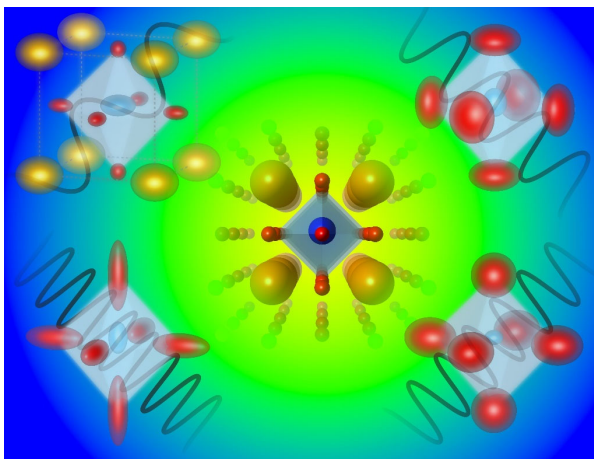
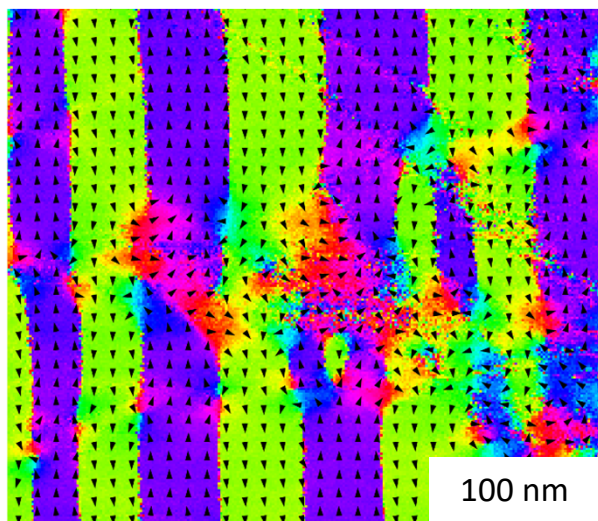
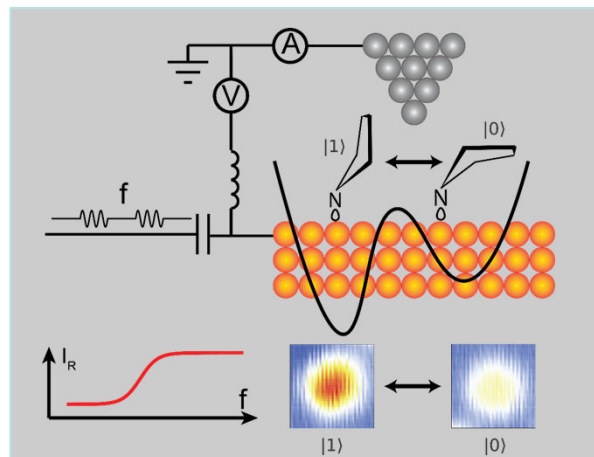
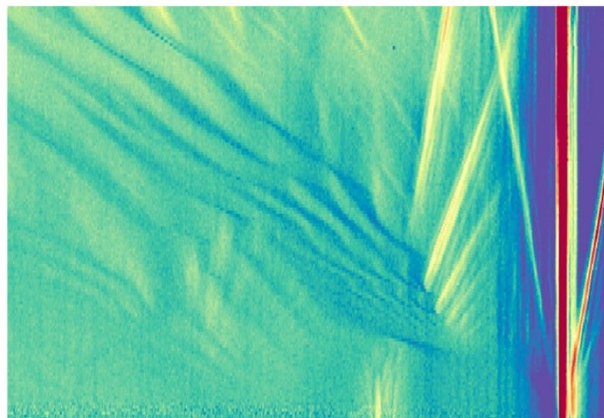


Electron and Scanning Probe Microscopies

2026 Principal Investigators' Meeting



Hilton Washington DC/Rockville Hotel & Executive Meeting Center
Rockville, Maryland
April 20-22, 2026



U.S. DEPARTMENT OF
ENERGY

Office of
Science

Office of Basic Energy Sciences
Materials Sciences and Engineering Division

On the Cover

- Top Left: *Magnetic Cascade in a Semiconductor Bilayer*. Inverse electronic compressibility $d\mu/dn$ as a function of moiré filling factor ν and magnetic field B or equivalently flux quanta per unit cell Φ/Φ_0 . A cascade of magnetic transitions indicate changes in spin occupation of Hofstadter states. Work published in *Nature Physics* **21**, 1942 (2025).
Courtesy: Ben Feldman, Stanford University
- Top Right: *Quantum Stochastic Rectification in a Molecular Qubit*. Researchers have advanced a new method of inducing nonequilibrium transitions between two structural conformations of a single pyrrolidine molecule by coupling a periodic voltage drive to the random noise and observing a resonance in the rectification current. Work published in *Phys. Rev. Lett.* **135**, 026201-1-6 (2025).
Courtesy: Wilson Ho, University of California, Irvine
- Bottom Left: *Origin of Magnetic Anisotropy in a 2D Magnet*. Lorentz 4D-STEM image shows the competition between in-plane and out-of-plane magnetic anisotropy causing a disturbance in the magnetic order on the mesoscale. Work published in *Adv. Mater.* e15150 (2025).
Courtesy: Miaofang Chi, Oak Ridge National Laboratory
- Bottom Right: *Visualizing Frequency-Dependent Phonon Anisotropy*. Newly developed momentum-selective electron energy-loss spectroscopy (q-selective EELS) method reveals that the oxygen atoms at different sites of tetragonal BaTiO₃ crystals undergo contrasting phonon anisotropies as illustrated in the thermal ellipsoids at different frequencies. Work published in *Nature* **645**, 893 (2025).
Courtesy: Xiaoqing Pan, University of California, Irvine

Foreword

This volume comprises the scientific content of the 2026 Electron and Scanning Probe Microscopies Principal Investigators' (PIs) Meeting sponsored by the Materials Sciences and Engineering Division (MSED) in the Office of Basic Energy Sciences (BES) of the U. S. Department of Energy (DOE). Held on April 20-22 in Rockville, Maryland, this marks the tenth PI meeting organized by BES in the Electron and Scanning Probe Microscopies (ESPM) area. The purpose of the meeting is to bring together researchers funded in this core research area, to facilitate the exchange of new results and research highlights, to foster new ideas and collaborations among the participants, and to discuss how to advance electron and scanning probe microscopy, spectroscopy, and associated theoretical tools, in order to address forefront scientific challenges. Additionally, the meeting provides BES program managers an opportunity to assess the state of the entire program collectively on a periodic basis, to chart future directions and to identify new programmatic needs.

