias for x=0.25 [1]. In PrScGe, Pr moments align with the magnetic field direction, but when the mixed-lanthanide Pr_{0.75}Gd_{0.25}ScGe is cooled in a weak external magnetic field, Gd moments arrange parallel and Pr moments self-organize antiparallel to the magnetic-field vector. This developed magnetic-moment texture remains stable (i.e., is "memorized") at elevated temperatures, and requires an order of magnitude higher opposing magnetic field for moment reversal. Strong exchange bias – conventionally



Figure 1. Magnetic compensation in $Pr_{0.75}Gd_{0.25}ScGe$ (top left) arising from antiparallel coupling of Pr and Gd magnetic moments (right) probed with element-specific XMCD (bottom left).

seen in artificial multilayers – arises naturally in the layered, single-phase $Pr_{0.75}Gd_{0.25}ScGe$ system as a result of minor Pr/Gd compositional perturbations in otherwise uniform single-phase material.

Understanding peculiar magnetic phase transition and large magnetocaloric effect in Nd₂In: We studied *an unusual borderline* $1^{st}/2^{nd}$ -order magnetoelastic phase transition in Nd₂In by physical property measurements, temperature-dependent crystallography, and electronic-structure calculations [2]. While our analysis indicates that paramagnetic-ferromagnetic transformation is first-order in nature, the temperature-dependent crystallographic study reveals no changes in lattice symmetry and lack of discontinuities both in phase volume and lattice parameters. This unique combination of physical behaviors results in excellent magnetocaloric properties with the *highest reported* magneticentropy change (-13 J/Kg K for $\Delta H = 20$ kOe) among potential magnetocaloric materials at temperatures near the boiling point of natural gas, while the thermal hystere is is negligible. Our theoretical study of Nd₂In with other R₂In compounds shows that peculiar features at the Fermi surface are associated with this unconventional nature of the transition in Nd₂In [3].

Magnetoelastic contribution on magnetothermal properties of GdNi_{1-x}**Co**_x: Experimental and mean-field theory modeling study of magnetothermal properties in GdNi_{1-x}Co_x system uncovered a rare second-order transition with concurrent changes in both magnetic and crystallographic sublattices [4]. A microscopic model of magnetothermal and magnetoelastic interactions in GdNi was developed, in which results of density-functional theory (DFT) calculations were used as inputs into a model Hamiltonian that includes elastic energy of an anisotropic crystal lattice, exchange interactions, and Zeeman effect. We demonstrated that such models can qualitatively and, in some cases, quantitatively describe anisotropic changes of lattice parameters and elastic contribution to magnetoelastic correction are required to accurately model experimental heat capacity of GdNi and this model can be applicable to describe different caloric parameters for different other rare-earth intermetallic systems even where anisotropic magnetoelastic effect presents.

Future Plans

Focusing on model systems well-suited for anticipated breakthroughs in materials science, chemistry, and physics of rare earth intermetallics, we will continue to enhance the basic understanding of magneto-responsive behaviors originated from complex interactions involving 4f electrons. Below

we describe several key research directions, each pursuing specific basic science goals, which we believe are best suited to achieve the stated basic-science objectives.

Truly discontinuous magnetoelastic transitions: We will work to uncover the underlying mechanism(s) of discontinuous phase transformations in R₂In compounds [2] that occur without noticeable thermal irreversibilities. Most of the R₂In compounds adopt *hex*-Ni₂In-type structure, whereas two of them (Eu₂In, Yb₂In) stabilize with the *orth*-Co₂Si-type structure. Our earlier work discovered first-order magnetic phase transitions in several R₂In compounds (Eu₂In, Pr₂In, Nd₂In), but those transitions are isostructural and we found no evidence of *hex*-Ni₂In-type \leftrightarrow *orth*-Co₂Si-type transition that is common in transition-metal alloys. We will focus our experimental and theoretical work on (R'_{2-x}R''_x)In pseudobinary systems [*e.g.*, Pr_{2-x}Eu_xIn or Er_{2-x}Yb_xIn, where end members adopt Ni₂In-type (R'= Pr, Er) and Co₂Si-type (R''= Eu, Yb) structures] aiming to design theoretically and observe experimentally the *hex* \leftrightarrow *orth* magnetostructural transition in these compounds. However, if we find that it is not possible, we will reveal why not and, then, moving beyond R₂In compounds, use alloying science to create this transition by co-alloying and hybridizing the 3*d*- and 4*f*-elements to mimic effects observed in 3*d* -only (Ni₂In- and Co₂Si-type) systems.

Extraordinarily large magnetic anisotropy with nearly-zero magnetic moment in noncentrosymmetric R₇Pd₃ compounds: With potential for magneto-optical and thermomagnetic recording, materials that maintain long-range magnetic order yet possess low or near-zero net

magnetization are in the spotlight for modern spin-transfer and memory applications. An absence of noticeable stray fields and ultra-fast spin dynamics are enabling faster switching and higher storage density. Our preliminary lowtemperature data (Fig. 2) reveal such a magnetic state in a Sm₇Pd₃, non-centrosymmetric compound where an extraordinarily large magnetic coercivity co-exists with small saturation magnetization (~1 $\mu_B/f.u.$) and exchange bias. Sm₇Pd₃ orders magnetically via sharp transition at $T_{\rm C} = 167$ K and shows anisotropic and mildly discontinuous change in lattice parameters below T_C. The preliminary theoretical results suggest a ferrimagnetic groundstate configuration. In future, we will explicate the fundamental origin of this



Figure 2. Magnetic hysteresis curves of Sm₇Pd₃ at 10, 50, 100, and 150 K.

extraordinary behavior via comprehensive experimental and theoretical studies and explore pathways for tailoring those properties using pseudobinary $(R_{1-x}R'_x)_7Pd_3$ model systems [R'= Gd, Nd]. We plan to grow a single-crystal Sm₇Pd₃ and study the anisotropic magnetic behavior at the National High Magnetic Field Laboratory.

Enabling magnetically responsive films and heterostructures: We will extend the science of extraordinary responsive magnetic rare-earth materials and 4*f* interactions toward low-dimensional materials using pulsed-laser deposition (PLD) method. Making use of epitaxy and controlling length scales, interfaces and surfaces are expected to provide additional controls not available in the bulk for tailoring, understanding and, in the future, exploiting the unique structural, magnetic, transport, and thermal properties of responsive rare-earth compounds. In the near future, we will standardize experimental parameters for deposition via PLD for successful synthesis and characterization of films of elemental Er, them address deposition of R_5T_4 -based compounds, which will be our model systems for this study. Further optimization of the deposition conditions for controlling thickness, surface rougness, compositions of the film, and selecting buffer layers (Mo, Ta) will be carried out to permit study of magnetic and electron transport properties of films.

Spin-current dynamics associated with phase transformations in rare-earth materials: We aim to exploit the coupling between phonons and magnetic excitations during magneto-structural transition to generate and manipulate spin currents. Our working hypothesis in this context is that

both intrinsic and induced structural and magnetic instabilities in a material in the vicinity of a phase transition can enhance the magnitude of spin current by way of dynamically evolving phonon and magnon spectra. To enable this research, a new experimental tool, compatible within the existing PPMS equipment, to measure Spin-Seebeck-Effect (SSE) is being designed and fabricated. Once the development and equipment calibration are completed, we will study SSE using Gd₅Si₂Ge₂ as a model system, exploring the influence of magnetic and crystallographic lattice changes on SSE and the effect on the generation of spin current.

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Metamaterials as a Platform for the Development of Novel Materials for Energy Applications

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Metamaterials, metasurfaces, deep learning, inverse design,

Research Scope

We propose to explore the fundamental properties of metamaterials and metasurfaces and their potential for control of energy at the sub-wavelength scale in support of the mission of the Department of Energy and the office of Basic Energy Sciences. Electromagnetic metasurfaces fashioned from dielectrics provide a new platform for the discovery and design of materials with novel structures, functions, and properties. The assembled team proposes to advance the knowledge base of these

through materials fundamental investigations of the experimental properties and theoretical of metamaterials for the discovery, prediction and design of new materials with novel structures, functions, and properties. The proposed research activities are synergistic, and emphasize а complete basic research program including the conceptual computational design, machine learning, fabrication / synthesis of the materials. and the characterization and analysis of their electromagnetic properties.

The proposed project is summarized in Fig. 1 and uses machine learning to explore the fundamental properties of metamaterials /



Figure 1. Top left: Depiction of a fully connected neural network used in machine learning for the current effort. Top right: SEM image of an all-dielectric metasurface which supports bound-statein-the-continuum modes. Bottom left: rendering of a zero-rank absorber. Bottom right: simulation of the field of a symmetry protected bound-state-in-the-continuum mode.

metasurfaces and their potential for energy applications. There are four main objectives: 1) Machine Learning the Interactions of Light and Matter, 2) Zero Rank and Coherent Perfect Absorbers, 3) Bound States in the Continuum, and 4) Spatial—Temporal Metasurfaces.

The program implements a complete basic research program consisting of theory, machine learning, modeling, characterization, and analysis, in order to fully characterize metamaterials and metasurfaces, while minimizing iterations necessary to achieve the proposal goals.

Recent Progress

Machine Learning the Interactions of Light and Matter

We have published several papers related to deep learning light matter interactions in metamaterials and metasurfaces. These works cover specific topics related to deep learning inverse methods, comparison and benchmarking inverse methods, physics informed neural networks, a review of the field of deep learning in photonics, and a tutorial manuscript on deep learning applied to artificial electromagnetic materials. Additionally, we have made available all our deep learning datasets online, as well as the code used for various deep learning studies.
In our inverse study we used an all-dielectric metasurface (ADM) to achieve an emission which matches that of the external quantum efficiency (ECE) of gallium antimonide (GaSb). [1,2] The neural adjoint (NA) inverse method determines the geometry of an all-dielectric metasurface which will yield an emissivity that matches the EQE of GaSb. What is found here is that the NA method indicated that better solutions would be found by increasing the heigh of the ADMs. Indeed that is what has been found, i.e. the MSE values in the expanded range suggested by NA exhibits lower MSE values than our initially explored geometry space. There are several difficulties associated with inverse design and, in particular, there are three major difficulties which are often described in terms of the so-called Hadamard well-posed criteria. These are: H1 the condition of non-existence, the condition of non-uniqueness, and the condition of non-continuity. Each of these present a major challenge to inverse design, and our developed deep learning inverse approach is able to find excellent inverse solutions despite the fundamental challenges.

We also investigated a physics informed neural network (PINN), [3] which we have formed through use of a Lorentz oscillator model. In particular, we enforce the condition of causality through the Lorentz layer which is incorporated within the deep neural network. The Lorentz NN (LNN) takes in the geometry of an all-dielectric metasurface, and outputs the causal frequency-dependent permittivity and permeability. Additionally, the LNN gives the spatial dispersion (k) inherent in the effective material parameters. The ability of the LNN to learn metasurface physics was shown through several examples, and the results are compared to theory and simulations.

Zero Rank and Coherent Perfect Absorbers

We have published four papers where we have studied all-dielectric metasurface and metamaterial absorbers. These papers are: a review paper where we have shown various types and applications of absorbers, a deep learning paper where we studied the physics of all-dielectric metasurfaces, a review paper on imaging with metamaterials, and a study of the Kerker conditions and their application to all-dielectric metamaterial absorbers.

The deep Lorentz network makes predictions of the absorptivity for an all-dielectric metasurface and we have compared these results to both temporal coupled mode theory (TCMT) [4] and numerical simulations. The LNN is also capable of predicting the individual even and odd resonances that are the eigenvalue modes of a mirror symmetric resonator. [5] We also studied the electric and magnetic polarizabilities resulting from simulations and performed a Kerker analysis using these values. We find excellent agreement with Kerker theory [6] and in this published paper have extended Kerker's original analysis.

Future Plans

The proposed future research builds from the current effort and will advance the state-of-the-art in new unexplored metamaterials phenomena. As a primary objective of the future work, we have identified three main areas that are technologically relevant, practically realizable, and ideally suited to our expertise – summarized below.

1) Deep Learning the Physics of Light Matter Interactions – We will develop deep learning (DL) neural networks that are capable of inferring fundamental physics, the way that humans do through the scientific method. We will explore, understand, and develop novel physics informed neural networks (PINNs) and deep learning distillation methods (DDMs). These models will represent a deep learning based approach for discovering new physical insights from data thereby achieving interpretable DL models that are unbiased by prior knowledge. An outcome will be a materials

knowledge-base which will impact other related fields and open exciting new frontiers in physics, materials science, optics, and nano-science.

2) Fundamental Limits of Absorption and Emission – The control of energy at surfaces – including absorptivity and emissivity – is paramount to the understanding of numerous areas of fundamental physics. Despite its importance there are only a few established fundamental relations governing the limits of absorptivity and emissivity. One such result gives the relationship between the thickness of a metal-backed absorber and its absorption bandwidth. [7] We will theoretically, computationally, and experimentally explore the fundamental limitations of absorption bandwidth versus angular, frequency, and polarization dependence, as well as thickness for other materials systems including non-continuous metal-backed materials, metasurfaces, and other artificial electromagnetic materials. Our results will be based on fundamental physical causal relations termed the Kramers-Kronig relations and thus will be universally applicable to a wide range of materials and systems.

3) Radiation Equilibrium – The quantities of absorption and emission are fundamental processes related to the energy contribution of radiative heat transfer. Kirchhoff's law of thermal radiation derives from the second law of thermodynamics and indicates that the emissivity (E) and absorptivity (A) of a surface are identical in thermal equilibrium over spectral, directional, and solid angle degrees of freedom. [8] Therefore, for any material in thermal equilibrium an understanding of the relationship between radiation and the distribution of internal degrees of freedom is critically important. The study of the basic mechanisms which influence these related distributions, and the extent to which they can be modified will help to advance fundamental investigations. Only after gaining a thorough understanding of the fundamental dependencies of radiation equilibrium can more complex scenarios in radiative transfer can be explored.

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Evidence of Hot Carrier Extraction in Metal Halide Perovskite Solar Cells

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Keywords: Hot carriers, perovskites, carrier dynamics

Research Scope: An increasing global demand for renewable energy and the sustainable implementation of these technologies is challenging the solar research community to develop new materials and increase the power conversion efficiency, while continuing to reduce the operational costs of photovoltaic (PV) systems. Recently, metal halide perovskite solar cells have stimulated tremendous interest due to their facile fabrication and the potential for large area inexpensive roll-to-roll manufacturing protocols. Moreover, in less than 10 years these materials have demonstrated solar cell power conversion efficiencies in excess of thin film or multi-crystalline silicon at > 25% [1]. While tremendous effort has been given to the realization of the potential of these materials in PV, the fundamental properties of these systems continue to stimulate significant debate in the scientific community.

In this program particular emphasis has been given to the properties of electron-phonon interaction, carrier transport, and hot carrier dynamics in these materials. Several recent studies have indicated the presence of long-lived hot carriers in perovskites [2-5] along with evidence of a phonon bottleneck [2] and inhibited heat dissipation in these systems [BES 2]. This suggests perovskites may have potential in advanced concept PV such as the hot carrier solar cell. In our work, we have leveraged our considerable knowledge of hot carrier effects in the III-V systems to investigate such effects in the in the metal halide systems in collaboration with experts in the perovskite hot carrier community at NREL.

Recent Progress:

The specific facet of this work presented here, is related to the dynamics of hot carriers in solar cell architectures rather than the thin films that have dominated this discussion historically. It will be shown that the presence of hot carriers can be observed *in the photovoltaic response* of FA_{0.8}Cs_{0.2}PbI_{2.4}Br_{0.6}Cl_{0.02} solar cells at ambient temperatures and under practical solar concentration conditions further supporting the potential of these systems for hot carrier devices. The ability to observe such effects in CW measurements is a direct consequence of the stability of the perovskites under investigation, which enables high power laser excitation and low decomposition under such illumination at high temperatures.

At 100 K, where parasitic processes can be deconvolved from the carrier dynamics clear evidence of hot carriers is observed in both the high energy tail of the photoluminescence (PL) spectra and from the appearance of a non-equilibrium like photocurrent at higher fluence in light J-V



Figure 1. (a) Power dependent photoluminescence at 100 K, and (b) the simultaneously measured monochromatic current density-voltage measurements from 0.2 X suns to 80 X suns equivalent.

measurements. This is shown in Figure 1 where both broadening of the high energy tail in the PL and evidence of hot photocurrent extraction in the light J-V measurements indicate hot carrier generation and extraction under high laser fluence.

At room temperature, the presence of hot carriers in the emission at elevated laser fluence is screened *somewhat* by a gradual red shift in the PL peak energy as photo induced halide segregation begins to occur at higher lattice temperature. However, despite the difficulty of resolving hot carriers in PL at ambient temperatures, simultaneous *J-V* measurements continue to suggested the role of hot carriers in the PV performance of the device even at 300 K.

Future Plans

Future and current work involves assessing hot carriers in operational devices under bias in transient absorption measurements. In these measurements, we have observed the presence of a parasitic barrier to carrier transport that inhibits current extraction at low temperatures that is circumvented by a high energy non-equilibrium carrier distribution at high excitation density. Current measurements are assessing full and half stack structures to elucidate the carrier dynamics at the front and back of the cell and on a more fundamental level – understand the transport of electron and holes in these systems.

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Spin-Dependent Quantum Phenomena in 2D Heterostructures

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Keywords: van der Waals heterostructures, spin transport, proximity-induced phenomena, 2D magnet, ferromagnetic quantum spin Hall insulator.

Research Scope

This research program focuses on exploring interfacial spin interactions and the resulting novel quantum phenomena in all-2D van der Waals (vdW) heterostructures consisting of different 2D materials such as quantum spin Hall insulators and magnetic insulators down to single- or a few-atomic layers in thickness. Due to the atomically flat and chemically sharp interfaces in the vdW heterostructures, the proximity effect is expected to be stronger than that in heterostructures made with three-dimensional materials.

Recent Progress

Using an automated transfer microscope, we have fabricated various heterostructures of 2D materials



Figure 1. Schematic views of monolayer (ML) 1T'-WTe₂ with few-layer CGT composite (upper left) and multi-level device (upper right). Optical image of the actual device (lower left) is before shown the composite is transferred for better clarity. The dashed contours of WTe2, CGT and BN are in yellow, white, green, and respectively. Anomalous Nernst voltages between three pairs (3-8, 4-7, and 4-5) of electrodes that are labeled in the left image (from Ref. P1).

including air-sensitive materials. By exfoliation and capsulation inside a glovebox, we are able to maintain their intrinsic properties down to single- and a few-atomic layer in thickness. These materials include ferromagnets (e.g., CrI₃, Cr₂Ge₂Te₆ or CGT, Fe₃GeTe₂), antiferromagnets (e.g., MnPS₃, FePS₃), quantum spin liquid (a-RuCl₃), and quantum spin Hall insulator (e.g., 1T'-WTe₂) [R1, R2]. We set out to study the proximity-induced ferromagnetism in quantum spin Hall insulator similar to our previous studies on graphene [R3] and 3D topological insulator [R4]. As illustrated in the upper right panel of Fig. 1, we have fabricated devices consisting of several 2D materials in the multi-level stack. At the bottom level, there is a few-layer graphene flake (cyan) as a local back gate, and a few microns away there is a Cr/Au line (red) serving as a local heating source to generate a temperature gradient. On the second level from the bottom, there is a boron nitride (BN) layer (orange) serving as an insulating layer. On top of the BN layer, Pt electrodes (gold) are fabricated by electron beam lithography. After introducing the patterned Pt electrodes back to the glovebox, a composite layer of monolayer 1T'-WTe₂ (green) and few-layer CGT (blue) is picked up by the top

BN layer (orange) and transferred onto the Pt electrodes. The two BN flakes are sufficiently large to capsulate the active device area to prevent oxidation. The sideview of the composite layer is shown in the upper left panel of Fig. 1. An optical micrograph of the device prior to the transfer is shown in the lower left panel of Fig. 1. In this entire device, only the 1T'-WTe₂ layer is conducting. The voltages from three pairs of electrodes show clear hysteresis in response to heater current which we ascribed to the anomalous Nernst effect (ANE) due to proximity-induced ferromagnetism in WTe₂. Similar voltage responses were observed in WTe₂/CrI₃ devices but the ANE origin was excluded by other researchers [R5]. In addition to the ANE responses, we have also observed anomalous Hall and anisotropic magnetoresistance responses, both of which corroborate the induced ferromagnetism. In a different device configuration with electrodes contacting different parts of the device, we have separated the ANE signals from the edge channel with respect to the bulk channel. This work demonstrates for the first time that with proximity coupling, the ML-WTe₂ can turn to a ferromagnetic quantum spin Hall insulator which supports partially spin-polarized edge currents. It enriches our current understanding of the edge states in quantum spin Hall insulators and quantum anomalous Hall insulators which have non-spin-polarized and fully spin-polarized edge currents, respectively. Our paper appeared in Nature Communications in 2022 [P1].

We are currently working on two other vdW heterostructures: antiferromagnetic MnPS₃ with $1T'-WTe_2$ and above-room temperature 2D ferromagnet Fe_3GaTe_2 with WTe_2 . In the antiferromagnetic case, we measure quantum oscillations in WTe_2 to investigate the interfacial exchange interaction strength. We also use the WTe_2 layer as a detector to measure the spin-flop transition in the antiferromagnet. Recently we have characterized the magnetic properties of Fe_3GaTe_2 , an above room-temperature 2D ferromagnet. We are working on the fabrication and transport measurements of the heterostructure devices. We will study spin-orbit torque switching in these devices.

Future Plans

We will continue our current work on the aforementioned heterostructure devices and advance our understanding of the 2D antiferromagnetism and spin-orbit torque switching efficiency in all-2D heterostructures. In addition, we plan to study the phase diagram and antiferromagnetic properties of quantum spin liquid a-RuCl₃ using proximity effect in heterostructures with WTe₂. We will first work on the exfoliated materials. In the meantime, we will explore the molecular beam epitaxy growth of large-area films which would allow us to conduct nonlocal spin transport measurements to investigate the spin-wave excitations in both edges and the bulk of the films.

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Electron Spin Polarization in Large Electric Fields

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Keywords: spintronics, electron spin dynamics, pump-probe optical spectroscopy, Gunn effect

Research Scope

This research program investigates the effect of large accelerating electric fields on electron spin polarization in semiconductors. The goals of this research are to understand the mechanisms that enable and limit the electrical generation of spin polarization in non-magnetic materials, the role of spin-orbit effects and spin scattering in a strongly driven regime, and to determine whether a high-electric field regime that preserves or even amplifies spin polarization that has been theoretically predicted can be realized experimentally. The experimental approach uses ultrafast optical techniques to monitor the motion and dynamics of spin-polarized electrons with sub-micron and sub-picosecond resolution using spatial- and time-resolved pump-probe optical spectroscopy and electrical device design and measurement techniques to produce large electric fields while minimizing excessive electrical heating. The expectation is that this research will improve our understanding of the fundamental processes that cause the electrical generation of spin polarization and contribute to spin dephasing. This knowledge will contribute to the development of robust spin-based devices for information processing, storage, and communication.

Recent Progress

Devices utilizing electron spin polarization to encode information or manipulate magnetization can benefit from electrically-driven methods to produce robust spin polarization. In 2006, Qi, Yu and Flatté predicted a spin Gunn effect that could enable the creation of sizeable spin polarization in gallium arsenide (GaAs) and indium phosphide (InP) at room temperature [1]. The mechanism for this effect is an amplification of spin polarization that occurs when a term proportional to the spatial derivative of the product of the charge density, electric field, and mobility exceeds the spin decay rate. They showed that this could occur near a Gunn domain, which is a dipole layer which forms in GaAs and InP at high electric fields due to the lower mobility of electrons in the L valley and results in a negative differential resistance (NDR) characteristic. The repeated process of Gunn domain nucleation at the cathode, transit through the device at the electron drift velocity, and domain annihilation at the anode causes current oscillations, which is Nown as the Gunn effect [2]. The threshold for nucleating a Gunn domain in gallium arsenide is 3.2 kV/cm, which poses practical challenges, including sample heating and breakdown.

In order to limit sample heating effects, measurements were performed using voltage pulses from a high-voltage source. The size and shape of the semiconductor channels can also be designed to reduce

the dissipated power. Since the electric field required to sustain a Gunn domain is lower than the electric field required to nucleate a Gunn domain, a tapered wedge-shaped geometry near the cathode connected to a rectangular region should lower the threshold voltage required to observe the Gunn effect. А schematic of the device geometry is shown in the top panel of Fig. 1. The dimensions of this device are chosen to be compatible with the optical pump-probe measurements. Previously, experimentally we demonstrated that a wedge-shaped tapering results in a Gunn threshold voltage reduction when the wedge ratio is sufficiently low [3].

In order to investigate electron spin properties in applied electric fields, our approach was to use optical pump-probe techniques, which are sensitive to small changes in electron spin polarization magnitude and is capable of detecting spin polarization with sub-micron spatial resolution and sub-picosecond temporal resolution. Therefore, even transient effects that only occur in close proximity to the Gunn domain could be detected. Since the optical pump pulse can also be tuned to a laser wavelength that will excite carriers in the semiconductor, we are also interested in whether optical pulses can be used to trigger the formation of Gunn domains or affect Gunn oscillation properties. An example of time-resolved Kerr rotation data of optically-pumped spin



Time-resolved Kerr rotation measurement showing electron spin precession and decay when the laser wavelength is 819.5 nm and the applied external magnetic field is 200 mT. Reproduced from Ref. [P3].

polarization is shown in the bottom panel of Fig. 1. The data is fitted to determine the spin lifetime and precession frequency.

In Ref. [P1], we illuminated a GaAs Gunn device and studied the light-induced changes of Gunn oscillation properties. We performed measurements as a function of laser wavelength and illumination power and with the laser both mode-locked, producing picosecond duration pulses at a repetition rate of 76 MHz, and in continuous-wave output mode. We observe that illumination leads to the modulation of the Gunn threshold voltage, the Gunn oscillation magnitude, and the coherency of Gunn oscillation, with the nature of the modulation dependent on which part of the device was illuminated. For example, we showed that near-anode illumination at an applied voltage of 98 V increases the coherency of Gunn oscillations and increases the oscillation magnitude by a factor of 3 compared to no illumination, whereas near-cathode illumination decreases the coherency of Gunn oscillation magnitude is decreased by a factor of 2 compared to no illumination.

We attribute these effects to the generation of optically-excited carriers, which produces a change in the conductivity and the electric field profile along the device.

In Ref. [P3], we examine what happens to optically-pumped electron spin polarization at high external electric fields using spatially-resolved Kerr rotation measurements. As shown in Fig. 2, the applied

electric field causes the spin-polarized electrons to drift. When the applied electric field is zero, the spin polarization generated by the pump pulse remains centered at zero pump-probe spatial separation. In addition, the applied electric field produces additional spin depolarization due to increased inhomogeneous broadening and hot electron effects, which can be observed in the decreasing amplitude of the Kerr rotation with increasing applied electric field. We increase the electric field to exceed the Gunn threshold and do not observe spin polarization signal or evidence of spin amplification due to the spin Gunn effect in the measured device and using our measurement scheme. Future work could focus on finding a sample and experimental conditions in which spin polarization can be measured even at electric fields that exceed the Gunn threshold.

In order to improve the spatial resolution of our measurements, we developed a 4-f set up to steer the position of a pump laser beam relative to the probe beam when both beams are focused on the sample using a microscope objective. Whereas the measurements described above focused the pump



Figure 2. Kerr rotation as a function of pumpprobe separation measured with a pump-probe time delay of 1000 ps at an external electric field of 0.10 (blue), 0.19 (green), and 0.28 kV/cm (purple). The curves are Gaussian fits to the data and show that the peak drifts by 14, 29, and 35 microns with respect to the zero-field peak position. The signal magnitude decreases to 44%, 15%, and 8 % of the zero-field signal magnitude. Reproduced from Ref. [P3].

and probe beams to have diameters of 30 microns on the sample, the microscope objective can focus the pump and probe beams to a 2-micron diameter on the sample. In Ref. [P2], we demonstrate using this set up to conduct time- and spatially-resolved Kerr rotation measurements on small flakes of monolayer tungsten diselenide.

Future Plans

Future efforts to demonstrate the spin amplification predicted by the spin Gunn effect using pumpprobe optical spectroscopy would be aided if it is possible to design a device in which Gunn domains can be triggered by an optical pulse; this would allow for synchronization of the optical measurements with the transient charge domains produced by the Gunn effect. These efforts will also need to account for the additional spin depolarization that can occur in some materials at high electric fields. **References**

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Stimuli-Responsive Materials from Mesoscale Self-Assembly of Plasmonic and Quantum Nanoparticles

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Self-identify keywords: mesostructured materials, nanoparticles, colloids, self-assembly, optical properties.

Research Scope

Our research within this project focuses on understanding and control of self-assembly of anisotropic organic molecules and metal and semiconductor nanoparticles at the mesoscale, as well as on material behavior arising from their ordered self-organization and alignment. The design and realization of physical properties in these composites are based on the following three strategies: (1) discovery of new condensed matter phases of hybrid molecular-colloidal systems enriched by diversity of colloidal particle's geometric shapes, surface charging and boundary conditions for molecular alignment; (2) topology of continuous & singular field configurations in the molecular-colloidal systems; (3) effective medium behavior and plasmon-exciton interactions in colloidal assemblies formed by different types of nanoparticles co-assembled at mesoscopic scales. The main objective of this project's activities is to explore self-organization of pre-engineered anisotropic functional units into colloidal composites with ordered mesoscopic structures that can be tuned and switched by weak external stimuli, such as light and low-voltage electric fields. Tunable composite materials with interesting physical behavior are designed through integrating unique properties of solid nanostructures with the facile responses of soft matter to weak external stimuli. The fundamental studies of interactions and ordering of nanoparticles reveal underpinning physical mechanisms that guide mesoscale morphology and ultimately determine material properties of the self-assembled composites. Mesoscale self-assembly of anisotropic nanoparticles dispersed in responsive liquid crystalline host media is used to enable new composites with properties controlled by applying fields, changing temperature, and using other external stimuli. The focus is on fundamental understanding and control of nanoscale self-assembly and alignment of metal and semiconductor nanoparticles that enable new material behavior arising from orientationally and positionally ordered self-organization of anisotropic molecules and nanoparticles into tunable long-range structures. Electrical realignment of the liquid crystal host, like that used in displays, allows for rearrangement and reorientation of anisotropic nanoparticles, leading to an unprecedented control over self-assembled nanostructures and to dramatic changes in the material's emergent properties. The effective-medium optical properties are characterized and correlated with the hierarchical structure and composition of selfassembled configurations, as well as with plasmon-excition and other interactions separately studied at the level of individual nanoparticles. Within the project, experiments are conducted in parallel with analytical and numerical modeling of interactions and effective-medium optical properties, providing important insights. We explore how ensuing novel composite materials can be used to control transmission and directional scattering of light, as needed for applications in smart windows, displays and electro-optic devices. This research transcends traditional disciplinary boundaries of physics, chemistry, engineering, and materials science. The research in this project broadly advances our knowledge of the nanoscale self-organization phenomena and the ensuing physical behavior.

Recent Progress

The main recent progress in our research project is the demonstration that vortex lines and their arrays interact with light similar to that of cosmic strings, allowing for pre-programmed steering of laser beams (*Nature Mater* 2023) [1], discovery of new topological defect structure with both singular and nonsingular twists (*Nature Physics* 2023) [2], as well as that optical and topological solitons can

organize into co-self-assembled spatial structures (*Nature Photonics* 2022) [3], yielding new physical behavior; there were many other recent breakthroughs as well [4-12]. Due to space constraints, we only describe the recent research findings that just appeared in *Nature Materials* [1], where we developed metamaterial-like behavior with nematic optical axis patterns in uniaxial birefringent host media and demonstrated switching them by unstructured light and low-voltage fields, as well as using them to guide propagation of laser beams

Topology can define material properties and behavior of physical systems at subatomic to cosmic scales but its role in controlling light by liquid crystals (LCs) remains unexplored. We have used optical solitons to demonstrate how LC's optical axis patterns with singular vortex lines mimic the theoretically predicted, imagination-capturing light steering action of cosmic strings, elusive defects in cosmology, albeit at different length scales. We have found that external stimuli, including electric field and light itself, allow for reconfiguring these unusual light-matter interactions by, for example, reconfiguring wide-angle laser beam steering and dramatically changing light deflection angles. We also observed that periodic arrays of vortices obtained by photopatterning enable the vortex-mediated fission of optical solitons, yielding their lightning-like propagation patterns. Furthermore, pre-designed patterns and spatial trajectories of vortex lines in high-birefringence liquid crystals can steer light into closed loops and various other geometrically and topologically complex configurations. Our vortex lattices might find technological uses in beam steering, telecommunications, virtual reality, anticounterfeiting, as well as may offer a model system for probing interaction of light with patterns of defects.