The Electron and Scanning Probe Microscopies Core Research Activity supports basic research in materials sciences through advanced electron and scanning probe microscopy and related spectroscopy techniques to understand the atomic, electronic, and magnetic structures and properties of materials. This activity also supports the development of new methods and techniques to advance basic science and materials characterizations for energy applications. The goal is to achieve a fundamental understanding of materials, including quantum phenomena, via advanced microscopy, spectroscopy, and theoretical tools. This year's meeting highlights topical areas such as imaging of magnetic and topological materials, quantum phenomena and microscopic responses of 2D materials, energy materials, emergent quantum phenomena, frontiers of functional imaging, and simulations and advanced 3D imaging. Notably, this year's meeting features two panel discussions on current PI interests: (i) instrumentation challenges and opportunities, and (ii) AI for microscopy.

I extend my gratitude to all meeting attendees for their active participation and for sharing innovative ideas and research results, which offer fresh insights for the continued development of this field and its value to the DOE. Special appreciation goes to meeting Co-Chairs Abhay Pasupathy and Miaofang Chi for their dedicated efforts and invaluable assistance in organizing this event. My sincere thanks also to all session moderators, Kerry Gorey of BES, and Stephanie Fox and her colleagues at the Oak Ridge Institute of Science and Education for their excellent logistical support.

Jane Zhu
Program Manager
Electron and Scanning Probe Microscopies
Materials Sciences and Engineering Division
Office of Basic Energy Sciences
U. S. Department of Energy

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**10th Electron and Scanning Probe Microscopies
Principal Investigators' Meeting**

April 20-22, 2026

Meeting Organizer: Jane Zhu (DOE-BES)
Co-Chairs: Abhay Pasupathy (BNL) & Miaofang Chi (ORNL)

Monday, April 20

7:30-8:30 am	Registration & Breakfast
8:30-8:50 am	<i>Welcome and Program Updates</i> Jane Zhu, Program Manager, Electron and Scanning Probe Microscopies Andrew Schwartz, Deputy Associate Director, DOE-BES
Session 1	Imaging of Magnetic and Topological Materials Chair: Gregory Fuchs
8:50-8:55 am	<i>Session Introduction</i> Gregory Fuchs, Cornell University
8:55-9:15 am	<i>Emergent Behavior in Nanoscale Functional Heterostructures</i> Charudatta Phatak, Argonne National Laboratory
9:15-9:35 am	<i>Magnetic Imaging of Emergent Phenomena in Topological Quantum Materials</i> Weida Wu, Rutgers
9:35-9:55 am	<i>Spin-resolved Imaging of Quantum Materials</i> Ilija Zeljkovic, Boston College
9:55-10:15 am	<i>Direct Probing Polarization and Magnetization Behaviors in Ferroics by In Situ Cryogenic-(S)TEM</i> Myung-Geun Han, Brookhaven National Laboratory
10:15-10:35 am	Break
Session 2	Quantum phenomena in 2D materials Chair: Abhay Pasupathy
10:35-10:40 am	<i>Session Introduction</i> Abhay Pasupathy, Brookhaven National Laboratory
10:40-11:00 am	<i>Emergent Phenomena in 2D Quantum Materials and Nanostructures Probed via STEM and EELS</i> Miaofang Chi, Oak Ridge National Laboratory
11:00-11:20 am	<i>Nanoscale Imaging of Correlations, Topology, and Magnetism in WSe₂ Layers</i> Ben Feldman, Stanford University
11:20-11:40 am	<i>Nano-Polaritonics in layered van der Waals heterostructures</i> Guangxin Ni, Florida State University

11:40-12:40 pm Working Lunch (discussion of the scientific presentations)

Session 3 Emergent Quantum Phenomena

Chair: Eduardo da Silva Neto

12:40-12:45pm *Session Introduction*

Eduardo da Silva Neto, Yale University

12:45-1:05 pm *Visualization of the finite-momentum pairing state in $\text{EuRbFe}_4\text{As}_4$*

Kazuhiro Fujita, Brookhaven National Laboratory

1:05-1:25 pm *Probing Unconventional Superconductivity with Advanced Tunneling Probes*

Xiaolong Liu, University of Notre Dame

1:25-1:45 pm *Visualizing Topological States at Dislocations in Fe-Chalcogenides and Symmetry-Breaking Electronic Orders in Kagome Magnet*

Lian Li, West Virginia University

1:45-2:05 pm *The Identification, Characterization, and Control of Two-Level Quantum Systems*

Wilson Ho, University of California, Irvine

2:05-2:30 pm **Break**

Session 4 Simulations and Advanced 3D Imaging

Chair: Yu-Tsun Shao

2:30-2:35 pm *Session Introduction*

Yu-Tsun Shao, University of Southern California

2:35-2:55 pm *Combining quantum calculations and electron microscopy to unveil nanostructure properties*

Sokrates Pantelides, Vanderbilt University

2:55-3:05 pm *Inelastic Scattering of Structured Matter Waves for Quantum Materials Characterization*

David Masiello, University of Washington

3:05-3:25 pm *Sub-angstrom Convergent Beam Electron Diffraction for Valence Electron Mapping*

Susanne Stemmer, University of California, Santa Barbara

3:25-3:45 pm *Ptychographic Atomic Electron Tomography: Mapping Heavy and Light Atoms in 3D*

Jianwei (John) Miao, University of California, Los Angeles

3:45-4:10 pm **Break**

4:10-5:10 pm **Panel Discussion: Instrumentation Challenges and Opportunities**

Panelists: Andy Lupini, Oak Ridge National Laboratory

Juan Carlos Idrobo, Pacific Northwest National Laboratory

Chong-Yu Ruan, Michigan State University
Markus Raschke, University of Colorado
Ali Yazdani, Princeton University
Moderator: Yimei Zhu, Brookhaven National Laboratory

5:10-6:30 pm **Poster Session I**

6:30-7:30 pm **Working Dinner (Group Discussions)**

Tuesday, April 21

7:30-8:30 am Breakfast

8:30-8:45 am *Program Guidelines*
Jane Zhu, DOE-BES

Session 5 Frontiers of Functional Imaging

Chair: Sergei Kalinin

8:45-8:50 am *Session Introduction*

Sergei Kalinin, University of Tennessee, Knoxville

8:50-9:10 am *Unveiling the Atomic Vibrational Anisotropy and Electron-Phonon Coupling via Momentum-Selective Electron Microscopy*

Xiaoqing Pan, University of California, Irvine

9:10-9:30 am *Nanoscale Microwave Impedance Microscopy of Complex Materials*

Keji Lai, University of Texas at Austin

9:30-9:50 am *Scanning Thermal Microscopy for Probing Nanoscale Energy Transport, Dissipation and Quantum Friction*

Pramod Reddy, University of Michigan

9:50-10:10 am *Towards Universal Hall Transport Mapping at the Nanoscale in the Electron Microscope*

Juan Carlos Idrobo, Pacific Northwest National Laboratory

10:10-10:35 am **Break**

Session 6 Microscopic Responses of 2D Materials

Chair: Abhay Pasupathy

10:35-10:40 am *Session introduction*

Abhay Pasupathy, Brookhaven National Laboratory

10:40-11:00 am *Probing Correlated Phenomena in Graphene Constrictions*

Fereshte Ghahari Kermani, George Mason University

11:00-11:20 am *Visualizing Correlated and Topological Quantum Phases in Two-Dimensional Materials*