LCs are known to offer a fascinating structural diversity, rich phase behavior and physical properties that allow them to be used as model systems in studies of topological defects and solitons in many physical systems. For example, formation of topological defects at the order-disorder transitions are described by the Kibble-Zurek mechanism for both LCs and the Early Universe Cosmology. Dynamics of vortices upon quenching LC materials through a transition from isotropic to nematic phase, a material analogue of the Big Bang, were used to model the analogous behavior of cosmic strings well before recent attempts to directly probe their very existence by gravitational wave experiments. However, due to quick annihilation of LC vortices after the isotropic-nematic phase transition and strong light scattering in the nematic medium caused by LC director fluctuations, these ideas could not be experimentally tested, as well as the technological potential could not be utilized till now. In our recent study [1], we have defined configurations of vortex lines stretched across the nematic LC bulk by microscale surface photopatterning of the LC director alignment (Figs. 1 and 2). This patterning of surface boundary conditions pins LC vortices in desired spatial locations and precludes their annihilation. We then generate optical solitons to form non-spreading light valves that robustly traverse our LC with vortices and, in the simplest cases, closely mimic interaction of light with cosmic strings. This similarity in light-defect interactions for certain cosmic strings and nematic LC vortices arises from the Fermat's principle stating that the spatial trajectory of light propagation in all media is the one travelled within the shortest amount of time. While optical nonlinearities enable the very formation of our optical solitons, also called "nematicons", these nonlinearities are weak and linear approximation robustly describes how topological defects steer the solitonic light. Using azobenzene-based photo-responsive alignment layers and the coupling of the dielectric LC medium with applied electric fields, we showed how this physical behavior can be robustly controlled and reconfigured with external stimuli for wide-angle beam steering and light localization within closed loops or knots. Continuously bending beams of light, the strongest lightsteering effects are found in large- Δn materials. To enhance Δn , LCs can be doped with plasmonic or other nanoparticles, including MoS2 with $\Delta n \sim 3.054$, or, alternatively, metamaterials and metasurfaces with giant Δn (Fig. 1d). Although solitonic light was used in our experiments, topological steering can be achieved for nonsolitonic beams by suppressing scattering through polymerizing LCs or by miniaturizing samples, so that the beams experience little intensity loss while guided by slowly varying patterns of optical axis. We foresee that cosmology-inspired topological steering of light could find technological uses in telecommunications, virtual reality designs, anticounterfeiting, nanophotonics and light-based energy storage.

Fig. 1. Steering of light by LC vortices & cosmic strings. a-c, Conical spacetime (green) and deficit angle $\Delta \phi$. Light trajectories (red lines) are distorted due to either a cosmic string or the LC vortex with concentric **n**(**r**) in (c). $\Delta \phi$ and the light deflection angle θ are marked in (a) and (c). d, θ of light rays passing near a cosmic string (blue) or a k=1, $\Psi_0=\pi/2$ LC vortex line (red). Red dots correspond to LCs CCN-47 ($\Delta n=0.015$), E7 ($\Delta n=0.24$), and SHB-6 ($\Delta n=0.79$). The inset in linear scale shows the values obtained from Hamiltonian-based simulation (open



circles, with dashed line serving as a guide to the eye) and from theoretical prediction (solid line). Examples of deflections by extraterrestrial objects are shown on the same scale as θ . e, (left) Polarizing optical micrograph of a k=1, $\Psi_0=\pi/2$ vortex, obtained between crossed polarizers (yellow arrows), and (right) the corresponding deflection of 650 nm laser beams incident parallel to the horizontal edge of the image from its left side (red arrows with yellow glow). f-j, Comparison of (left) computer-simulated light trajectories (red and dashed green lines), overlaid atop of $\mathbf{n}(\mathbf{r})$ (white cylinders), with (right) experimental trajectories generated by 1064 nm beams for: (f) k=1, $\Psi_0=\pi/2$; (g) k=1, $\Psi_0=0$; (h) k=1/2, $\Psi_0=\pi/4$; (i) k=-1/2, $\Psi_0=\pi/4$ and (j) k=-1/2, $\Psi_0=5\pi/8$. Insets in (h) and (i) show polarizing and brightfield optical micrographs of the corresponding vortices. All scale bars are 100 µm.

Fig. 2. Interactions of optical solitons with arrays of vortices. a, Polarizing optical micrograph of an array containing k=3, k=-1 and k=-1/2 vortices. The brightfield optical micrograph in the inset shows dark dots that correspond to the singular/melted cores of half-integer vortices, depicting how k=3, k=-1 cores split into 6 and 2 half-integer defects in cell midplane, respectively. b, corresponding $\mathbf{n}(\mathbf{r})$ (white streamlines) within the blue-box region in (a); different vortex locations are marked by filled red diamonds, blue squares and orange triangles, respectively. c, Computer-simulated splitting of the k=3defect core into a hexagon of half-integer vortices, with the red isosurfaces showing regions of reduced scalar order parameter of 0.43 and lower. d, (left) Beam trajectories with accumulating light deflections bending them backwards (red) or into closed loops (green) and (right) their computersimulated analogues obtained with the Hamiltonian approach, overlaid atop of corresponding polarizing optical micrographs. e, Distinct vortex-guided (left) experimental and (right) computer-simulated ray trajectories distinguished by false colours. f,g, An array with k=1



vortices shown like in (\mathbf{a}, \mathbf{b}) with an experimental micrograph and simulation of $\mathbf{n}(\mathbf{r})$ and defects. Inset micrograph shows local splitting of k=1 vortex cores into 2 half-integer defects. **h**, Simulated splitting of k=1 vortex core showing $\mathbf{n}(\mathbf{r})$ and regions of reduced scalar order parameter of 0.5 and lower (green). Scale bars are 200 µm.

Future Plans

Within the next year, the focus will be on developing stimuli-responsive materials that combine properties of solid nanostructures (quantum dots and plasmonic nanoparticles) and facile responses of soft matter, along with emergent new behavior enabled by various aspects of topology in the order parameter fields. Using LC materials and its mixtures doped with magnetically monodomain colloidal

platelets, PI will explore topological transformations between different phases. Other nanoparticles will include mesoporous silica nanorods and nanoplatelets recently successfully synthesized on our group, which appear to be ideal for exploring the phase behavior. In-depth studies will reveal how mesoscale self-organization, which can yield centimeter-large mono-crystals of colloidal nanoparticles with tunable center-to-center separations, leads to new physical behavior and material properties arising from a combination of unique properties of nanoparticles and structural organization at nanometer to macroscopic scales. Effective medium properties of pre-engineered metamaterials will be studied. By exploiting unique properties of solid nanostructures, PI intends to develop a new breed of composites with novel physical behavior, pre-engineered properties, and facile response to external fields. For example, PI's preliminary studies already show that mesostructured composites made of perovskite quantum nanoparticles dispersed in thermotropic nematics can exhibit ultra-strong responses to light and electric fields; this work will be now systematically extended to different particle sizes and geometric shapes.

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Program Scope

The objective of this project is to discover and explore new solid-state caloric materials, and to understand the origins of their physical behaviors including magnetocaloric effects, barocaloric effects, and transport properties. We explore new materials that exhibit magnetic or magnetostructural

transitions near room temperature that form as a result of doping, thermal quenching, hydrostatic pressure (during measurement), and the application of pressure during synthesis, leading to metastable magnetostructural phases.

Recent Progress

One goal of this project is to induce coupled, magnetostructural transitions in materials near room temperature by creating metastable phases through thermal quenching, or by applying pressure during synthesis. The application of hydrostatic pressure during measurement (i.e., not during synthesis) can shift magnetostructural transitions, or even cause them to form by forcing structural and magnetic transitions to coincide in temperature. This process can result in large magnetocaloric or barocaloric effects, but these are temporary behaviors since the transitions return to their normal (standard pressure) temperatures when the hydrostatic pressure is removed.

In order to permanently create a magnetostructural transition, or to tune an existing one to occur near room temperature (where such a material could perform as



Fig. 1. The permanent shifting of phase transitions in MnNiGe as a function of thermal treatment. SC1100 was "slow cooled" from 1100 °C. The "AQ" curves were quenched from the indicated temperatures.

refrigeration working material), elemental substitutions are often made in some parent compound. In some cases, this can dilute the magnetization, and therefore the overall effectiveness as a magnetocaloric material, since magnetic species are often replaced with nonmagnetic atoms.

An alternative strategy to *permanently* to shift, or induce, a magnetostructural transition in a ferromagnetic parent compound that undergoes a structural transition at a higher temperature (sometimes hundreds of Kelvin above the Curie temperature) is to generate a metastable phase through thermal quenching, or through synthesis at high pressure. Such processes can permanently alter the behaviors of the phase transitions and physical properties of the materials. A good example of where this can happen is in the thermal quenching of Mn*TX* alloys, where T = Ni, Co, or Fe and X = Si or Ge.¹ Alloys of the form Mn*TX* have been of great interest for solid-state cooling since they have been shown to exhibit large magnetocaloric effects (MCEs) and barocaloric effects (BCEs), and sometime *both*.^{2,3} In many of these cases, however, complex atomic substitutions had to be made in order to couple the magnetic and structural transitions at room temperature.

Consider the case of $(MnNiSi)_{1-x}(FeCoGe)_x$: The parent compound is MnNiSi, which has a magnetic transition at $T_C = 662$ K, and a structural transition at $T_M = 1200$ K, above which it has a

Ni₂In-type hexagonal structure and below which it has a TiNiSi-type orthorhombic structure.⁵ No single-element substitution was able to couple the two transitions near room temperature, thus the isostructural substitution of FeCoGe was required. The saturation magnetization of NiMnSi is $M_{\rm S}$ = 2.6 μ_B per formula unit, whereas that of FeCoGe is 2.0 μ_B , which is lower, but at least comparable to the parent compounds. Other isostructural substitutions have larger negative effects on the total moment, such as FeNiGe, for which $M_{\rm S} = 0.5 \,\mu_{\rm B}/{\rm fu}$. Therefore, one objective was to explore synthesis processes in which the high-temperature hexagonal phases of parent or modestly-doped MnTX compounds were made metastable near room temperature (through quenching or high-pressure synthesis). This may reduce or alleviate the undesirable effects of atomic substitution. Two methods to stabilize the magnetostructural transition at lower temperature were employed in this study: thermal quenching and high-pressure synthesis. The recent results on which we focus here regard doped and undoped MnNiGe.



Fig. 3. Magnetization of MnNiGe as a function of temperature at the indicated hydrostatic pressures (during measurement). Pressure further shifts the transition of a quenched sample (AQ1100) to room temperature.

Figure 1 shows the magnetization and calorimetric data on MnNiGe with systematic thermal treatments that range from slow-cooled from 1100 °C (SC1100) to quenched in liquid nitrogen from 1200 °C (AQ1200). The slow-cooled sample shows three transitions: structural ($T_{\rm M} = 470$ K), spiral (simple) antiferromagnetic ($T_{\rm N1} = 360$ K), and spiral (cycloidal) antiferromagnetic ($T_{\rm N2} = 250$ K). A phase diagram showing the magnetostructural phases is shown in Figure 2.

As can be seen in Figure 1, even at the highest quenching temperature (1200 °C, AQ1200), the magnetostructural transition temperature does not shift to room temperature (~300 K). In this case, however, the application of hydrostatic pressure can be used to shift the transition to even lower temperature, and it reaches room temperature when P = 9.17 kbar (see Fig. 3). This not only results in large magnetocaloric effects (MCEs), but also suggests that this material will exhibit significant barocaloric effects (BCEs), since the transition is pressure sensitive with dP/dT = -8 K/kbar. The interesting final result is as follows: through quenching and applied hydrostatic pressure, stoichiometric MnNiGe can be transformed into a standalone MCE or BCE material (i.e., with no elemental substitutions).

As demonstrated above, the final step in shifting the magnetostructural transition in stoichiometric MnNiGe to room temperature was the application of hydrostatic pressure (see Fig. 3). This final shift, however, is not permanent, i.e., the transition shifts back to its original position upon the release of pressure. We can, however, shift the transition *permanently* with a small amount of doping (5 - 8% of Co for Mn), which has the effect of shifting the transition to lower temperature, together with *highpressure synthesis*, which shifts it further.⁴

In Figure 4(a) are the magnetization data of $Mn_{1-x}Co_xNiGe$ (x = 0.05) for samples that were annealed at 800 °C and then slow-cooled (Co5_SC), rapidly-



Fig. 2. A phase diagram of MnNiGe as a function of quenching temperature.

cooled (Co5_RC), and synthesized at high pressure (P = 3.5 GPa) and subsequently slow-cooled



Fig 4. Magnetization and magnetic entropy changes in $Mn_{1-x}Co_xNiGe$ (x = 0.05. and 0.08). (a) Slow cooled (SC), rapidly-cooled (RC), and high-pressure synthesized and rapidly-cooled (HP-RC) magnetization for x = 0.05; (b) Same as in (a) but for x = 0.08; (c) and (d) The corresponding magnetic entropy changes for x = 0.05 and 0.08, respectively.

(Co5-HP-SC). Similar data are shown in Fig. 4(b) for x = 0.08 at the same synthesis pressure. In the case of x = 0.05, high-pressure synthesis followed by rapid cooling shifted the incompletely formed magnetostructural transition from about 365 K to 300 K, where it also became fully coupled. Unlike the shifts illustrated in Figure 3 for NiMnGe, these shifts are *permanent*. This phase is metastable, but durable, i.e., the transition does not revert to the "pre-pressure-synthesized" state after repeated thermal and field cycling. Figure 4(b) shows similar measurements for the sample with x = 0.08, for which the transition of the high-pressure-synthesized sample has shifted to about 250 K, so that it is in the metastable, high-temperature hexagonal phase at room temperature.

Figure 4 (c) and (d) show the corresponding magnetic entropy changes of these materials, the peaks of which shift to lower temperatures in correspondence with their respective transitions. For both x = 0.05 and 0.08, the MCEs of the samples synthesized at high pressure are either maintained or improved relative to those fabricated at atmospheric pressure. For x = 0.08, for example, $\Delta S_{max} = 80 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$ for $\Delta H = 7 \text{ T}$, whereas the slow-cooled sample had a value of 60 $\text{J}\cdot\text{kg}^{-1}\text{K}^{-1}$. For x = 0.05, $\Delta S_{max} = 16 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$ for $\Delta H = 7 \text{ T}$, but the relative cooling power, defined as RCP = $\Delta S_{max} \times \delta_{FWHM}$, where ΔS_{max} is the maximum magnetic entropy change and δ_{FWHM} is the full width at half maximum, is enhanced in the high-pressure sample (205 J/kg) relative to the rapidly-cooled (180 J/kg) and slow-cooled (25 J/kg) samples. A major conclusion drawn from this study is that, through thermal quenching and high-pressure synthesis, metastable phases can be created such that magnetostructural transitions occur in materials in which they are not present under conventional fabrication processes. In the end, a material can be transformed into a solid-state caloric material through quenching and high-pressure synthesis.

Future Plans

Future and in-progress projects include: (1) Perform direct adiabatic temperature change (ΔT_{ad}) measurements of antiperovskite magnetocaloric compounds, (2) carry out high-pressure synthesis and characterization of stoichiometric MnNiSi (attempt to create a room-temperature metastable

phase), (3) investigate the synthesis and solid-state caloric properties of the Mn-based, antiperovskites Mn₃GaC and Mn₃ZnC, and (4) explore the phase transitions and magnetic entropy changes in 2-D van der Waals ferromagnets (Fe₄GeTe₂).

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* Two additional manuscripts are currently in preparation.

Elucidating Chirality-induced Magnetism and Magnetoelectric Functionalities in Layered Chiral Hybrid Metal Halide Perovskites

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Keywords: Chiral hybrid metal halides, chirality-induced spin selectivity, chiral phonons, magnetism, magneto-optics.

Research Scope

2D layered Hybrid Metal Halides (2D-HMHs) are a new class of synthetic semiconductors prepared by low-temperature solution processing with a large chemical and structural 'universe' benefiting from their synthetic versatility. By implanting chiral organic cations into the HMH superstructure, the 2D-chiral-HMH would simultaneously exhibit ferromagnetic, ferroelectric, and magnetoelectric functionalities stemming from a Chirality-Induced Spin Selectivity (CISS) effect that may not be subject to thermal fluctuations. The goal of this program is to elucidate the fundamental origins of chirality-induced magnetism via the CISS effect and their electrical tunability in 2D layered HMH material systems. To date, we focused our efforts on developing two ultrasensitive detection themes based on spin-orbitronics and magneto-optics to probe the CISS-induced magnetism and magnetoelectric functionalities in this hybrid material. Specific research activities include preparation and structural characterization of the chiral 2D-HMHs, development of magneto-optical detection under light illumination, and theoretical modeling.

Recent Progress

[1] "Chiral-phonons-activated spin Seebeck effect" - Observation of the chiral phonon-activated spin Seebeck effect using transient magneto-optical Kerr effect technique.

The invigorated field of spin caloritronics examines the interplays between spin and heat transport in various magnetic materials and even exotic non-magnetic semiconductors. For example, coupled thermal spin transport provides conceptually new mechanisms for solid-state thermal-to-electron spin energy conversion. There are many recent advancements related to processes through which thermal-induced spin currents can be generated, manipulated, and detected, with an emphasis on the discoveries related to the spin Seebeck effect (SSE) [1-4]. It is noteworthy that the spin current can be also generated by angular momentum conversion, usually among magnetization, photon angular momentum, and intrinsic spin. It comes to our attention that the mechanical angular momentum carried by condensed matter systems, including rigid rotation and elastic deformation has been theoretically proposed. At the microscopic scale, the lattice vibrations, i.e., phonons, can also carry angular momentum. The **phonon angular momentum**, i.e., **chiral phonons**, have been experimentally observed in 2018 [5]. It represents a microscopic local rotational motion of the nuclei around their equilibrium positions. When the system is driven out of equilibrium, the non-zero



Figure 1. Transient spin current generation via the CPASS effect. a, Schematic illustration of chiral phonon activated spin Seebeck (CPASS) effect. **b**, A skech of the measurement geometry (not to scale) of the CPASS in layered Cu/chiral HMH heterostructures using the time-resolved MOKE technique. The expanded panel depicts the schematics of the 2D chiral HMH structure used in this work consisting of alternating PbX₆ framework and chiral organic ligands with opposite chirality. An ultrafast temperature gradient is built across the heterostructure by a laser pump pulse that is incident on a Cu layer. The generated diffusive spin current in the Cu layer via the CPASS is detected by a probe pulse. **c**, Transient Kerr rotation signals measured on the Cu layer side of the Cu/(S-MePEA)₂PbI₄ (blue), Cu/(R-MePEA)₂PbI₄ (red) heterostructure, respectively. The laser-induced change in the Kerr rotation in each heterostructure is plotted as a function of time delay. All measurements are performed at room temperature.

phonon angular momentum will be generated. This effect requires crystals with sufficiently low total crystallographic symmetries, making the chiral system perfect for this condition. From the perspective of chiral phonons, since its early prediction and recent observation in two-dimensional monolayer in 2018 [5], researchers, especially those who are in the field of 'topological materials', are searching for materials that possess chiral phonons. They aim for identifying materials systems where chiral phonons couple with other carriers and become beneficial for the desired properties. Therefore, it is natural to launch a scenario where chiral phonons can transfer their angular momentum and drive a non-equilibrium spin current in an adjacent conductor in the same way as the SSE but without the need for magnetic elements.

<u>Generation of oscillating spin current via CPASS.</u> We report the observation of a Chiral Phonons Activated Spin Seebeck (CPASS) effect in non-magnetic chiral-HMHs by applying a transient temperature gradient induced by ultrafast laser pulses. A schematic overview of our experiment is described in Figure 1a. Figure 1b shows time-resolved Kerr rotation signals probed on the Cu side of two different types of chiral-HMH-based heterostructures having opposite chirality, i.e.,

Cu/(S-MePEA)₂PbI₄ and Cu/(R-MePEA)₂PbI₄. An unprecedented long-lived oscillating Kerr signal in the gigahertz frequency (~2 GHz) is observed, exhibiting a slow decay persisting up to ~4 ns. We found that when the chirality of the HMH films changes from the left-handed (S, red) to the right-handed (R, blue), the phase of the oscillating Kerr signal is inverted.

<u>CPASS-driven spin transfer torque (STT).</u> We examined the torque exerted on an adjacent ferromagnetic layer induced by the generated spin current. By absorbing this spin current, the NiFe layer acts as a spin sink via the STT process, leading to a precessional motion of magnetization that will be detected by the polar TR-MOKE measurements. We found the direct evidence of CPASS-driven STT by measuring the time-resolved Kerr signal on the NiFe layer of the NiFe/Cu/(S-MePEA)₂PbI₄ sample at zero fields (B = 0 mT). A clear long-lived oscillating Kerr signal is observed in the same gigahertz frequency (~2 GHz), consistent with that in **Figure 1c**. The phase of the oscillating Kerr signals inverts when the chirality flips.

[2] "Comprehensive demonstration of spin Hall Hanle effects in epitaxial Pt thin films" – *Probing spin physics in heavy metals without the need for adjacent magnetic materials.*

Spin Hall Effect (SHE) and inverse spin Hall effect (ISHE) are fundamental spintronic processes in strongly spin-orbit coupled materials, such as a heavy metal, Pt [6]. On the other hand, it is difficult to probe SHE and ISHE using a magnetic field, since its effect is limited by the short momentum relaxation time in heavy metal. In this work, we demonstrate that in heavy metal thin films, the magnetic field can effectively modulate spin diffusion due to the reflection of spin current (from SHE) by spin precession (see **Figure 2**). The effect manifests in the field-dependence of the longitudinal and transverse charge transport via ISHE, referred to spin-Hall Hanle effect (SHHE). We show that SHHE can be used to probe the spin-Hall angle as the key parameter for SHE and ISHE, as well as spin relaxation time and spin diffusion length, without the need for a magnetic interface. This can be particularly important for probing spin relaxation time in many other strongly spin-orbit coupled materials that have low spin relaxation time. In addition, the simplicity of SHHE suggests they are ubiquitous and paves the way for unraveling more complicated spin transport processes in heavy-metal thin film structures adjacent to complex magnetic systems, particularly for ferroelectric and multiferroic hybrid materials.

[3] "Observation of Spatially-Resolved Rashba States on the Surface of CH₃NH₃PbBr₃ Single Crystals" – Solving paradoxical diversity of the Rashba state in hybrid perovskites.



Figure 2. (a) Schematics of the spin-Hall Hanle effects at the film/substrate interface. Top: no spin precession in zero field. Bottom: spin precession when the field is perpendicular to the interface (z direction). \vec{J}_c and \vec{J}_s are the charge current and corresponding spin current generated via SHE respectively. $\vec{J}_{S,R}$ and $\vec{J}_{c,R}$ are the reflected spin current and the corresponding charge current generated via ISHE respectively. (b) Measured change of longitudinal resistivity normalized with the zero-field resistivity. B_x , B_y , and B_z are the magnetic field along the x, y, and z direction. (c) Transverse Hall resistivity normalized with the zero-field resistivity. Reproduced from *Phys. Rev. B*, 106, 184420 (2022). https://doi.org/10.1103/PhysRevB.106.184420

Solution-processed hybrid metal perovskites (HMHs) are prime candidates for exploring the potential Rashba effect given their large spin-orbit coupling induced by the heavy metal atoms in their hybrid organic-inorganic framework [7].



Figure 3 A suite of experimental work and theoretical calculations shows that specific terminations on the surface of a CH3NH3PbBr3 single crystal yield surface Rashba states at room temperature induced by local symmetry breaking. Reproduced from Appl. Phys. Rev. 8, 31408 (2021). https://doi.org/10.1063/5.00538 84

Unfortunately, the origin of the presumed Rashba effect in HMHs is still a puzzle in the community, causing extensive debates that remained unsettled. In the present work, we aim to solve this paradoxical diversity of the Rashba state in CH3NH3PbBr3 (MAPbBr3) by presenting the first experimental observation of Rashba state domains on the crystal surface. The unique spin-dependent features in the presence of the Rashba effect are demonstrated using novel spatially resolved 'photon-to-spin conversion' approaches, namely the circular photogalvanic (CPGE) effect and the photoinduced inverse spin Hall effect; which are further corroborated by multi-photon microscopy of the crystal surface (see **Figure 3**). We show the existence of domains on the MAPbBr3 crystal surface with various degrees of Rashba effect depending on the surface terminations, in agreement with DFT calculations. By reconstructing different surface terminations on the same MAPbBr3 crystal, we found that the computed Rashba parameter varies in the interval 0 to 2 eV·Å, which accounts for the observed inhomogeneity of Rashba states. Our results simultaneously offer a cautionary note in measuring and reporting this important phenomenon in HOIPs, as well as helping design semiconductor surfaces and interfaces that may maximize these effects even in materials that nominally do not fulfill conditions for bulk Rashba splitting.

Future Plans

The goal of future work is to perform temperature and field orientation-dependent magnetotransport and magneto-optical studies of the 2D chiral HMH films interfaced with ferromagnet and nonmagnetic materials. We will continue to elucidate the fundamental mechanism of chiralityinduced magnetism, chiral spin texture, and chiral-phonons activated spin Seebeck effect in the chiral-HMH materials. We will also continue studying the temperature-dependent magnetic hysteresis switching and interactions between chiral phonons and spin current generation across the heavy metal and 2D chiral hybrid perovskite interfaces. This will help to unravel rich synergistic effects from the junction of quantum chemistry, materials design, spintronics, and emergent chiral magnetism. We anticipate launching a promising testbed by employing the spin Hall Hanle effect to encompass a variety of chiral-HMHs for multiferroic spintronic studies.

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Spin Functionality at Interfaces through Complex Oxide Heteroepitaxy

PI: Yuri Suzuki Department of Applied Physics, Stanford University

Keywords: spin current, low magnetic loss, complex oxide thin films

Research Scope

The main research objective of the program is to develop low damping complex oxide thin films and heterostructures with perpendicular magnetic anisotropy (PMA) to realize isotropic spin wave excitation and propagation as well as efficient spin wave control. gWe have brought our expertise in atomic scale synthesis of complex oxide thin films and heterostructures together with our recent discovery of spinel ferrite thin films with low magnetic damping: (i) to develop an understanding of the key factors that govern charge-to-spin (and spin-to-charge) conversion and spin wave propagation and (ii) to demonstrate how PMA ferromagnetic insulators (FMI) can enable isotropic and efficient excitation of coherent spin waves and their propagation in extended spatial regions. We have applied specific design criteria to optimize for low magnetic damping and PMA via chemical doping and epitaxial strain in spinel ferrite thin films. More specifically, we have chosen to study low damping spinel ferrite thin films based on L=0 Fe³⁺ cations placed under tensile epitaxial strain to induce PMA in (Ni,Zn)(Al,Fe)₂O₄, and Li_{0.5}(Al,Fe)_{2.5}O₄. These epitaxial spinel ferrite films are then interfaced with strongly spin-orbit coupled layers in heterostructures for spin excitation, propagation and magnetization switching.

Recent Progress

Highlights of recent work include (i) the discovery and synthesis of lithium aluminum ferrite Li_{0.5}(Al,Fe)_{2.5}O₄ films with extremely low damping and perpendicular magnetic anisotropy and (ii) demonstration of energy efficient spin-orbit torque switching of these spinel ferrite films in heterostructures with a heavy metal. Additional highlights include demonstration of emergent long range magnetic order in ultra-thin LaNiO₃ films.

Ultra-Low-Loss Epitaxial Spinel Ferrite Films with Perpendicular Magnetic Anisotropy. Ultra-thin

FMIs with PMA are an important class of materials not only in studying exotic magnetic phenomena but also in realizing spin wave control, thereby enabling energy efficient spin-wave based electronics. They support the manipulation and isotropic propagation of spin waves in the absence of dissipative charge currents, providing a new paradigm for energy efficient spin-based computing and memory. Two critical characteristics of these PMA FMIs are that they exhibit extremely low magnetic damping and can form excellent interfaces with adjacent spin-to-charge conversion layers. Previous reports of FMI thin films with low damping and PMA are largely devoted to garnet structure ferrite films [1-3]. However they suffer from difficulty in integrating with materials other than garnet structure materials, high deposition temperatures and a magnetic dead layer at the film-substrate interface due to interdiffusion.



Figure 1. Cross sectional image of the interface between $Li_{0.5}AlFe_{1.5}O_4$ and the (001) MgGa₂O₄ substrate.

We have realized ultra-thin, low-loss $Li_{0.5}(AlFe)_{2.5}O_4$ (LAFO) films that exhibit bulk saturation magnetization values and PMA for film thicknesses as low as 4nm (or 5 unit cells). We attribute such bulk static magnetic properties to the high interfacial quality and crystallinity at the film/substrate interface. A



Figure 2. (a) Ferromagnetic resonance peak of a 15nm thick MAFO film on $MgGa_2O_4$ (001). (b) The slope of the frequency dependence of the linewidth.

cross sectional transmission electron microscope image of the interface between $Li_{0.5}AlFe_{1.5}O_4$ and the (001) MgGa₂O₄ substrate shows a sharp interface with minimal disorder (Figure 1).

This interface provides for not only bulk saturation magnetization of our ultra-thin LAFO films but also low damping as can be deduced from the frequency dependence of the ferromagnetic resonance (FMR) linewidth. Figure 2(a) shows a typical FMR peak for a single LAFO film with narrow linewidth. From the slope of the frequency dependence of the linewidth, we deduce the Gilbert damping parameter that characterizes the magnetic loss to be typically 6 x 10⁻⁴ (Fig.2(b)).

<u>Spin-Orbit Torque Switching of Lithium Aluminum Ferrite Thin Films</u>. One of the important features of a spin-wave based system is to efficiently switch the magnetic state of our spin wave material with an electrical current. To this end, spin-orbit torque switching of ferromagnets via an adjacent spin-to-charge conversion layer has been extensively studied. The analysis is complicated by current shunting through the ferromagnet if it is a metal. But in the case of FMI, the analysis is straightforward. We have studied spin-orbit torque switching in LAFO/Pt bilayers where Pt is the spin-to-charge conversion layer. In contrast to the garnet/Pt bilayers, our spinel/Pt bilayers can be grown epitaxially and therefore improve the interface quality. Figure 3 shows an in-plane f scan of the (111) Pt and LAFO peaks in x-ray diffraction where the 12 fold symmetry and 4 fold symmetry of the Pt and LAFO peaks respectively correspond to the four types of epitaxial relationships shown in Figure 3(b).



Figure3. (a) In-plane x-ray diffraction scan of a Pt/LAFO bilayer showing registry of the Pt(200) peaks with the (111) spinel peaks and (b) the epitaxial relationship between LAFO (001) and Pt (111) lattices.

We patterned the LAFO/Pt bilayers into Hall bars and performed spin-orbit torque switching experiments comprised of sending charge current through the Pt layer to magnetically switch the adjacent LAFO layer. Figure 4 shows how we can switch the LAFO magnetization with a critical current density in (b) in the same way that we can switch it with external applied field in (a). The significant accomplishments here are that the switching occurs at critical current densities more than an order of magnitude lower than previous work and that it is reversible and repeatable as observed in Figure 4(c).



Figure 4. Hall resistance measured as a function of magnetic field (a) and electrical current (b) through the Pt layer in a LAFO/Pt bilayer is indicative of the magnetic state of the LAFO layer. The electrical switching of the magnetic state of the LAFO is repeatable and reversible (c).

Long Range Magnetic Order in Ultra-Thin (111) LaNiO₃ Films. LaNiO₃ (LNO) is the only rare earth nickelate that does not exhibit a metal-insulator or magnetic transition in the bulk. When grown in thin film with an (111) orientation, LNO films exhibit signatures of long-range magnetic ordering (LRMO). Previous work identified the LRMO to be ferromagnetic but we have more recently acquired evidence that suggests antiferromagnetism. Transport and structural studies of (111) LNO films indicate that NiO₆ octahedral distortions stabilize a magnetic insulating phase at the film/substrate interface and result in a thickness-dependent metal-insulator transition at t = 8 unit cells. Away from this interface, distortions relax and bulk-like conduction is regained. Synchrotron x-ray diffraction and dynamical x-ray diffraction simulations confirm a corresponding out-of-plane unit-cell expansion at the interface of all films. X-ray absorption reveals that distortion stabilizes an increased concentration of Ni²⁺ ions. Evidence of long-range magnetic order is found in anomalous Hall effect and magnetoresistance measurements, likely due to magnetic superexchange interactions among Ni²⁺–Ni³⁺ ions. More recently we have found that low energy muon spin relaxation measurements reveal the entire film to be magnetically ordered below 50K. Given the fact that magnetic profiling by polarized neutron reflectivity does not indicate ferromagnetic ordering at these same conditions, we are led to conclude that (111) LNO films exhibit long range antiferromagnetic ordering. Together, these results indicate that long-range magnetic ordering and metallicity in (111) LNO films emerges from a balance among the spin, charge, lattice, and orbital degrees of freedom.

Future Plans

Our future plans include spin wave, or magnon, characterization in LAFO thin films via non-local transport measurements. We also plan to explore Al doping of the $Li_{0.5}Fe_{2.5}O_4$ films to improve lattice match of the film and substrate, minimize defects and hence reduce damping further. We will also incorporate an antiferromagnetic insulator between the FMI and spin-to-charge-conversion layer to improve spin wave transmission as well as suppress a magnetic proximity effect in the spin-to-charge conversion layer due to the ferromagnet.

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Coherent control of strongly interacting spins in the solid-state

PI: Jeff Thompson, Princeton University

Keywords: nanophotonics, rare earth ions, quantum optics, spin interactions

Research Scope

We are exploring single erbium (Er^{3+}) ions in solid-state crystals as a platform for quantum networks. In particular, we are interested in harnessing the interaction between electron spins, or between electron and nuclear spins, to generate and manipulate entanglement.