Ali Yazdani, Princeton University

11:20-11:40 am *Programming and imaging active defect arrays in layered materials via atomic lock-on*

Frances Ross, Massachusetts Institute of Technology

11:40-12:00 pm *Atomic-scale characterization of strain-tunable moiré quantum materials*

Matthew Yankowitz, University of Washington

12:00-1:00 pm Working Lunch (discussion of the scientific presentations)

Session 7	Energy Materials
	Chair: Robert Klie
1:00-1:05 pm	<i>Session Introduction</i> Robert Klie, University of Illinois at Chicago
1:05-1:25 pm	<i>Cryogenic Electron Microscopy for Electrochemical Energy Materials</i> Yi Cui, SLAC National Accelerator Laboratory
1:25-1:45 pm	<i>Imaging of Charge-Containing Soft Matter on Atomic and Mesoscopic Length Scales</i> Nitash Balsara, Lawrence Berkeley National Laboratory
1:45-2:05 pm	<i>New Cryo-EM Tools for Studying Dynamic Interfaces in Battery Materials</i> Yuzhang Li, University of California, Los Angeles
2:05-2:25pm	<i>Liquid Cell Electron Microscopy: Heterogeneity and Fluctuations at Solid-Liquid Interfaces</i> Haimei Zheng, Lawrence Berkeley National Laboratory
2:25-2:45 pm	<i>4D-STEM Based Electron Diffraction Contrast Tomography of Charge-Lattice Coupled Materials</i> Qian Chen, University of Illinois at Urbana-Champaign
2:45-3:05 pm	<i>Probing the electric double layer through 3D atomic force microscopy and multiscale simulation</i> Tao Ye, University of California, Merced
3:05-3:30 pm	Break
3:30-4:40 pm	Panel Discussion: AI for Microscopy Panelists: Rama Vasudevan, Oak Ridge National Laboratory (<i>invited</i>) John Miao, University of California, Los Angeles Yimei Zhu, Brookhaven National Laboratory David Ginger, University of Washington Abhay Pasupathy, BNL/ Columbia U. Moderator: Sergei Kalinin, University of Tennessee, Knoxville
4:50-6:30 pm	Poster Session II
6:30-7:30 pm	Working Dinner (Group Discussions)

Wednesday, April 22

7:30-8:30 am	Breakfast
Session 8	Electron-Lattice Interactions
	Chair: Jordan Hachtel
8:30-8:35 am	<i>Session Introduction</i>
	Jordan Hachtel, Oak Ridge National Laboratory
8:35-8:55 am	<i>Exploring Charge and Lattice Correlations and Dynamics in Quantum Materials</i>
	Yimei Zhu, Brookhaven National Laboratory
8:55-9:15 am	<i>Uncovering Nonequilibrium Order in Quantum Materials: Multimodal Ultrafast Electron Microscopy Platform</i>
	Chong-Yu Ruan, Michigan State University
9:15-9:35 am	<i>Visualizing light-induced non-equilibrium states in correlated insulators with ultrafast electron diffraction and nonlinear optics</i>
	Anshul Kogar, University of California, Los Angeles
9:35-10:05 am	Break
Session 9	Electron Dynamics in Solids
	Chair: Miaofang Chi
10:05-10:10 am	<i>Session Introduction</i>
	Miaofang Chi, Oak Ridge National Laboratory
10:10-10:30 am	<i>Sub-diffraction Imaging of Carrier Dynamics in Perovskite Semiconductors: Passivation, Ion Motion, and Applying Convolutional Neural Networks</i>
	David Ginger, University of Washington
10:30-10:50 am	<i>Development of Atomic Resolution Spin Dynamics Imaging Scanning Tunneling Microscopy (SDI-STM)</i>
	Jay Gupta, Ohio State University
10:50-11:10 am	<i>Control, Order, and Melting of 2D Charge Density Waves</i>
	Robert Hovden, University of Michigan
11:10-11:30 am	<i>Nano-optical Imaging, Spectroscopy, and Control of Quantum Materials</i>
	Markus Raschke, University of Colorado, Boulder
11:30-12:00 pm	Closing Remarks
Noon	Adjourn

Poster Session I
Monday, April 20, 5:10-6:30 PM

- P-I.1 *Topological solitons and transport in nanomagnetic structures*
Hanu Arava, Argonne National Laboratory
- P-I.2 *Magnetic imaging of emergent phenomena in topological quantum materials*
Weida Wu, Rutgers Univ.
- P-I.3 *Direct Probing Polarization and Magnetization Behaviors in Ferroics by In Situ Cryogenic-(S)TEM*
Myung-Geun Han, Lijun Wu, Yimei Zhu, Brookhaven National Laboratory
- P-I.4 *Visualizing the atomic-scale dynamics of charge-ordered phases in quantum materials*
Christopher Gutiérrez, University of California, Los Angeles
- P-I.5 *Emergent Phenomena in 2D Quantum Materials and Nanostructures Probed via STEM and EELS*
Miaofang Chi, Andrew R. Lupini, Jordan A. Hachtel, Elizaveta Tiukalova, Eric Hoglund, ORNL
- P-I.6 *Atomic-scale characterization of strain-tunable moiré quantum materials*
Matthew Yankowitz, University of Washington
- P-I.7 *Ptychographic Atomic Electron Tomography: Mapping Heavy and Light Atoms in 3D*
Jianwei (John) Miao, UCLA
- P-I.8 *Nanoscale Imaging of Correlations, Topology, and Magnetism in WSe₂ Layers*
Ben Feldman, Stanford University
- P-I.9 *Liquid Cell Electron Microscopy: Heterogeneity and Fluctuations at Solid-Liquid Interfaces*
Haimei Zheng, Peter Ercius, Emory Chan, David Limmer, LBNL
- P-I.10 *Probing Correlated Phenomena in Graphene Constrictions*
Fereshte Ghahari Kermani, George Mason University
- P-I.11 *Cryogenic Electron Microscopy for Topological Spin Textures in Two-Dimensional van der Waals Magnetic Materials*
Kai He, University of California, Irvine
- P-I.12 *Deciphering Electrochemical Transformation Pathways on the Nanometer Scale: Advancing Fundamental Discovery for Material Innovation*
Sergei Kalinin, University of Tennessee, Knoxville
- P-I.13 *4D-STEM Based Electron Diffraction Contrast Tomography of Charge-Lattice Coupled Materials*
Qian Chen, Jian-Min Zuo, Kejie Zhao, University of Illinois at Urbana-Champaign
- P-I.14 *Sub-angstrom convergent beam electron diffraction for valence electron mapping*
Susanne Stemmer, University of California, Santa Barbara
- P-I.15 *New Cryo-EM Tools for Studying Dynamic Interfaces in Battery Materials*
Yuzhang Li, University of California, Los Angeles
- P-I.16 *Development of Atomic Resolution Spin Dynamics Imaging Scanning Tunneling Microscopy*
Jay A. Gupta, Roland Kawakami, Michael E. Flatte, Ohio State University
- P-I.17 *Cryogenic Electron Microscopy for Electrochemical Energy Materials*
Yi Cui, Wah Chiu, Paul McIntyre, Arun Majumdar, Jennifer Dionne, SLAC
- P-I.18 *Visualizing interactions and inhomogeneity in magnetic van der Waals materials*
Eduardo H. da Silva Neto, Yale University
- P-I.19 *Control, Order, and Melting of 2D Charge Density Waves from 20K to 700K*
Robert Hovden, University of Michigan
- P-I.20 *Nano-Polaritonics in layered van der Waals heterostructures*
Guangxin Ni, Florida State University