This is enabled by a novel experimental platform consisting of individually controlled Er^{3+} ions coupled to a silicon nanophotonic cavity (Fig. 1). The cavity provides an efficient optical interface to the spin despite the forbidden nature of the intra-4f optical transition in the Er^{3+} ions [1]. Moreover, slight inhomogeneous broadening in the crystal allows for individual addressing of single ions in the frequency domain, without regard for their spatial separation [2]. These features make Er^{3+} ions a unique platform for harnessing and studying spin-spin interactions in the solid state.

Recent Progress

We have made two major advances in the last year. The first is demonstrating coherent interactions between an electron spin and a nearby nuclear spin, and also between the nuclear spin and two other "dark" modes. The second is the development of a new host material for implanted Er³⁺ ions, CaWO₄, that offers significantly improved spin and optical coherence times compared to previously studied



Figure 1 (a) Our experimental platform consists of fiber-coupled silicon nanophotonic cavities stamped on top of single crystal substrates doped with extremely low concentrations of Er^{3+} ions. (b) Inhomogeneous broadening allows multiple ions to be resolved in a single, sub-micron device. (c) We demonstrate simultaneous initialization, manipulation and readout of four spins.

materials. This allowed us to demonstrate indistinguishable single photon emission for the first time, and is a promising starting point for studying electron-electron interactions.

In our first effort, we demonstrated coherent coupling between the electron spin of a single Er^{3+} ion in yttrium orthosilicate (Y₂SiO₅) to a single nearby nuclear spin [4]. This work was a collaborative project with Slava Dobrovistkii (TU Delft) and Chris van de Walle (UCSB). The nuclear spin is controlled via microwave-driven, dynamical decoupling sequences on the electronic spin, realizing one-qubit and two-qubit gate operations that let us probe the coupling strength and coherent dynamics of the nuclear spin (Fig. 2). We observe a nuclear spin T₂ time (with a Hahn echo) of 1.9 ms, about three orders of magnitude longer than the same quantity in the Er^{3+} electron spin alone. With a SWAP operation, we also demonstrate that the state of the nuclear spin in the computational basis survives electron spin readout and re-initialization. The properties of the nuclear spin suggest that it is a fortuitously located proton (¹H), whose location we determine by measuring the coupling strength for several magnetic field configurations. This work adds a key component to the toolkit of individually-addressed REIs, and also demonstrates a potentially powerful approach to engineering nuclear spin ancillae using non-native atomic species.



Figure 2 (left) Schematic of single electron spin interacting with nuclear spin and two dark spins. (a) Gate sequence used to couple electron and nuclear spin. (b) Ramsey precession of nuclear spin. Coherent evolution at short times gives way to noisy behavior at long time. (c) Fourier analysis reveals a discrete spectrum, which we believe originates from two spin-1/2 dark spins in the environment. Single-shot readout of the dark spins gives a lifetime of ~ minutes.

In our second effort, we demonstrated indistinguishable single photon emission from a single Er^{3+} ion coupled to a nanophotonic optical cavity, which is a major milestone towards the development of quantum networks based on this platform [5]. This is enabled by shallow ion implantation of Er³⁺ into calcium tungstate (CaWO₄), a host material satisfying the above criteria and for which long electron spin coherence has recently been demonstrated in Er³⁺ ensembles at millikelvin temperatures [3]. By coupling the ions to silicon nanophotonic circuits, we observe individual ions with single-scan optical linewidths of 150 kHz, and emission rate enhancement by a factor of P = 850 via the Purcell effect. Using a 36 km delay line, we observe Hong-Ou-Mandel (HOM) interference between successively emitted photons with a visibility of V = 80(4)% (Fig. 3). We also demonstrate spin initialization and single-shot readout with a fidelity F = 0.972, as well as the preservation of electron spin coherence for more than 200 µs, limited by paramagnetic impurities in the sample. This demonstration is a key step for the development of quantum repeaters based on single rare earth ions, and Er³⁺ in particular. The development of the materials, implantation and annealing techniques was done in close collaboration with Nathalie de Leon and Robert Cava (Princeton).



Figure 3 (a) Schematic of Hong-Ou-Mandel interferometer. (b) Indistinguishability between subsequent photons gives rise to suppressed two-photon coincidences at zero delay, which return when the indistinguishability is destroyed with a noise source in one arm [panel (c)].

Future Plans

We are currently investigating two avenues. The first is to study erbium-erbium interactions in CaWO₄. By using patterned ion implantation, we will create "puddles" of 10-20 Er ions within a 20 nm radius, which should have dipolar interactions in the range of 10-100 kHz, considerably longer than the Er spin coherence time. Using optical addressing techniques to individually manipulate the spins, we will study their interactions, and harness them for elementary entangling operations that will be useful in quantum networks.

The second avenue is to continue to improve the spin and optical coherence of Er:CaWO4. Our spectroscopy in Ref. [5] indicates that we are limited not by nuclear spins, but by paramagnetic impurities. We are currently setting up an experiment in a dilution refrigerator to freeze the impurities out, and in parallel working on materials analysis and improved growth with collaborators to remove the impurities. Ultimately, combining these techniques with isotopically enriched precursors to eliminate the ¹⁸³W nuclear spins may allow seconds-scale coherence.

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Excitons in Low-Dimensional Perovskites

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Program Scope

The goal of this research effort is to obtain a deeper understanding of strongly bound excitonic states in low-dimensional halide perovskites. Experiments will address how excitons in these quantumconfined materials move, how they interact with the polar lattice, and how their behavior can be manipulated through chemical or structural modification. Having established a strong understanding of intrinsic exciton physics in 2D and 0D perovskite nanomaterials during the first 3 years of this project, we shift our focus now to emergent excitonic phenomena in perovskite nanomaterial assemblies and mixed dimensional heterostructures. In particular, we focus our attention on excitations that extend across multiple low-dimensional building blocks and how the facile synthetic tunability of perovskite nanomaterials can be leveraged to direct excited state behavior.

Recent Progress

Quantification of exciton fine structure splitting in a two-dimensional perovskite compound. Applications of two-dimensional (2D) perovskites have significantly outpaced the understanding of many fundamental aspects of their photophysics. The optical response of 2D lead halide perovskites is dominated by strongly bound excitonic states. However, a comprehensive experimental verification of the exciton fine structure splitting and associated transition symmetries remains elusive. Here we employ low temperature magneto-optical spectroscopy to reveal the exciton fine structure of

(PEA)₂PbI₄ (here PEA is phenylethylammonium) single crystals. We observe two orthogonally polarized bright in-plane free exciton (FX) states, both accompanied by a manifold of phonon-dressed states that preserve the polarization of the corresponding FX state. Introducing a magnetic field perpendicular to the 2D plane, we resolve the lowest energy dark exciton state, which although theoretically predicted, has systematically escaped experimental observation (in Faraday configuration) until now. These results corroborate standard multiband, effective-mass theories for the exciton fine structure in 2D perovskites and provide valuable quantification of the fine structure splitting in (PEA)₂PbI₄.



Figure 1. Photoluminescence spectra of a 2D perovskite compound under no magnetic field and under high magnetic field, showing brightening of the dark exciton state. Inset = orthogonal polarization of the two in-plane bright exciton states. *Published work from this award* (Posmyk *et al., J. Phys. Chem. Lett.* (2022)).

Power-dependent photoluminescence efficiency in manganese-doped 2D hybrid perovskite nanoplatelets. Substitutional metal doping is a powerful strategy for manipulating the emission spectra and excited state dynamics of semiconductor nanomaterials. Here, we demonstrate the synthesis of colloidal manganese (Mn^{2+})-doped organic-inorganic hybrid perovskite nanoplatelets (chemical formula: L₂[APb_{1-x}Mn_xBr₃]_{n-1}Pb_{1-x}Mn_xBr₄, L: butylammonium, A: methylammonium or formamidinium, n(=1 or 2): number of Pb_{1-x}Mn_xBr₆⁴⁻ octahedral layers in thickness) via a ligand-assisted reprecipitation method. Substitutional doping of manganese for lead introduces bright (approaching 100% efficiency) and long-lived (>500 µs) mid-gap Mn²⁺ atomic states, and the doped nanoplatelets exhibit dual emission from both the band edge and the dopant state. Photoluminescence quantum yields and band-edge-to-Mn intensity ratios exhibit strong excitation power dependence, even at very low incident intensity (<100 µW/cm²). Surprisingly, we find that saturation of long-lived



Figure 2. Schematic illustration of nonradiative recombination processes in a (Mn^{2+}) -doped 2D perovskite nanoplatelet. *Published work from this award* (Ha *et al.*, *ACS Nano* (2021)).

 Mn^{2+} dopant sites cannot explain our observation. Instead, we propose an alternative mechanism involving the cross-relaxation of long-lived Mn-site excitations by freely diffusing band-edge excitons. We formulate a kinetic model based on this cross-relaxation mechanism that quantitatively reproduces all of the experimental observations, and validate the model using time-resolved absorption and emission spectroscopy. Finally, we extract a concentration-normalized microscopic rate constant for band edge-to-dopant excitation transfer that is ~10x faster in methylammoniumcontaining nanoplatelets than in formamidiniumcontaining nanoplatelets. This work provides

fundamental insight into the interaction of mobile band edge excitons with localized dopant sites in 2D semiconductors and expands the toolbox for manipulating light emission in perovskite nanomaterials.

Persistent enhancement of exciton diffusivity in CsPbBr₃ nanocrystal solids. In semiconductors, exciton or charge carrier diffusivity is typically described as an inherent material property. Here, we show that the transport of excitons (i.e., bound electron-hole pairs) in CsPbBr₃ perovskite nanocrystals (NCs) depends markedly on how recently those NCs were occupied by a previous exciton. Using fluence- and repetition-rate-dependent transport in CsPbBr₃ NC solids. Surprisingly, we observe a striking dependence of the apparent exciton diffusivity on excitation laser power that


Figure 3. *Persistent enhancement of exciton diffusivity*. (a) Experimentally measured diffusivity relaxation curve. Exciton diffusivity of CsPbBr₃ NCs with OLA/OA ligands as a function of time between NC excitation events. (b) Schematic illustration of the excitation memory effect leading to persistent enhancement of exciton diffusivity. (c) Potential energy surface description of the phenomenon illustrated in panel (b). Black curves indicate the electronic excited state and electronic ground state of the NCs. (d) Snapshot of a kinetic Monte Carlo (KMC) simulation of exciton transport in a 2D NC array, which includes excitation memory effects. (e) KMC simulation results plotted as a function of time between NC excitation events, showing consistency with the experimentally measured phenomenon. *Work from this award submitted for publication* (Shcherbakov-Wu *et al., arXiv* (2022)).

does not arise from nonlinear exciton-exciton interactions nor from thermal heating of the sample. We interpret our observations with a model in which excitons cause NCs to undergo a transition to a metastable configuration that admits faster exciton transport by roughly an order of magnitude. This metastable configuration persists for ~microseconds at room temperature, and does not depend on the identity of surface ligands or presence of an oxide shell, suggesting that it is an intrinsic response of the perovskite lattice to electronic excitation. The exciton diffusivity observed here (>0.15 cm²/s) is considerably higher than that observed in other NC systems on similar timescales, revealing unusually strong excitonic coupling in a NC material. The finding of a persistent enhancement in excitonic coupling between NCs may help explain other extraordinary photophysical behaviors observed in CsPbBr₃ NC arrays, such as superfluorescence. Additionally, faster exciton diffusivity under higher photoexcitation intensity is likely to provide practical insights for optoelectronic device engineering.

Future Plans

Future plans focus heavily on the investigation of exciton dynamics in nanocrystal superlattices, including multinary superlattice structures and superlattices containing anisotropic nanocrystals. A particular area of emphasis will be on low-temperature behavior and the emergence of partially-coherent exciton transport processes.

Publications

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1. "Power-Dependent Photoluminescence Efficiency in Manganese-Doped 2D Hybrid Perovskite Nanoplatelets"

S.K. Ha, W. Shcherbakov-Wu, E.R. Powers, W. Paritmongkol, <u>W.A. Tisdale</u> *ACS Nano* 15, 20527-20538 (2021).

 "Temperature-Independent Dielectric Constant in CsPbBr₃ Nanocrystals Revealed by Linear Absorption Spectroscopy"
W. Shcherbakov-Wu, P.C. Sercel*, F. Krieg, M.V. Kovalenko, W.A. Tisdale*

J. Phys. Chem. Lett. 12, 8088-8095 (2021).

- 3. the Halide Perovskite Nanocrystals" "State of Art and Prospects for A. Dev al. (multi-author review) et ACS Nano. 15, 10775-10981 (2021).
- 4. "Colloidal Nano-MOFs Nucleate and Stabilize Ultra-Small Quantum Dots of Lead Bromide Perovskites"

L. Protesescu, J. Calbo, K. Williams, <u>W.A. Tisdale</u>, A. Walsh, M. Dinca; *Chem. Sci.* 12, 6129-6135 (2021).

 "Tuning the Excitonic Properties of the 2D (PEA)₂(MA)_{n-1}Pb_nI_{3n+1} Perovskite Family *via* Quantum M. Dyksik, S. Wang, W. Paritmongkol, D.K. Maude, <u>W.A. Tisdale</u>, [†] M. Baranowski, [†] P.

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- 6. "Light Emission in 2D Silver Phenylchalcogenolates" W.S. Lee, Y. Cho, E.R. Powers, W. Paritmongkol, T. Sakurada, H.J. Kulik, <u>W.A. Tisdale</u> *ACS Nano* 16, 20318–20328 (2022).
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- "Quantification of exciton fine structure splitting in a two-dimensional perovskite compound" K. Posmyk, N. Zawadzka, Mateusz Dyksik, A. Surrente, D.K. Maude, T. Kazimierczuk, A. Babinski, M.R. Molas, W. Paritmongkol, M. Maczka, <u>W.A. Tisdale</u>, Paulina Plochocka, M. Baranowski

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Non-Equilibrium Quantum Dynamics of Multi-Qubit Superconducting Circuits

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Keywords: Non-equilibrium Quantum Dynamics, Superconducting Circuits, Electrodynamic Modeling, Cavity QED, Quantum Simulation

Research Scope

The overarching goal of this project is to develop computational techniques that are able to accurately capture the evolution of the quantum state of Josephson junction (JJ) artificial atoms embedded in large-scale complex planar circuitry or 3D cavities, and driven by microwave and RF signals. This effort will build on quantum electrodynamic modeling tools we developed for superconducting circuits in the previous performance period [1,2], and extend them further to address phenomena that are of current interest in the field of superconducting circuits. The major goals are:

- 1. **3D** Quantum Electrodynamic Modeling of Cavity QED systems: The Heisenberg-Langevin (HL) approach developed in the previous period for planar circuit electrodynamic systems will be extended to three-dimensional solid-state structures.
- 2. Radiative corrections in solid state Cavity QED systems: Based on the formulation developed in 1. we will look into the calculation of radiative corrections of atoms in open resonators.
- 3. **Non-equilibrium dynamics in multi-qubit quantum circuits**: A general method will be developed to derive and parametrize effective Quantum Master Equations for microwave-driven superconducting quantum circuits.
- 4. **Dynamics of qubits coupled to high-impedance resonators**: The phase-diagram of drivendissipative high-impedance resonators with embedded superconducting qubits will be studied.

Recent Progress

Accurate modeling of superconducting microwave circuits incorporating non-linear Josephson junction (JJ) based elements is essential for the design, control, and deployment of quantum information processing systems involving qubits and their readout systems. With an increasing number of qubits and complex electromagnetic environments, there is a pressing need for efficient computational approaches that can produce reduced quantum models capable of capturing the relevant degrees of freedom. In pursuit of this goal (major goal 1), we have achieved a significant milestone. In our recent paper [3], we introduce DEC-QED, a computational approach for modeling superconducting non-linear elements in complex three-dimensional electromagnetic environments. The accurate 3D modeling of large superconducting devices that incorporate Josephson junctions poses a significant challenge. A major issue is the large discrepancy between the relevant length scales. The important charge degrees of freedom, such as those involved in the Josephson plasma oscillations near the junctions, vary at the nanometer scale, while the electromagnetic modes vary over millimeters. In typical superconducting processors, which include protecting 3D cavities, the full scale to be modeled can be of the order of many centimeters. Furthermore, the boundary and coupling between the relevant electromagnetic structure and its environment leads to finite dissipation rates for all relevant degrees of freedom (such as the important radiative contribution to the T₁ and T₂ times of the qubits embedded in the 3D structure). These challenges become even more critical for the quantum dynamics of excitations in the processor since each degree of freedom is associated with an entire Hilbert space. To address this profound multi-scale problem, our team has developed two technical tools: spatial coarse-graining and open boundary conditions that are compatible with field quantization. In our recent work, which is published in Ref. [3], we have completed the development of the coarse-graining methodology.