- P-I.21 *Imaging of Charge-Containing Soft Matter on Atomic and Mesoscopic Length Scales*
Nitash Balsara, Andrew Minor, Rui Wang, Xi Jiang, David Prendergast, Brooks Abel, LBNL
- P-I.22 *Visualizing Topological States at Dislocations in Fe-Chalcogenides and Symmetry-Breaking Electronic Orders in Kagome Magnet*
Lian Li, West Virginia University
- P-I.23 *Towards Universal Hall Transport Mapping at the Nanoscale in the Electron Microscope*
Juan Carlos Idrobo, Micah Prange, Di Xiao, Yingge Du, Libor Kovarik, PNNL
- P-I.24 *Probing the electric double layer through 3D atomic force microscopy and multiscale simulations*
Tao Ye (UC Merced), Ashlie Martini (UC Merced), David Prendergast (LBNL)
- P-I.25 *New Electron Microscopy Capabilities at the Center for Functional Nanomaterials*
Judith Yang, Brookhaven National Laboratory

Poster Session II
Tuesday, April 21, 4:50-6:30 PM

- P-II.1 *Advancements in Cryogenic and Monochromated STEM-EELS Experimentation for Quantum Materials*
J. Hachtel, E. Tiukalova, E. Hoglund, Y. Kim, J. Smith, A. Lupini, M. Chi, ORNL
- P-II.2 *Nanoscale Microwave Impedance Microscopy of Complex Materials*
Keji Lai, University of Texas at Austin
- P-II.3 *Inelastic Scattering of Structured Matter Waves for Quantum Materials Characterization*
David Masiello, University of Washington
- P-II.4 *The Identification, Characterization, and Control of Two-Level Quantum Systems*
Wilson Ho, University of California, Irvine
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- P-II.6 *Visualization of the finite-momentum pairing state in $\text{EuRbFe}_4\text{As}_4$*
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Anshul Kogar, University of California, Los Angeles
- P-II.8 *Non-Contact Near-Field Radiative Thermal Imaging to Understand the Energy Transport across a PN Junction*
Qing Hao (University of Arizona), Liping Wang (Arizona State University)
- P-II.9 *Discovering Ion-Electron Interactions at Electrochemical Interfaces Using Depth-Resolved Electron Microscopy*
David Stewart (UMD), Leonard Brillson (OSU), Yue Qi (Brown Univ.)
- P-II.10 *Spatiotemporal Imaging of Magnetization Dynamics of van der Waals ferromagnets*
Gregory Fuchs, Cornell University
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Y. Zhu, L. Wu, S. Reisbick, M.G. Han, Brookhaven National Laboratory
- P-II.12 *Spin-resolved imaging of quantum materials*
Ilija Zeljkovic, Boston College
- P-II.13 *Probing Lattice and Spin Order in van der Waals Magnetic Materials with Cryogenic and Multi-modal Electron Microscopy*
Yu-Tsun Shao, Univ. of Southern California
- P-II.14 *Visualizing Correlated and Topological Quantum Phases in Two-Dimensional Materials*
Ali Yazdani, Princeton University
- P-II.15 *Uncovering Nonequilibrium Order in Quantum Materials: Multimodal Ultrafast Electron Microscopy Platform*
Chong-Yu Ruan, Michigan State University
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- P-II.18 *Sub-diffraction Imaging of Carrier Dynamics in Perovskite Semiconductors: Passivation, Ion Motion, and Applying Convolutional Neural Networks*
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- P-II.24 *Emergent behavior in van der Waals ferromagnets*
Yue Li, Argonne National Laboratory
- P-II.25 *Quantum-Coherent Manipulation of Two-Level Systems via Wavefunction Engineering in a Scanning Electron Microscope*
William Putnum, University of California, Davis
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Lijun Wu and Yimei Zhu, Brookhaven National Laboratory

*Laboratory
Abstracts*

Imaging of Charge-Containing Soft Matter on Atomic and Mesoscopic Length Scales

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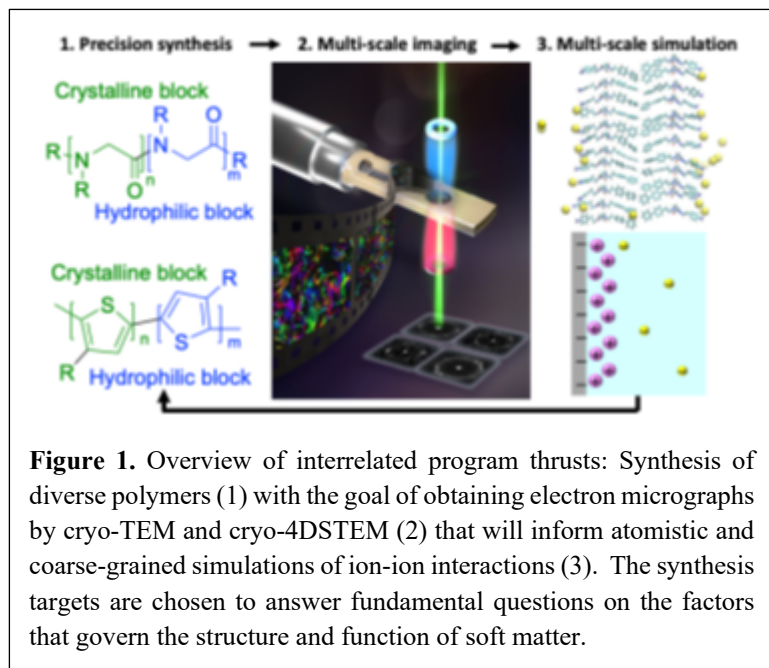
Keywords: Cryo-TEM; Cryo-4DSTEM; noncovalent interactions; charge-containing polymers; ML-acceleration.

Research Scope

Our mission is to obtain explicit experimental electron microscopy images at the most relevant scales that will provide constraints for the proposed theoretical work, allowing us to uncover the fundamental interactions and processes that govern structure formation and underpinnings of structure-property relations from atomic to micrometer length scales in synthetic soft materials.

The main barrier for the atomic-scale imaging of soft materials is preservation of the natural structure. Low-dose imaging at low temperatures and vitrification, first developed in the structural biology community, have provided an avenue for overcoming this barrier. To prevent the rupture of chemical bonds and unit cells, images must be obtained using very limited electron doses, usually less than $20 \text{ e}/\text{\AA}^2$ at liquid nitrogen temperature. This limit is slightly higher for materials that contain aromatic rings. Two imaging approaches, cryogenic transmission electron microscopy (cryo-TEM) and cryogenic four-dimensional scanning transmission electron microscopy (cryo-4DSTEM) are

used in this program to extract multimodal information from atomic to mesoscale. Limited electron dose leads to micrographs in position space or diffraction patterns in reciprocal space with low signal to noise ratio (SNR). Sorting and averaging algorithms are needed to average identical structures in many thousand images to increase signal to noise ratio after classifying different structures



based on the low dose images obtained by cryo-TEM to achieve atomic-scale resolution. Cryo-4DSTEM on the other hand utilizes an electron probe to scan the structures in thin films. It enables acquisition of diffraction patterns at precise scanning locations, providing detailed local structural information from nanometer to micrometer length scales, unlike the sample-averaged information obtained by conventional electron diffraction. The comparison of theoretical predictions and electron micrographs, particularly disagreement between theory and experiment, will be used to complete the feedback loop and design synthetic targets to test our hypothesis for the reason for the disagreement (Figure 1).

Recent Progress

We studied a positively charged nanofiber with chloride counterions suspended in water. Our main accomplishment was to determine the location of the counterions which are, in principle, free to diffuse into the surrounding water, subject to constraints provided by coulombic and van der Waals interactions. Pioneering work by Manning [1] indicated that the fiber would present two populations of counterions: condensed counterions that form an ion pair with the positive charge on the fiber and dissociated counterions that could be randomly dispersed in the surrounding water. These two types of counterions are shown schematically in Figure 2A. The polymer used for this study, shown in Figure 2B, has the presence of an ionically bound halogen ion instead of a covalently bonded halogen atom. The atomic-scale cryo-TEM image of a fiber with counter ions is shown in Figure 2C. The crystalline core (V-shaped) of the fiber and the locations of both condensed counterions and fixed charges on the polymer chain were determined

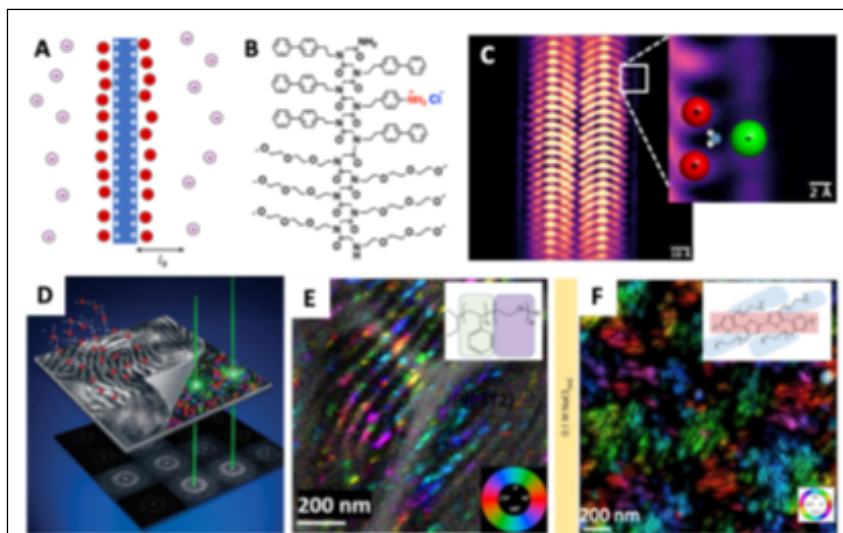
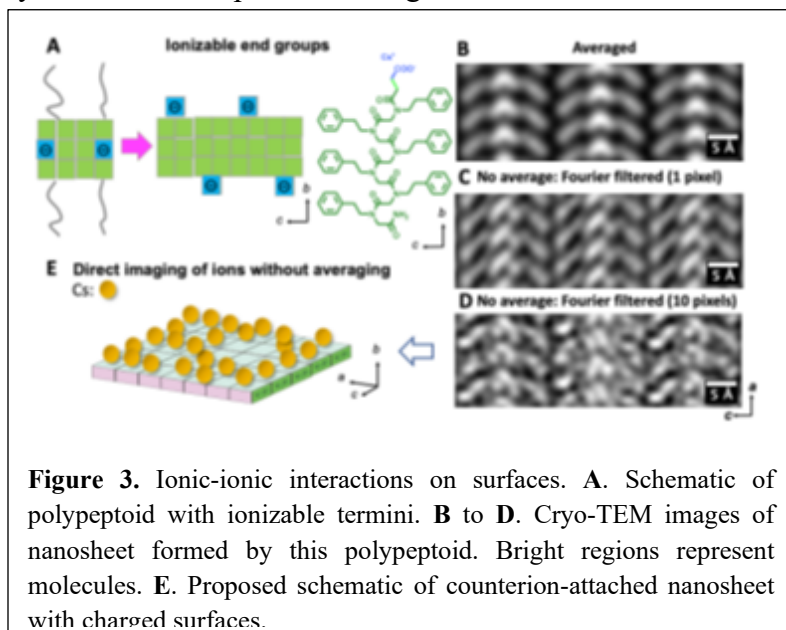


Figure 2. A. Diagram of a charged nanofiber. B. Chemical structure of charged polypeptoid. C. Cryo-TEM image of peptoid nanofiber with condensed counterions. Inset shows the positively charged nitrogen, water, and chloride counterion are superimposed over the image. D. Schematic of the 4D-STEM scanning over a polymer thin film. E. Orientation map of localized PEO crystallites in PS-b-PEO. F. The direction of p(g3T2) chains in crystallites. The chemical structures are shown as insets.

directly from atomic-scale images, as indicated in Figure 2C [2]. Our experimentally determined counterion distributions were peaked at a distance of about 5 Å away from the fixed positive charge, indicating the presence of a layer of water molecules between condensed ion pairs. We hypothesize that the formation of solvent-separated ion pairs is due to entropic considerations and hope that our study will motivate further study of these contributions. Our work opens the door to direct imaging of more complex

systems such as pairs of charged nanofibers wherein correlations between adjacent layers of



condensed counterions can be studied directly. This work shows that solvated ions in soft matter can be imaged at the atomic scale, which would allow us to design molecules with targeted ionic bonds to facilitate the selective capture of critical materials.

Electronic charge transport in polymers is closely related to local crystal structure and grain orientation. We used cryo-4DSTEM to study the local crystal orientation in soft materials (Figure 2D). We

investigated the structure of the PEO-rich lamellae of polystyrene-block-poly(ethylene oxide) (PS-b-PEO), a promising material for use as a polymer solid-state electrolyte, and the structure of a model organic mixed ionic-electronic conductor, polythiophene with ethylene glycol side chains p(g3T2). Using cryo-4DSTEM, we generated orientation maps that show crystallites exhibit a preferential alignment with respect to the PS-b-PEO interface. (Figure 2E) [3]. This is the first direct measurement of crystal orientation with respect to the local orientation of the interface between block copolymer lamellae. The cryo-4DSTEM image of p(g3T2) across multiple length scales in frozen hydrated states is shown in Figure 2F [4]. The orientation maps of frozen hydrated p(g3T2) thin films reveal that swelling-induced disorder is mostly localized in discrete regions, preserving the liquid crystalline order. These studies, along images shown in Figures 2-4, demonstrate our efforts to image materials from the atomic to continuum length scales, which would enable the direct imaging of the correlation between charge transport and local structures.