DEC-QED [3] captures the non-linear response and induced currents in BCS superconductors and accurately captures phenomena such as the Meissner effect, flux quantization and Josephson effects. Using a finite-element construction based on Discrete Exterior Calculus (DEC), *DEC-QED* can accurately simulate transient and long-time dynamics in superconductors. The expression of the entire electrodynamic problem in terms of the gauge-invariant flux field and charges makes the resulting classical field theory suitable for second quantization. This computational suite in the form of a Julia package is currently being tested through a collaboration with IBM Quantum. Work on 3D implementation of open boundary conditions is ongoing and builds on the fundamental approach developed in Ref. [4], described below, that provides a methodology for quantum electrodynamics of 1D (transmission-line based) systems in an open finite volume.

In ongoing work towards major goal 3, we developed a systematic perturbation theory for timecoarse-grained quantum dynamics of Josephson-junction-based non-linear elements embedded in electromagnetic resonators. This work, when completed, will complement DEC-OED in that it provides a systematic methodology for the derivation of an *effective* reduced quantum model, starting with an ab-initio quantum model potentially provided by DEC-QED. This numerical methodology is a response to the challenge of modeling strongly driven Josephson-junction based circuits, where strong renormalization effects are observed. One such problem is the dynamics of a qubit that is read out with a high-power pulse. It is found that the effective qubit decay time is strongly renormalized in a way that is dependent on the power delivered by the pulse. In addition, such pulses are known to lead to transitions out of the computational subspace of the qubit in a strongly power-dependent way, limiting read-out to a lower SNR in practice than desired. To tackle this and similar problems encountered for strong driving, we developed a systematic perturbation theory for obtaining the timecoarse-grained (TCG) dynamics of quantum systems where the resulting effective model is informed by the measurement channel and time resolution with which the system is initialized and observed. We derive a closed-form formula for the Effective Master Equation (EME) at arbitrary order in the perturbation theory, and provide a diagrammatic representation of each superoperator in the EME. As a demonstration of the method, we derive the fourth-order EME for an experimentally relevant model of the transmon readout problem, where the readout drive is found to significantly decrease the T₁ time of the first excited state of the transmon, as is suggested by recent experimental work analyzing limitations to fast and high-fidelity qubit readout. This approach reveals the emergent drive-induced incoherent transitions between the transmon energy levels when the system is prepared and observed with sub-GHz time resolution. In particular, we derive simple analytical expressions for the drive-induced relaxation and excitation rates of the transmon, and obtain effective equations of motion that allows efficient numerical solution.

Towards the major goals 2 and 4, we have completed an in-depth study of the non-equilibrium quantum dynamics of an artificial atom embedded in a superconducting *high-impedance* transmission line resonator. Recent experiments show that the system of a Josephson atom coupled to a high-impedance transmission line provides a tunable platform for realizing light-matter interactions across a wide range of coupling strength regimes [5,6]. These systems have also been considered as effective experimental platforms for quantum simulation of quantum impurity systems in novel regimes [7]. In our recent paper [4] we show that there are coupling regimes (reached in current experiments) where the radiative corrections to the properties of a Josephson-junction based atoms is ill-defined in perturbation theory. In [4], we study the radiative properties---the Lamb shift, Purcell decay rate and the spontaneous emission dynamics---of an artificial atom coupled to a long, multimode cavity formed by an array of Josephson junctions. Introducing a tunable coupling element between the atom and the array, we demonstrate that such a system can exhibit a crossover from a perturbative to non-perturbative regime of light-matter interaction as one strengthens the coupling between the atom and the Josephson junction array (JJA) providing a high-impedance resonator. Consequently, the concept

of spontaneous emission as the occupation of the local atomic site being governed by a single complex-valued exponent breaks down. This breakdown, we show, can be interpreted in terms of formation of hybrid atom-resonator modes with radiative losses that are non-trivially related to the effective coupling between individual modes. We develop a singular function expansion approach for the description of the open quantum system dynamics in such a multimode non-perturbative regime. This modal framework generalizes the normal mode description of quantum fields in a finite volume, incorporating exact radiative losses and incident quantum noise at the delimiting surface.

Future Plans

Our work in the remainder of the funding period will focus on the benchmarking and validation studies of *DEC-QED*, and the completion of our work on the time-coarse-graining approach.

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Uncovering and surmounting loss mechanisms in light emitters

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Keywords: first-principles calculations, recombination mechanisms, nonradiative recombination, nitride semiconductors, halide perovskites

Research Scope

The aim of this project is twofold: to develop reliable first-principles methodologies for calculating loss mechanisms in optoelectronic devices, and to apply them to technologically important materials. A main focus over the past few years has been on halide perovskites, materials that excel in photovoltaics and are being considered for light emitting diodes (LEDs), but for which a fundamental understanding of defect physics has been lacking. In addition, we have continued our investigations of nitride semiconductors, the key materials for solid-state lighting.

The evaluation of loss mechanisms requires accurate calculations of radiative and nonradiative recombination. A major effort within the project has been to develop and implement first-principles techniques that take full account of accurate electronic structure and electron-phonon interactions without any fitting to experiment.

Our overall goal is to generate the fundamental knowledge that is essential for improving efficiencies, and to provide guidelines for overcoming the limitations.

Recent Progress

Loss mechanisms in halide perovskites

A major part of our effort over the past two years has been devoted to the halide perovskites. Hybrid perovskites, such as methylammonium lead iodide (MAPbI₃), have emerged as promising materials for highly efficient solar cells and light emitters. Despite the remarkable success, the fundamental mechanisms that are responsible for the high efficiency are still vigorously debated.

The halide perovskites are frequently cited as being "defect tolerant". Our work firmly established that these materials are equally prone to defect-assisted nonradiative recombination as conventional semiconductors [R1, R2]. Point defects with levels deep in the bandgap can definitely form, but they do not cause detrimental nonradiative recombination because strong anharmonicity causes their capture rate to be low. Conversely, point defects that have states closer to the band edges and that traditionally would have been regarded harmless can actually act as strong recombination centers. In all cases, rigorous evaluation of capture coefficients based on configuration coordinate diagrams calculated with a hybrid functional and including spin-orbit coupling is essential [P9].

Our recent work addressed a hitherto overlooked type of defects, namely hydrogen vacancies (**Figure** 1), finding that they can be detrimental to device efficiency. They have relatively low formation energies, and also an extremely high carrier capture coefficient (**Figure 2**). A comparative study of hydrogen vacancies in MAPbI₃ and FAPbI₃ (FA: formamidinium) also reveals a fundamental difference: the hydrogen vacancies are much more difficult to form in FAPbI₃, and they have

substantially lower capture coefficients [P3]. To the best of our knowledge, this is the first time a rationale has been proposed as to why adding FA is essential for achieving high efficiency (as is empirically well established).

Our work clearly shows that the presence of the organic cation could potentially be detrimental to efficiency. This suggests that all-inorganic halide perovskites might actually have better performance. However, there is a common belief that the organic cation somehow suppresses defect-assisted nonradiative recombination. Using rigorous first-principles calculations we have shown that the dominant nonradiative recombination centers in inorganic perovskites such as CsPbI₃ cause similar nonradiative capture as in their hybrid perovskite counterparts. Indeed, we found that, similar to MAPbI₃, the iodine interstitial acts as a dominant nonradiative recombination center in CsPbI₃; it can be choosing suppressed by iodine-poor synthesis conditions. However, the MA cation can give rise to additional strong nonradiative recombination centers



Figure 1. The hydrogen vacancy (a missing hydrogen atom on the methylammonium molecule), a likely microscopic origin of efficiency losses in methylammonium-lead iodide solar cells.

such as hydrogen vacancies, which are absent from CsPbI₃. The inorganic perovskites are therefore potentially superior [P8]. One outstanding problem is inadequate stability of the perovskite phase of the all-inorganic halides, which is a topic we are currently working on.

The bottom line is that point defects are an equally big concern for halide perovskites as they are for conventional semiconductors, and controlling them is essential for obtaining high efficiencies. The halide perovskites are therefore not really "defect tolerant"; a more accurate statement is that they can be grown with surprisingly high quality using low-cost deposition techniques. The insights obtained in our studies will not only help to establish a correct understanding of the defect physics in halide perovskites, but will also serve as a guide for experimentalists to further suppress the formation of strong recombination centers during synthesis, thus enabling optimal performance in both photovoltaic and light-emitting applications.



We have also continued our investigations of point defects and impurities that can impact the efficiency of nitride-based light emitters. We published a review paper [P2] that presents a comprehensive overview of which types of defects are most likely to impact efficiency, and how to characterize them





(**Figure 3**). We also investigated whether adding boron to GaN would result in stable alloys with desirable characteristics [P1].

In addition, we examined carrier transport processes, which are essential for overall device efficiency [P6, P10].

Methodology

We made our code for calculating nonradiative capture coefficients at defects or impurities publicly available on a <u>Github repository</u>, and published an accompanying paper [P5].



We also published our methodology for accurately studying polarization fields. Electric fields induced by spontaneous and piezoelectric polarization strongly impact device efficiencies, but are sometimes also employed for heterostructure engineering [P7]; they also complicate first-principles modeling of surfaces or nanostructures. Our novel approach enables accurately accounting for polarization effects in slab calculations [P4].

We advanced the evaluation of nonradiative recombination rates by going beyond the harmonic approximation for the potential energy surface. This assumption is valid for a wide variety of defects

and has enabled researchers to develop intuition and guiding principles for understanding nonradiative capture. However, important defects that deviate from the harmonic approximation have been uncovered. Figure 4 schematically illustrates how deviations from harmonicity can have a large effect on capture barriers and hence on rates; the coordinate Q is the configuration coordinate that represents the distortion of the atomic structure during the transition. We developed a methodology to explicitly treat the anharmonicity.

As seen in **Fig. 4**, anharmonicity has a particularly large impact if ΔQ , the difference in configuration coordinate between the minimum-energy defect structures in the two different charge states, is large. In **Fig. 4** ΔQ is so large that the intersection of the potential energy surfaces occurs *in between* their minima [unlike the more common case, where the intersection occurs either at Q



< 0 or $Q > \Delta Q$]. It turns out that in this regime, the simple rule of thumb relating capture barrier (or rate) to energy difference between the defect level and the band edge no longer holds. This makes it essential to perform explicit first-principles calculations, rather than rely on simple rules. A treatment of these issues has been published in Ref. [P9].

Future Plans

In terms of methodology, we have almost completed our development of a first-principles treatment of trap-assisted Auger-Meitner recombination, and we are in the process of applying the formalism to relevant defects and impurities in nitride semiconductors. We are also assessing the impact of going beyond the one-dimensional approximation in the treatment of nonradiative recombination. For halide perovskites, we are examining the impact of strain on the band structure, aiding in the interpretation of experimental measurements based on one- and two-photon transient absorption spectroscopy. We are also assessing the role of hydrogen vacancy formation in material degradation, and finalizing a study on iodine vacancies in a range of hybrid and inorganic halide perovskites. We are also pursuing the causes of unexpectedly high efficiency in a different materials system, namely lonsdaleite SiGe alloys [R3].

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Two-year Publication List

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- P2. J. L. Lyons, D. Wickramaratne, and C. G. Van de Walle, *A first-principles understanding of point defects and impurities in GaN*, J. Appl. Phys. **129**, 111101 (2021). [doi: <u>10.1063/5.0041506</u>]
- P3. X. Zhang, J.-X. Shen, M. E. Turiansky and C. G. Van de Walle, *Minimizing hydrogen vacancies to enable highly efficient hybrid perovskites*, Nat. Mater. 20, 971 (2021). [doi: <u>10.1038/s41563-021-00986-5</u>]
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Light-Matter Quantum Control: Coherence and Dynamics

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Self-identify keywords to describe your project: ultrafast dynamics, coherent control, terahertz optics, nano-optics, topological and quantum materials

Research Scope The proposed research will advance our understanding and enable manipulation of photoenergy conversion and photocurrent generation through the study of coherence-mediated and/or topology-protected transport against impurities, across grain boundaries and/or microstructures. There is growing evidence that harnessing coherence and non-equilibrium dynamics may push highly efficient initial charge transfer into simultaneously the multi-terahertz and multi-nanometer regime and enable exceptionally robust quantum transport. Harnessing nearly dissipationless current underlines entire fields of microelectronics and quantum information systems. We will reveal how exceptional photocurrent generation and nearly dissipationless transport against impurity scattering can be realized by coherence, symmetry and topological protection. Such cross-cutting principles will provide the foundational knowledge for spin and topological electronics, photovoltaics and quantum computing applications. The work will characterize time, space, and energy evolution of electronic, vibrational, and quantum geometric properties of matter, such as Berry curvature. This work will engage important scales of nanometer, terahertz and femtosecond, in a variety of model systems with strong quantum coherent, geometric and photovoltaic properties. Special emphases for the current grant period are on dynamic topological stability, quantum phase switching, nano-imaging of quantum and photovoltaic materials. The work brings together a team of experimentalists, including experts in ultrafast, terahertz and nano optics, with theorists skilled in out-of-equilibrium simulations. This research directly addresses DOE Transformative Opportunities: Harnessing Coherence in Light and Matter and Exploiting Transformative Advances in Imaging Capabilities across Multiple Scales. **Recent Progress**

1. Spontaneous Symmetry Breaking by Twisting Weyl Nodes

Topology-symmetry interplay has been mostly studied "one-way", i.e., topological states are examined subject to a specific fixed symmetry. Recently, a light-induced *phononic* symmetry switch, that works by twisting the crystal lattice with selective mode symmetry [1, 2], coherently induces Dirac or Weyl semimetals in ZrTe₅. Here we demonstrate that the topology-symmetry interplay can be mutual in ZrTe₅. On the one hand, we show that crystalline symmetries (e.g., inversion symmetry) and time-reversal symmetry may turn fragile when topological phase transitions are triggered, which are manifested by the off-resonant excitation of infrared (IR) phonon mode and the generation of strong non-field-driven photocurrents. On the other hand, we formulate a theory of geometric pumping and dephasing at topological phase transition. The theory helps understand the mysterious charge pumping experiments observed in ZrTe₅ reported in the last grant period, wherein the band gap is apparently higher than the energy quanta, but electronic hopping still happens. Such observations establish a generic framework to link between light-induced symmetry and topological transitions.

2. Ultrafast Martensitic Phase Transition by Terahertz Driven Phonons

We report on an ultrafast nonequilibrium phase transition with a strikingly long-lived martensitic anomaly driven by above-threshold single-cycle terahertz pulses with a peak field of more than 1 MV/cm [3]. A nonthermal, terahertz-induced depletion of low-frequency conductivity in Nb₃Sn indicates increased gap splitting of high-energy Γ_{12} bands by removal of their degeneracies, which induces the martensitic phase above their equilibrium transition temperature. In contrast, optical pumping leads to a Γ_{12} gap thermal melting. Such light-induced nonequilibrium martensitic phase exhibits a substantially enhanced critical temperature up to ~100 K, i.e., more than twice the equilibrium temperature, and can be stabilized beyond technologically relevant, nanosecond time scales. Together with first-principle simulations, we identify a compelling terahertz tuning mechanism of structural order via Γ_{12} phonons to achieve the ultrafast phase transition to a metastable electronic state out of equilibrium at high temperatures far exceeding those for equilibrium states.

3. A sub-2 Kelvin Cryogenic Magneto-Terahertz Scattering-type Scanning Near-Field Optical Microscope (cm-THz-sSNOM)

We have developed a versatile near-field microscopy platform that can operate at high magnetic fields and below liquid-helium temperatures. We use this platform to demonstrate an extreme terahertz (THz) nanoscope operation and to obtain the first cryogenic magneto-THz time-domain nano-spectroscopy/imaging at temperatures as low as 1.8 K, magnetic fields of up to 5 T, and with operation of 0_2 THz. Our Cryogenic Magneto-Terahertz Scattering-type Scanning Near-field Optical Microscope, or cm-THz-sSNOM, instrument is comprised of three main equipment: i) a 5 T split pair magnetic cryostat with a custom made insert; ii) a custom sSNOM instrument capable of accepting ultrafast THz excitation; and iii) a MHz repetition rate, femtosecond laser amplifier for broadband THz pulse generation and sensitive detection. We apply the cm-THz-sSNOM to obtain proof of principle measurements of superconductors and topological semimetals. The new capabilities demonstrated break grounds for studying quantum materials that requires extreme environment of cryogenic operation and/or applied magnetic fields in nanometer space, femtosecond time, and THz energy scales.

4. Terahertz Nanoimaging of Perovskite Solar Cell Materials

Direct visualization and quantitative evaluation of charge filling in grain boundary traps require dynamic conductivity imaging simultaneously at the terahertz frequency and nanometer spatial scales, not accessible by conventional transport and imaging methods used thus far. A major limiting factor is our inability to "see" local conductivity across grain boundaries at terahertz-nanometer (THz-nm) limit and our understanding of device physics to efficiently engineering photo-conversion efficiency. Here we apply a THz near-field nano-conductivity mapping to the archetypal hybrid metal halide perovskite film and demonstrate it as a powerful tool to reveal distinct dielectric heterogeneity due to charge trapping and degradation at the granular level [4]. Our approach visualizes the filled defect ion traps by local terahertz charge conductivity and allows extracting a quantitative profile of trapping density in the vicinity of grain boundaries with sub-20nm resolution. Furthermore, imaging the material degradation by tracking local nano-defect distributions over time identifies a distinct degradation pathway that starts from the grain boundaries and propagates inside the grains. The nano-terahertz conductivity mapping demonstrated here can be extended to benchmark various perovskite materials and devices for their global photoenergy conversion performance and local charge transfer proprieties of absorbers and interfaces.