Future Plans

Building on our recent progress in atomic-scale imaging of soft matter and polymers, we propose to explore new frontiers in molecular design and noncovalent interactions. We will leverage 1D nanofibers and 2D nanosheets, comprising sequence-defined polymers, as two nanoplatforms to explore how to advance our understanding of molecular design and noncovalent interactions. Specifically, we aim to investigate how precisely tunable interactions can promote selectivity for *critical materials*.

Atomic-scale imaging of ions is the key for understanding how engineered nanostructures can improve separation efficiency and selectivity for single ions and localized ions during

separation, processing, and recycling of critical materials, ultimately leading to more efficient separation processes.

To achieve this goal, we will leverage our expertise in cryo-TEM and cryo-4DSTEM imaging, as well as our experience with sequence-defined charge-containing polymers and conjugated polymers.

In addition to engineering the ionizable side chains in nanofibers shown in Figure 2, we propose studying molecules with a single charged head group, analogous to ionic surfactants but with crystallizable hydrophobic tails (Figure 3A). An example molecule with a COO^-Cs^+ head group forms nanosheets that can be imaged by cryo-TEM. Preliminary images show a V-shaped crystal motif and atomic-scale features of the nanosheet without ions in the non-averaged image (Figures 3B to 3D, which is critical for imaging localized ions. We will use a hybrid deep learning workflow that combines Machine-Learning-based self-supervised denoising, feature-aware restoration, and architectural flexibility to detect the location of counterions. If successful, this platform could enable locating individual ions or local ion clusters without averaging, allowing observation of condensed and dissociated counterions. We will synthesize different molecules and study the effect of ionic strength and size on heterogeneity, using strategies to minimize ice thickness and beam-induced motion, thereby enabling the imaging of individual counterions in a vitreous state on nanosheets.

The overall goal of the program is to integrate experimental images and simulations on matched length scales. To achieve this, atomic-scale images will be compared with predictions of molecular dynamics simulations. Meso-scale images will be compared with predictions of continuum theories. We will demonstrate that the continuum theories can be used to identify the missing interactions that cause departures between theory and experiment on the atomic scale. We will adopt an approach where the evaluation of local atomic energies and forces is relegated to a trained deep-learning model based on convolutional or graph neural networks, thereby retaining accuracy without increasing computational cost.

References

1. G.S. Manning. *Limiting Laws and Counterion Condensation in Polyelectrolyte Solutions I. Colligative Properties*. J. Chem. Phys. **51**, 924–933 (1969).
2. M. Seidler, T. Yu, X. Luo, D. Prendergast, R.N. Zuckermann, X. Jiang, and N.P. Balsara, *Atomic-Scale Imaging of Condensed Counterions*, Macromolecules. **57**, 10016–10022 (2024)
3. M. Chen, K. C. Bustillo, V. Patel, B. H. Savitzky, H. Sternlicht, J. A. Maslyn, W. S. Loo, J. Ciston, C. Ophus, X. Jiang, N.P. Balsara, and A.M. Minor, *Direct Imaging of the Crystalline Domains and Their Orientation in the PS-*b*-PEO Block Copolymer with 4D-STEM*, Macromolecules **57**, 5629-5638 (2024).
4. Y. Tsarfati, K.C. Bustillo, B.H. Savitzky, L. Balhorn, T. J. Quill, A. Marks, J. Donohue, S. E. Zeltmann, C.J. Takacs, A. Giovannitti, I. McCulloch, C. Ophus, A. M. Minor and A. Salleo, *The hierarchical structure of organic mixed ionic–electronic conductors and its evolution in water*. Nat. Mater. **24**, 101–108 (2025).

Publications

1. M. Chen, K. C. Bustillo, Y. J. Lee, C. Ophus, J. Ciston, B. A. Abel, X. Jiang, N. P. Balsara, A. M. Minor, *In Situ 4D-STEM Imaging of the Orientation of Lamellar Clusters in Polymer Crystallization*. Macromol. Rapid Commun. e00450 (2025)
2. X. Luo, F. Roncoroni, T. Yu, N.K. Li, R.N. Zuckermann, X. Jiang, N.P. Balsara, D. Prendergast. *Cooperative Role of Mixed Solvent in the Evaporation-Induced Self-Assembly of Polypeptoid Nanocrystals*, ACS Appl. Nano Mater. **8**, 12909–12919 (2025).
3. Y.J Lee, M. Seidler, X. Luo, G.L Butterfoss, T. Yu, B. Rad, S. Xuan, C. Zhu, D. Prendergast, N.P. Balsara, B.A. Abel, R.N. Zuckermann, X. Jiang, *Crystalline Peptoid Nanofibers with a Single-Unit Cell Cross*, J. Am. Chem. Soc. (2025)
4. Y.J Lee, X. Luo, M. Seidler, T. Yu, D. Prendergast, R.N Zuckermann, N. P. Balsara, B.A. Abel, X. Jiang, *Key Intermediate Nanostructures in the Self-Assembly of Amphiphilic Polypeptoids Revealed by Cryo-TEM*, Macromolecules **58**, 3795–3803(2025)
5. Y. Tsarfati, K.C. Bustillo, B.H. Savitzky, L. Balhorn, T. J. Quill, A. Marks, J. Donohue, S. E. Zeltmann, C.J. Takacs, A. Giovannitti, I. McCulloch, C. Ophus, A. M. Minor and A. Salleo, *The hierarchical structure of organic mixed ionic–electronic conductors and its evolution in water*. Nat. Mater. **24**, 101–108 (2025).
6. X. Luo, M. Seidler, Y. J. Lee, T. Yu, R. N. Zuckermann, N. P. Balsara, B. A. Abel, D. Prendergast, X. Jiang, *Evaluating Cryo-TEM Reconstruction Accuracy of Self-Assembled Polymer Nanostructures*. Macromol. Rapid Commun. **46**, 2400589(2024)
7. M. Seidler, T. Yu, X. Luo, D. Prendergast, R.N. Zuckermann, X. Jiang, and N.P. Balsara, *Atomic-Scale Imaging of Condensed Counterions*, Macromolecules. **57**, 10016–10022 (2024)
8. X. Jiang, R.N. Zuckermann, and N. P. Balsara, *Relationship between molecular structure and corrugations in self-assembled polypeptoid nanosheets revealed by cryogenic electron microscopy*, Phys. Rev. Materials **8**, 020301, (2024).
9. M. Chen, K. C. Bustillo, V. Patel, B. H. Savitzky, H. Sternlicht, J. A. Maslyn, W. S. Loo, J. Ciston, C. Ophus, X. Jiang, N.P. Balsara, and A.M. Minor, *Direct Imaging of the Crystalline Domains and Their Orientation in the PS-*b*-PEO Block Copolymer with 4D-STEM*, Macromolecules **57**, 5629-5638 (2024).
10. X. Luo, T. Yu, N.K. Li, R.N. Zuckermann, X. Jiang, N.P. Balsara, and D. Prendergast, *Thermodynamic Driving Forces for the Self-Assembly of Diblock Polypeptoids*, ACS Nano **18**, 14917-14924 (2024).

Emergent Phenomena in 2D Quantum Materials and Nanostructures Probed *via* STEM and EELS

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Keywords: Cryogenic, Scanning Transmission Electron Microscopy, Monochromated EELS, Quantum materials

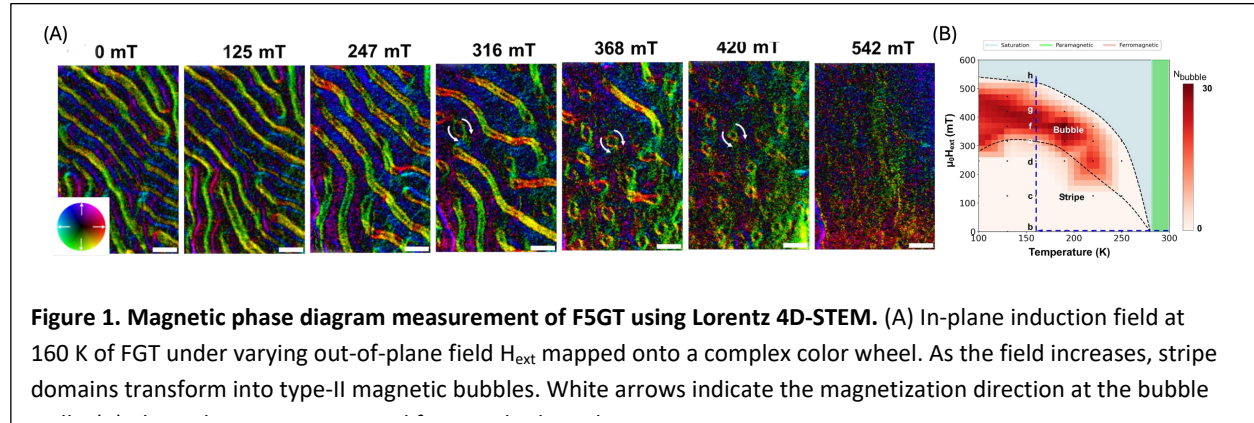
Research Scope

Two-dimensional (2D) quantum materials and nanostructures offer an exceptional platform for exploring emergent physics driven by reduced dimensionality and nanoscale heterogeneity. Materials such as 2D magnets, transition metal dichalcogenides, and functional oxide superlattices exhibit geometric constraints that give rise to phenomena, including magnetism, topological states, and superconductivity, that are absent in their bulk counterparts. These systems also exhibit extreme sensitivity to external stimuli and local disorder, including defects, strain, and dopants. As a result, the coupling among lattice, spin, and charge can be significantly altered, giving rise to complex and tunable quantum behaviors. The overarching goal of this project is to understand local emergent spin-charge-lattice correlations and quasiparticle interactions in 2D quantum materials and heterostructures. A central goal is to develop and apply advanced STEM techniques with high spatial, energy, and momentum resolution for correlative measurements of structural, electronic, and vibrational properties, while integrating these methods with cryogenic stages to access ultra-low temperatures where delicate quantum states can be revealed.

Recent progress

To uncover the fundamental mechanisms driving spin–charge–lattice interactions and quasiparticle dynamics in 2D quantum materials and nanostructures, we are actively pursuing two tightly connected and ambitious goals. First, we are advancing and integrating the frontiers of STEM by developing next-generation capabilities: cryogenic microscopy for *atomic-resolution* imaging and spectroscopy at liquid nitrogen (~100 K) and liquid helium (<10 K) temperatures; monochromated EELS offering high spatial, energy, and momentum resolution; and machine learning-driven workflows that enable low-dose, high-efficiency data acquisition that is crucial for mitigating stage instability in cryogenic experiments and preserving beam-sensitive 2D materials. These ongoing technical innovations, detailed in our companion abstract, are already opening new avenues in quantum materials research. Here, we highlight our recent scientific advances enabled

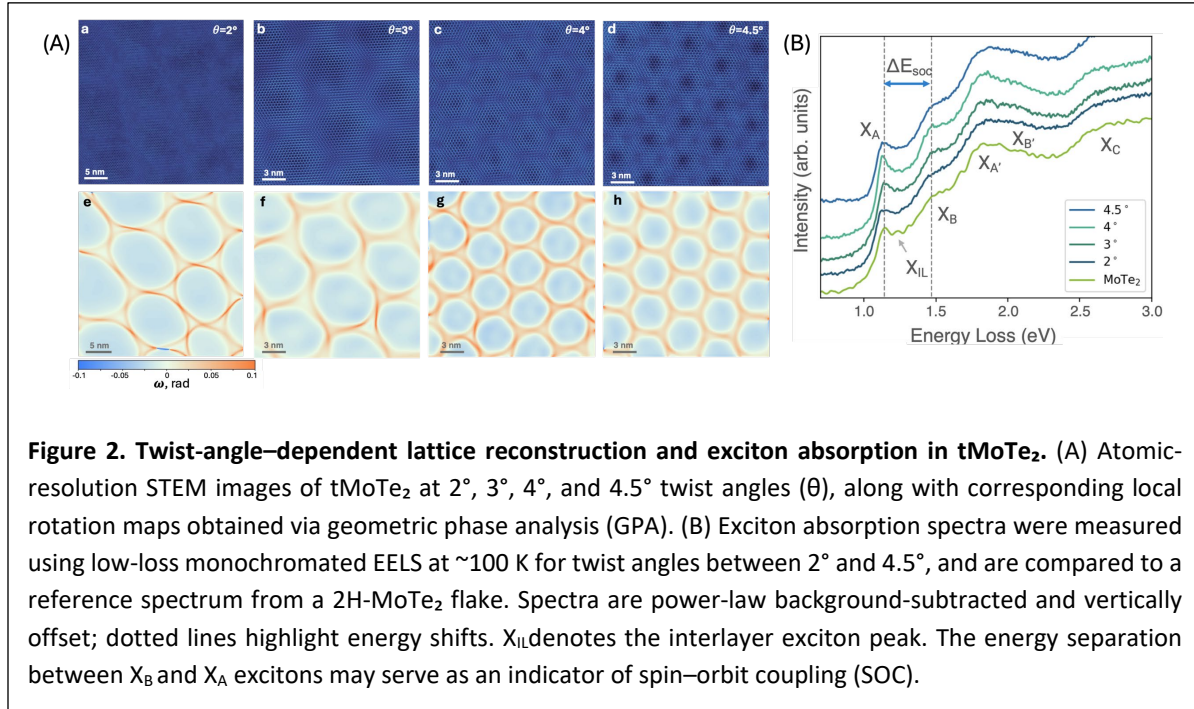
by these capabilities, including real-time observation of spintronic phase transitions in 2D magnets, twist-angle control of spin-orbit-entangled quantum states, and the discovery of topological and lattice-driven phonon behavior. Together, these efforts represent an important step toward atomically resolved, quantum-sensitive imaging of complex correlated systems at relevant temperatures.