5. Nano-optical imaging of exciton-plasmon polaritons in WSe2/Au heterostructures

We report a nano-optical imaging study of exciton-plasmon polaritons (EPPs) in WSe2/Au heterostructures with scattering-type scanning near-field optical microscopy (s-SNOM) [5]. By mapping the interference fringes of EPPs at various excitation energies, we constructed the dispersion

diagram of the EPPs, which shows a strong exciton-plasmon coupling with a sizable Rabi splitting energy (~0.19 eV). Furthermore, we found a sensitive dependence of the polariton wavelength on WSe2 thickness (d). When d is below 40 nm, polariton wavelength decreases rapidly with increasing d. As d reaches 50 nm and above, the wavelength drops to 210 nm, which is over 4 times smaller than that of the free-space photons. Our simulations indicate that the high spatial confinement of EPPs is due to the strong localization of the polariton field inside WSe2. Our work uncovers the transport properties of EPPs and paves the way for future applications of these highly confined polaritons in nanophotonics and optoelectronics.

Future Plans

Quantum coherence tomography of light-induced quantum geometric properties such as Weyl/Dirac points and surface Fermi arcs. We will address several key questions/hypotheses: *How to coherently generate quantum geometry and topology by light, such as Weyl and Dirac points, and control their properties, such as Weyl point separation and surface Fermi arcs? Can we image topological plasmons as an unambiguous evidence for light-induced Weyl points and surface Fermi arcs?* We will measure the coherent dynamics and quantum geometry, controlled by vibrational and electronic excitations.

Advance Theory and Experiment of Coherent Light-Matter Interactions in Topological Electrons and Correlated Magnons. First, we plan to improve a real-time time-dependent density functional theory code, which allows us to carry out quantum dynamics simulations of materials in the presence of spin-orbit interaction. The goal is to show that accompanying the periodic topological switching by coherent phonon in some topological materials, carriers can be gradually pumped from valence band to conduction band despite the orders of magnitude smaller of the phonon energy relative to the insulating gap. Second, we will perform high-order nonlinear response function calculations. As a further step beyond the coherent phonon induced quantum dynamics simulations in the last period, we will focus on quantum dynamics simulations of quantum lattice models with light-matter interactions explicitly included, which allows direct investigation of nonlinear effects of correlated magnons. The quantum dynamics simulations will also be compared with semi-classical approach.

Investigate how correlation effects affect spin, charge and magneto-gyrotropic photocurrents: We will extend our polarization-dependent ultrafast THz photocurrent emission and nano-imaging measurements to compare bulk vs 2D perovskite. We will use physical models with parameters obtained from these experiments and first principles calculations to calculate the charge transfer distance and charge separation rate.

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Weyl Semimetals for High-Thermopower Transverse Thermoelectric Transport

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Topological materials, thermoelectric transport, thermo-magnetic transport, Nernst effect

Research Scope

Topological materials have gained much interest in solid-state physics fields since their discovery, with recent work showing that Dirac semimetals and Weyl semimetals (WSMs) are excellent candidates for both longitudinal and transverse magneto-thermoelectric transport applications, including the conversion of waste heat to useful electric power. Because WSMs are two-carrier systems, it was predicted that these materials would possess a very large Nernst effect and a minimal Seebeck effect. However, WSMs were theoretically expected to simultaneously exhibit a large magneto-Seebeck effect and Nernst effect due to their gapless band structure not seen in traditional semimetals [1]. Because both a longitudinal and transverse TE voltage can be produced in the presence of a magnetic field, this class of materials presents a unique opportunity to utilize magneto-thermoelectric effects.

The long-term goal of this project is to determine, and be able to manipulate and enhance, the transport mechanisms present in WSMs, making these materials viable as solid-state energy conversion materials. In doing so, transport in both polycrystalline and single-crystalline samples from candidate materials in all

Table 1: Candidate WSM materials used in this work.

	Type I (Symmetric Dirac Bands)	Type II (Tilted Dirac Bands)
Breaks Inversion Symmetry	NbP	WTe ₂
Breaks Time- Reversal Symmetry	HgCr ₂ Se ₄	YbMnBi ₂

four categories listed in Table 1 will be explored as polycrystalline samples are more practical for device applications. Recent work in polycrystalline NbP observes the simultaneous existence of both a large Nernst and magneto-Seebeck effect, while the magneto-Seebeck effect was explicitly not observed in single-crystalline NbP [2]. Since grain boundaries do not preferentially scatter holes or electrons, doping has been attributed as the cause for the existence of a reduced Nernst effect but majorly increased magneto-Seebeck effect in polycrystalline NbP in comparison to single-crystalline NbP. If both magneto-thermoelectric voltages could be harnessed simultaneously, the thermoelectric figure of merit, zT, could be significantly enhanced. While NbP hosts symmetric Dirac bands, WTe₂ hosts tilted Dirac bands - thermoelectric transport is compared between the two to determine the effects of Dirac band tilting. Recent progress in polycrystalline WTe₂ also demonstrates the simultaneous presence of both a magneto-Seebeck and Nernst effect, although only the magnitude of the Nernst effect is appreciably decreased from that observed in single-crystalline WTe₂ [3]. While both NbP and WTe₂ break inversion symmetry, the breaking of time-reversal symmetry is associated with the presence of a net Berry curvature, which could ultimately enhance magneto-thermoelectric effects. Ongoing work in polycrystalline YbMnBi2 seeks to determine if the giant anomalous Nernst conductivity observed in single-crystalline YbMnBi₂ [4] is maintained in polycrystalline YbMnBi₂ while concurrently minimizing both electrical resistivity and thermal conductivity to ultimately maximize the thermoelectric figure of merit. Future work in both single-crystalline and polycrystalline HgCr₂Se₄ will determine how band symmetry specifically affects magnetothermoelectric effects in the presence of a non-zero net Berry curvature.

Recent Progress

We have observed a simultaneously large magneto-Seebeck (S_{xxz}) and Nernst (S_{xyz}) effect in two polycrystalline samples of NbP, with a significantly reduced thermal conductivity (k_{xxz}) from that of single-crystalline values [2] and reasonably low electrical resistivity (r_{xxz}) . The simultaneous presence of both a large Nernst effect and a magneto-Seebeck effect, where the thermopowers from each effect are on the same order of magnitude, is not typically found in a single material. In a two-carrier system, the two signs of charge carrier typically counteract each other in a longitudinal geometry as both polarities of charge carriers condense on the cold side. However, the unique band structure of WSMs leads to a large longitudinal thermoelectric effect in the presence of a transverse magnetic field. This result implies that, in



Figure 1: Temperature dependence of the thermoelectric figure of merit, zT, in polycrystalline NbP. $zT_{effective}$ exhibits the largest value of 0.041 at 196 K, 9 T.

the presence of a magnetic field, the total effective thermopower of NbP can include contributions from both longitudinal and transverse thermoelectric effects, which effectively doubles the total thermopower if a thermoelectric device is setup appropriately. We have calculated the effective



Figure 2: Theoretical calculation of combined magnetic thermopowers $(|S_{xxz}| + |S_{xyz}|)$ as a function of T_F at two externally applied discrete fields: a) 2 T and b) 9 T.

compared to the highest figure of

merit for an independent thermoelectric effect. Both experimental and theoretical findings indicate that thermoelectric effects in NbP, and more broadly in Type I WSMs, are highly sensitive to doping, altering not only the maximum values of thermoelectric transport properties but the temperatures at which these maxima occur. We conclude that changes in the Fermi temperature, T_F , through doping can be used as a sensitive tuning mechanism for thermoelectric properties and the temperatures at which they are maximized, as shown in Figure 2.

Unlike single-crystalline results in NbP [2], previous work in single-crystalline WTe₂ observed a magneto-Seebeck effect in addition to an ultrahigh Nernst effect [3]. Our current results in polycrystalline WTe₂, shown in Figure 3, indicate a reduction in Nernst thermopower by approximately three orders of magnitude at low temperatures in comparison to single-crystalline WTe₂, but no anomalous Nernst effect is observed in either data set as it is in both single-crystalline and polycrystalline NbP. Furthermore, we only observe an appreciable magneto-Seebeck effect below 100 K in polycrystalline WTe₂, and the effect is of the same order of magnitude as that in single-crystalline WTe₂. Ongoing experiments in conjunction with theoretical results will determine the underlying mechanisms responsible for the differences observed in single-crystalline and polycrystalline WTe₂ along with the differences in these trends in comparison to those observed in NbP to ultimately determine the effects of Dirac band tilting on thermoelectric transport in WSMs that break inversion symmetry.

Future Plans

Because NbP possesses the unique simultaneous presence of both a large magneto-Seebeck and Nernst effect, we propose a device which utilizes both thermopowers produced in the presence of a magnetic field. The resulting

zT of such a device was found to be significantly higher than the zT observed by the individual thermoelectric effects (Figure 1) and is greater than zT found in other competitive WSMs. We plan to design a device that harnesses both longitudinal and transverse voltages with only one magnetic field direction being needed for the entire device. Figure 4 shows the concept of such a device, which would need further optimization to operate appropriately.

Previous work in YbMnBi₂ [4] and other WSMs that break time-reversal symmetry indicate anisotropy in transport properties dependent on crystallographic orientation. However, polycrystalline samples have multiple grains in multiple orientations, such that a degree of each crystallographic orientation can exist in each direction, which should allow thermoelectric transport dependent on a Berry curvature to be present in all physical directions, albeit reduced. In the coming year of this project, we will synthesize polycrystalline samples of YbMnBi₂ and characterize their

coupled thermal, electrical, and magnetic transport, with emphasis on the Nernst effect. From this, we will determine how magneto-thermoelectric transport in WSMs that break timereversal symmetry are altered by the introduction of grain boundaries.

Literature for theoretical results in $HgCr_2Se_4$ indicates that an anomalous Hall effect should exist in the absence of magnetic field due to an existent Berry curvature [5], although experimental





Figure 21: Schematic of a single thermoelectric leg for the proposed device utilizing contributions from both the Nernst and Seebeck effects.



results have not explored the Nernst effect. Published work in YbMnBi₂ indicates that Berry curvature can serve as a source of a skew force in transverse transport, including thermoelectric effects. In the coming year of this project, will we characterize coupled thermal, electrical, and magnetic transport in single-crystalline HgCr₂Se₄ to determine temperature-, magnetic field-, and angular-dependence of the Nernst effect, emphasizing comparison between results in the presence of and in the absence of magnetic field. Comparison of the temperature dependence of the Nernst thermopower in zero-field and the angular dependence of the Nernst thermopower with that of YbMnBi₂ will indicate the effects of anisotropy in Dirac bands on the Berry curvature-induced transport phenomena.

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Photoelectrochemistry of Halide Perovskites: from Stability to Chirality

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Keywords: halide perovskites; photoelectrochemistry; solar fuels; chirality; spin-polarized

photocurrent;

Research Scope

Organic-inorganic halide perovskites (OIHP) offer attractive opportunities for designing semiconductors with tailored properties, because they can combine useful attributes of both organic and inorganic materials at the molecular scale. Organic components provide great tunability in functional groups, electronic properties, chirality and processability, while inorganic components may offer high electronic mobility, bandgap tunability and mechanical stability. Therefore, OIHPs are promising semiconductors for photoelectrochemical solar fuels. However, previous studies of halide perovskite photoelectrochemistry (PEC) have been limited to few materials such as methylammonium lead(II) halides and cesium lead(II) halides, and their vulnerability to corrosion and photo-corrosion impedes their applications.

The renewal project will address the corrosion challenge of OIHPs in PEC through a holistic design of OIHPs, orthogonal electrolytes, and their interphases. OIHPs based on aromatic quaternary ammonium such as viologens will be explored due to their stability in liquid water, as well as their small and tunable bandgaps from the charge-transfer excitation. Highly fluorinated electrolytes will be used as the orthogonal electrolytes because they do not dissolve OIHPs but dissolve CO_2 well for CO_2 reduction. The water- and thermal-stability of the proposed OIHPs will also enable the passivation of OIHP surfaces, which will further stabilize OIHPs in PEC solar fuels.

In addition, this renewal project will investigate PEC properties of chiral OIHPs. Based on the previously observed chirality-induced spin selectivity, we hypothesize that photoexcitation of chiral OIHPs may induce spin-polarized photocurrent, which may be applied for enantioselective recognition and asymmetric organic synthesis. Furthermore, designing new chiral semiconductors will be interesting for other basic materials sciences such as spintronics.

This project will generate knowledge in understanding how the structures of OIHP constituents control the stability and performance in photoelectrochemical solar fuels. The results may enable predictive science for durability at the molecular, material, and component levels. In addition to the impact in basic energy science for durable solar fuels, the proposed studies on chiral OIHPs may generate a new direction in spin-polarized photoelectrochemistry.

Recent Progress

(1) Toward understanding the composition-structure relationship of halide perovskites: impact of secondary structures of organic cations

In the studies of organic-inorganic halide perovskites (OIHP), understanding the compositionstructure relationship is important for controlling their optical, optoelectronic, spintronic, and ferroelectric properties. Prior knowledge has only considered the primary structure of organic cations to predict the dimensionality of OIHPs. However, with the existence of noncovalent interactions (especially hydrogen bonding), the structure-directing organic cations may form secondary structures, which change their shape and steric hindrance when the cations are packed inside OIHPs. To our best knowledge, the role of secondary structures of organic cations has not been systematically investigated yet. In our recent progress, we report a systematic investigation of the influence from the secondary structure of ammonium ions induced by hydrogen bonding. We use a serious of alkoxy-ammoniums as the model system to investigate how the NH···O hydrogen bonding induces the folding of the organic cations into ring structures. The folding increases the steric hindrance around the NH3+ end and thus reduces the dimensionality of OIHPs. By systematically changing the linker length between alkoxy and ammonium, we have established the 7-member ring forms the strongest intramolecular

hydrogen bonding. More intriguingly, the folded secondary structures become chiral, which provides a new approach for creating symmetry-breaking chiral OIHPs.

We think this study will be interesting for a broad range of researchers working on organichalide perovskite inorganic materials and solid-state chemistry. It provides a systematic investigation on how secondary structures via hydrogen bonding impact the whole structure of perovskites. The obtained new insight will be helpful for



Figure 1: Crystal structures of OIHPs using a serious of methoxyammonium as the structure-directing cations, showing the NH…O hydrogen bonding induces the folding of the organic cations into ring structures.

understanding the composition-structure relationship in low-dimensional OIHPs and controlling the optical, optoelectronic, spintronic and ferroelectric properties. Embed figures in the text like this.

(2) Photoelectrochemistry of Methylviologen Lead Iodide: Achieving Stability inside

Polar Solvent

Semiconductor photoelectrochemistry (PEC) is а promising technology for solar fuels and photovoltaics. However, the application of organic-inorganic halide perovskites (OIHPs) for PEC has been limited by their instability in polar solvents. In our recent progress, we report the use of a 1D OHIP, methylviologen lead iodide (MVPb₂I₆) as an unprotected photoelectrode which is stable inside acetonitrile-based polar electrolyte. Moreover, the charge- transfer absorption inside MVPb₂I₆ reduces its band gap to 2.1 eV and thus, makes it a suitable solar absorber. MVPb₂I₆ photoelectrode was fabricated via a mild-temperature solution process and shows preferred photoanodic behavior. Stable anodic photocurrent was observed with only 24% decay after 10 hours operation under 1 sun illumination and 0.9 V (vs NHE) applied bias towards the oxidation of iodide, I⁻. Characterization of the photoelectrode after long-time PEC reveals the dissolution



of $MVPb_2I_6$ to be one important factor that influences the stability. The stability of $MVPb_2I_6$ also allows the use of cyclic voltammetry to determine its energetics. $MVPb_2I_6/TiO_2$ has also been demonstrated based on their energy alignment. This work demonstrates the potential of using smallband-gap 1D OIHPs to achieve stable PEC inside polar solvents without protection.

Future Plans

We will first explore the orthogonal electrolyte concept. Highly fluorinated electrolytes will be used as the orthogonal electrolytes because they do not dissolve OIHPs but dissolve CO_2 well for CO_2 reduction. Furthermore, we will complete the synthesis of our proposed model chiral OIHPs and investigate PEC properties of chiral OIHPs. Based on previously observed chirality-induced spin selectivity, we hypothesize that photoexcitation of chiral OIHPs may induce spin-polarized photocurrent, which may be applied for enantioselective recognition and asymmetric organic synthesis. Furthermore, designing new chiral semiconductors will be interesting for other basic materials sciences such as spintronics.

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Semiconductor nanoshell quantum dots for energy conversion applications.

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Research Scope

The project focuses on a novel class of colloidal inorganic nanocrystals, called quantum shells (QSs), which enable a stronger suppression of Auger recombination than any other type of colloidal quantum dots.

Auger recombination is a process in which excitation energy in colloidal nanocrystals is converted into excess heat, which can significantly reduce the efficiency and longevity of nanocrystal-based photodetectors/X-ray scintillators, solar cells, lasers, and high-brightness LEDs. The proposed 2D quantum shell system appears to be a promising candidate for addressing this issue, which can yield advances across different energy disciplines. The development of quantum shells using various semiconductor combinations can result in a novel class of colloidal nanomaterials that offers an even performance under intense optical or electrical excitation. In addition to highbrightness LEDs, photodetectors, and X-ray scintillators, the ability to harvest multiple excitons by quantum shells would be also useful for developing concentrator photovoltaics, where Auger processes cause sizable energy losses. Meanwhile, a large optical extinction of quantum shell nanoparticles could ultimately be of interest for developing photocatalytic systems.

Recent Progress

During the last two years (12/2021 - 12/2023), we have demonstrated high-quality quantum shells that show encouraging performance in several categories of optoelectronic processes: Auger suppression, optical gain, up-conversion, and radio-luminescence (x-ray scintillation). Below, we provide a brief summary of these measurements.

Suppression of Auger decay in nanocrystals. Following several years of research, we have managed to unlock the synthetic mystery of fabricating high quality quantum shells with CdS_{bulk}-CdSe-CdS (Figures 1c,1d,1f) and more recently CdS_{bulk}-CdSe-CdS-ZnS (Figure 1e) compositions. This achievement has enabled the demonstration of remarkable multi-exciton properties. Particularly intriguing was the observation of long biexciton lifetimes, $\tau_{XX} = 5 - 25$ ns, and a large biexciton quantum yield reaching an impressive 50% - 90% range (Figures 1b, 2a-c). These parameters indicate a strong suppression of Auger recombination in quantum shells, which is the main mechanism of multi-exciton energy losses in semiconductor nanoparticles. It was attributed to a large volume of the 2D quantum-confined "shell" layer, where direct Coulomb interaction between multiple charges are reduced. Our most recent work (submitted for publication), reports on the synthesis of CdS-CdSe-CdS-ZnS core-shell-shell-shell colloidal QSs with an emission quantum yield of 90% for singleexciton and 80% for bi-exciton populations. The design of these QSs was optimized to reduce both surface and Auger recombination processes, which are two of the most common causes of nonradiative losses in nanocrystals. The biexciton Auger lifetimes of these QSs ($\tau_{Auger} = 90 - 120$ ns) were found to be an order of magnitude longer than those reported for other types of colloidal nanocrystals. Furthermore, the rates of Auger decay in QSs were found to increase slower with the number of excitons per particle than in 0D quantum dots, making QSs particularly well suited for multi-carrier optoelectronic processes.

Figure 1. (a). Absorption/PL of 4.5-nm-core CdS_{bulk} -CdSe-CdS quantum shells (b). Lagtime-dependence of the crosscorrelation function, $g^{(2)}$, showing the ratio of biexciton to exciton QY for 4.5-nm core (orange curve) and 6.0-nm core (blue curve) quantum shells. (c). High angle annular dark field (HAADF)-STEM images of 8.2-nm-core CdS_{bulk}-CdSe-CdS quantum shells, highlighting the location of the CdSe shell layer (lighter shade) (d). TEM image of 4.5-nm-core quantum shells. (e,f). High-resolution TEM images of 6.0-nm-core CdS-CdSe-CdS-ZnS (e) and 8.2-nm-core CdS-CdSe-CdS (f) quantum shells.



Our early experimental data on quantum shell scintillators demonstrates encouraging performance (Figure 2h). The radioluminescence lifetime of quantum shells measured using a pulsed X-ray source (collaborative project with Ben Diroll and Burak Guzelturk, Agronne) shows a decay constant (~ 4 ns) is one of the longest among colloidal semiconductors, exceeding those of CdS/CdSe/CdS nanoplatelets by a factor of 8. It was most surprising to see yet another characteristic of quantum shell scintillators reaching unprecedented performance levels. According to Figure 2h, the radioluminescence stability of spincoated CdS_{bulk}-CdSe-CdS QS solids exceeded that of similar-extinction CdSe/CdS giant core-shell NCs by a factor of >100 under X-ray beam synchrotron radiation. We attribute this phenomenon to a relatively low rate of Auger heating in QS solids. It appears that a greater biexciton Auger lifetime of quantum shells propagates into a much-improved efficiency of multi-exciton down conversion processes.

Our recent research has shown that quantum shells nanoparticles have a large two-photon absorption cross section. This means that two-photon pumping can induce similar optical properties as one-photon pumping, such as high-energy excitons, repulsive biexcitons, and biexcitons with long lifetimes. Figure 2g demonstrates amplified stimulated emission from QS solids through the process of upconversion, where a two 1.55-eV photons produce ASE at 2.0 eV. Such a process could potentially extend the absorption spectrum of solar cells, allowing them to absorb more sub-band-gap light and thus increase their efficiency.



Figure 2. (a,b). Examples of $g^2(\tau)$ functions for 8.2-nm-core CdS_{bulk}-CdSe-CdS quantum shells, showing BX QY of 80% and 97%. (c). Statistics of $g^2(\tau)$ values for the three quantum shell types. (d). A representative PL intensity trajectory of a single quantum shell along with (e) – a PL decay curve corresponding to the biexciton single-particle intensity level. The dependence of biexciton Auger lifetimes, τ_{Auger} , on particle volume for different types of colloidal nanocrystals (Adapted from *Nat. Rev. Mater.* **2021**, *6*, 382–401 2021. (g). Two-photon amplified spontaneous emission (ASE) spectra as a function of fluence for CdS/CdSe/CdS QS thin film samples. Pump photon energy is 1.55 eV. (g). Stability of the hard X-ray scintillation by quantum shell sample in constrast to a CdSe/CdS giant core/shell quantum dots. The radioluminescence signal is normalized to 1 for the maximum emission signal. (j,i). (HAADF)-STEM images of 8.2-nm-core CdS_{bulk}-CdSe-CdS quantum shells.

Single-exciton optical gain. In addition to long-lived multi-exciton populations, QSs exhibit a rare, single-exciton optical gain, for which Auger decay is inactive. The single-exciton gain results from splitting of exciton (X) and biexciton (XX) energy levels (Figure 3a), caused by the photoinduced electric field of a spatially-separated electron-hole pair. Previously, such exciton-biexciton energy splitting has been achieved only in composite nanocrystals with a substantial charge delocalization. In case of QSs, the splitting energy, $\Delta_{XX} \approx 60$ meV, is particularly large, resulting in the longest optical gain lifetime reported colloidal nanocrystals, to date ($\tau_{gain} > 6$ ns).

The presence of single-exciton and biexciton optical gain regimes is evident in amplified spontaneous emission (ASE) spectra of quantum shells in Figure 3b. The spectral position of the X ASE peak (E = 1.96 eV) matches the steady state PL (blue curve), indicating a single-exciton origin of this emission. The XX ASE evolves at higher photon energy indicating an X-X repulsion phenomenon ($\Delta_{XX} > 0$). Evidence of the single-exciton gain mechanism was corroborated by transient absorption (TA) gain spectra in Figure 3c, showing the optical gain at the PL photon energy. The TA spectrum was recorded at a relatively high excitation fluence (36 µJ/cm²) causing the saturation of X

and XX 1S transitions. As a result, optical gain ($\alpha + \Delta \alpha < 0$, where α is the sample absorbance) from higher-energy excitons develops, including 1S(e)-2S_{3/2}(h) and 1P(e)-1P_{3/2}(h) interband transitions. We note that optical gain due to 1P excitons is rarely observed in conventional, core-shell QDs because of relatively short multi-exciton lifetimes.^{Error! Bookmark not defined.} Such high-energy exciton gain allows demonstration of optical amplifications with a large spectral bandwidth (Figure 3c) and low excitation thresholds.



Figure 3. (a). The X-X repulsion in quantum shells produces an energy offset for an absorbing transition of the second incoming photon, allowing for a single-exciton optical gain. (b). The spectrum shows a dual-mode amplified spontaneous emission (ASE) involving both the single-exciton (X) and the biexciton (XX) gain mechanisms. (b). A 3D lifetime/bandwidth contour plot of the transient absorption optical gain in 4.5-nm-core CdS_{bulk}-CdSe-CdS quantum shells. The positive gain is achieved when $\alpha + \Delta \alpha < 0$, where α is the sample absorbance and $\Delta \alpha$ is the pump-induced absorbance change. The pump fluence is 36 µJ/cm².

Future Plans

Looking into future development of the quantum shell systems, we expect this nanoscale geometry to potentially evolve as an alternative to traditional 0D core-shell QDs. In this regard, it is important to explore the concept of quantum shells using non-toxic and abundant semiconductors. Furthermore, the ability to achieve a near-unity biexciton quantum yield in such material systems will significantly broaden the range of potential applications of colloidal nanostructures. By developing quantum shells with a broadly tunable band gap and variety of semiconductor material choices, we expect to provide the scientific community with new-generation nanomaterials for the solution-phase processing of optoelectronic devices.

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Microscopic understanding of growth, substrate engineering, and proximity coupling in twodimensional organic/inorganic hybrid systems

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Self-identify keywords to describe your project: stanene, boron nitride monolayer, Moire patterns, interfacial coupling, molecular assemblies

Research Scope

The rapid advances in materials synthesis and processing have enabled the growth of twodimensional (2D) thin film materials of various crystalline symmetry and chemical composition. For these 2D materials, the substrate effects are essential. Interfacial charge transfer, electrostatic screening, orbital or electronic reconstruction could all impact the properties of 2D materials. Furthermore, for hybrid heterostructures composed of versatile molecular systems, rich physical and chemical behaviors may emerge owing to the interfacial processes and proximity coupling. The overarching goal of the program is to establish microscopic understanding of heterostructures and heterointerfaces in organic/inorganic hybrid systems. Specifically, we aim to: 1) Study the effects of strain and Moiré patterns on topological properties of 2D tin (Sn); 2) Achieve a comprehensive understanding of 2D metal organic framework (MOF) properties, especially those driven by the interfacial coupling with supporting substrate; 3) Investigate proximity effects between 2D Sn and 2D MOF to enrich the functionalities of the hybrid system. The synergistic efforts on hybrid heterostructure design, along with the heterointerface control, are anticipated to lead to unprecedented advances in the tunability of 2D quantum materials and deep understanding of interfacial physics.

Recent Progress

1) Remote epitaxy of 2D Sn on metal substrate through a h-BN decoupling layer

With the enhanced spin orbit coupling (SOC), stanene was predicted to be a room temperature 2D topological insulator (TI, also called quantum spin hall, QSH, insulator).¹ In contrast to graphene which can be mechanically exfoliated from graphite, the bulk counterpart of stanene, i.e., α –Sn (face-centered diamond cubic structure), is not a layered material. As the result, stanene has to be realized through growth on a supporting substrate. Experimentally, electronic structures of low-buckled honeycomb stanene have been found to display large variations on different substrates, with some showing metallic properties and others trivial insulators. The inverted band structure of monolayer stanene was evidenced for Sn grown on Cu(111).² Nonetheless, the QSH conducting channels, even if existing, may not be electronically isolated from metallic substrates or accessible if they reside far away from the Fermi level. Hybridization with the substrate that is either metallic or has metallic surface states could significantly alter the physical properties of Sn adlayers.

Inserting an insulating monolayer (h-BN, Fig. 1) between stanene and the metallic substrate could help suppress the substrate hybridization, mitigate the electronic disturbance, while at the same time retaining some substrate influence on structure stabilization. In our recent work, we have demonstrated, for the first time via combined experimental and theoretical approach, that *Moiré patterns* on h-BN/metal can facilitate the formation of new 2D Sn phases (Fig. 2a).³ The insertion of h-BN monolayer significantly weakens the interaction between Sn adlayer and metal substrate at the Moiré wire locations, whereas at the Moiré pore regions the local interfacial charge transfer interaction



Figure 1. (a) Large-scale and high-quality h-BN monolayer on Ir(111) grown by UHV-CVD. (b) Moiré patterns with pore and wire locations marked by the corresponding arrows. The apparent heights of pore and wire in the STM image are influenced by the density of states (DOS) contribution, with the pores appearing brighter at the positive sample bias (2V).

triggers the formation of a novel Sn structure that is registered to a superlattice of the underlying metal surface (Fig. 2b). *This "remote" epitaxy scheme allows the epitaxial registry of 2D Sn to the highly crystalline metal surface and stabilizes its structure. The scheme also suggests the possibility to remotely tune 2D Sn through the h-BN "decoupling" layer.* Although the compressive strain developed in this specific 2D Sn structure in the preliminary study leads to a metallic behavior (Fig. 2c), this new Sn phase still displays distinct electronic properties, i.e., the opening of the local gap upon the application of a slight tensile effective strain, much like the case of low-buckled honeycomb stanene.



Figure 2. (a) Empty-state and filled-state images of the new 2D Sn phase (unit cell in red Rhombic) and Moiré pattern of the underlying h-BN/Ir(111) substrate (green Rhombic). (b) Side views of the charge density differences for Sn adlayers on different substrates. Insertion of h-BN monolayer reduces charge redistribution between Sn and Ir(111), but pore and wire locations exhibit drastic differences. Light yellow and light blue correspond to positive and negative, respectively. (c) DFT calculated band structure revealing a metallic behavior driven by the compressive strain.

This work advances fundamental understanding of substrate coupling on the formation and properties of 2D Sn and suggests a clear way to balance the strain and charge transfer interaction toward the desired 2D Sn with high thermodynamic stability. With the wide variety of choices of metal substrate including its *d*-orbital occupancy and the intercalation of foreign atoms that mediate the strength of interaction between h-BN and metal substrate, the coupling between Sn structures and the h-BN/metal template can be modulated accordingly. Various degrees of strain may also be introduced into Sn structures by varying the metal substrate of different lattice constants and/or

crystalline symmetry via the remote epitaxy scheme. It is desirable to establish topologically nontrivial 2D Sn phases with balanced interaction strength and strain on proper h-BN/metal systems. 2) Correlated organic molecular systems

We have been long interested in the growth and characterization of organic molecular thin films. Single-component molecular systems are typically semiconducting, however, in organic charge transfer complexes (CTC) made of donor and acceptor molecular moieties rich physical properties ranging from Mott insulator, metal, superconductor, ferroelectricty, to (aniti) ferromagnetism could emerge due to charge transfer beween donor and acceptor.



Figure 3. (a) STM image of a striped phase of K-TCNQ. K atoms occupy the center of the TCNQ meshes, correlating to the packing motif in the b-c plane of the bulk crystal. The unit cell is marked with the outline. (b) STS spectra taken on the TCNQ or K-TCNQ molecules shown in the STM topological image in the inset. The scale bar is 2 nm.

K-TCNQ (7,7,8,8-tetracyanoquinodimethane) is a quasi-one-dimensional CTC that can undergo a Mott insulator-to-metal transition under external electric or optical fields. Recently, Dr. Shenqiang Ren's group at University of Buffalo discovered a stable long-lived conducting state in K-TCNQ via laser-pulse-induced cooperative transition. In collaboration, we performed STM/STS experiments on a molecular heterojunction of TCNQ and K-TCNQ to obtain a microscopic understanding of the electrically inhomogeneous conducting state.^{4,5} The single-layer K-TCNQ shows the same packing structure as that of K-TCNQ crystal (Fig. 3a). The STS spectra taken near the heterojunction of TCNQ and K-TCNQ are shown in Fig. 3b. By tracking the spectral feature, we find that the peak located at ~0.6V broadens and moves towards the Fermi level from TCNQ, the interface of TCNQ/K-TCNQ, to K-TCNQ. The movement of the peak towards the Fermi level is associated with the electron population in TCNQ as a result of the K doping. When imaging K-TCNQ at the broadened peak, a significant delocalization along the molecular stripes is observed. If such delocalization exists in the bulk crystal, they could facilitate the flow of carriers from or to the *a* axis of the π - π stacked TCNQ molecules and open a potential channel for enhancing the metallic conductivity of the bulk.

Future Plans

h-BN/metal potentially provides a new avenue for engineering electronic properties of 2D Sn and achieving new topological phases with high thermodynamic stability that warrants futher studies. Meanwhile, 2D MOF, based on the versatility of its framework structure, could offer a tailorable template with topological properties by design. In our recently preliminary results, we have demonstrated long-ranged ordered 2D MOFs on surfaces. We will focus on examining the properties of the complex organic/inorganic hybrid system, particularly those driven by interfacial phenomena.

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