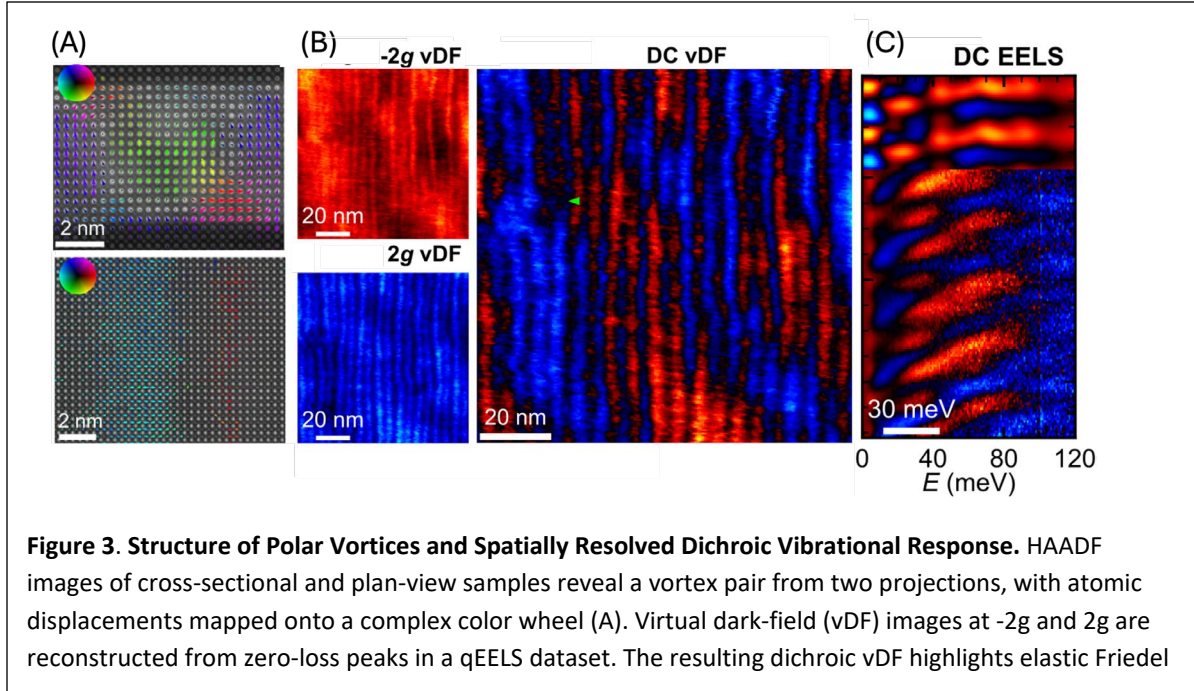


Probing Spintronic Phase Transitions in $\text{Fe}_{5-x}\text{GeTe}_2$ (F5GT) via Cryogenic Lorentz 4D-STEM. F5GT is a promising 2D ferromagnetic material due to its high Curie temperature, tunable spin textures, and potential for spintronic and topological applications [1]. However, its magnetic behavior shows considerable variability across samples, particularly in anisotropy and spin configurations. Using cryogenic Lorentz 4D-STEM and micromagnetic simulations, we mapped the magnetic phase diagram of quenched F5GT, identifying transitions from stripe domains to magnetic bubbles driven by external fields and thermal history (**Figure 1**). These transitions occur without significant Dzyaloshinskii-Moriya interaction (DMI) and instead result from the interplay of uniaxial anisotropy, dipolar interactions, and field orientation. Stripe domains form under zero-field cooling, while metastable bubbles emerge under applied fields, with type-I to type-II bubble transitions triggered by oblique field application. These results establish F5GT as a tunable platform for nanoscale topological magnetism [2]. While a high Curie temperature in F5GT is widely accepted, the origin of sample-dependent anisotropy remained unclear. We recently mapped magnetism, structure, and chemistry from atomic to micron scales and found that only mesoscale Fe-deficient secondary phases, introduced by quenching, significantly impact magnetic anisotropy. These inclusions lead to in-plane anisotropy, while slow cooling suppresses phase separation and maintains out-of-plane order. This work reconciles prior inconsistencies and provides a predictive framework for tailoring magnetic behavior in F5GT and related 2D magnets via thermal processing.

Cryogenic STEM-EELS Investigation of Moiré Reconstruction and Exciton Fine Structure in Twisted MoTe₂

Twisted bilayers of MoTe₂ form moiré superlattices that host rich excitonic and correlated quantum phenomena, strongly influenced by twist angle and stacking geometry, specifically, H-type (60°) or R-type (0°) [3]. Using cryogenic monochromated STEM-EELS, we directly correlated atomic-scale lattice reconstruction with excitonic fine structure in H-type twisted MoTe₂. Our results reveal that lattice relaxation and strain are maximized at ~4° due to moiré-induced reconstruction (**Figure 2**). We observed an enhancement in valence band spin-orbit coupling (SOC) at 4°, using the energy separation between X_A and X_B excitons as an indicator, which is closely linked to interlayer hybridization and local strain. Spatially resolved spectroscopy further revealed site-specific modulations of the X_B exciton within the moiré lattice, with distinct splitting at high-symmetry stacking sites, providing direct evidence that exciton behavior is governed not only by global twist angle, but also by local atomic registry and stacking environment. These findings demonstrate that moiré superlattices in TMDs offer a tunable platform for engineering excitonic properties and SOC at the nanoscale through twist-angle and stacking control. We are currently extending this work to R-type twisted MoTe₂ bilayers, where correlated topological phases, such as the fractional quantum anomalous Hall effect (FQAHE), have been observed in the 2.6°-3.8° range, beyond the theoretically predicted flat-band regime (~1°–2°). We hypothesize that extended lattice reconstruction, local strain, and interlayer coupling reshape the moiré potential in R-type stacks, stabilizing emergent quantum phases. Correlatively probing spatially resolved structural and excitonic modulations at cryogenic Ts will be essential to this study.





Vortex-Lattice Topology and Its Impact on Phonon Dynamics. Topologically ordered structures, such as polar vortex lattices, offer a new frontier for studying quantum phenomena in ferroic materials [4]. Using monochromated, momentum-resolved STEM-EELS with nanometer spatial and meV energy resolution, we reveal how the chiral vortex lattice in PbTiO_3 modulates the vibrational spectrum in both real and reciprocal space (**Figure 3**). These modulations enhance as periodic phonon softening at vortex cores, vortex-induced “swoop” features in the phonon dispersion, and strong dichroism associated with local chirality and lattice asymmetry. Importantly, topological defects such as dislocations and domain boundaries give rise to distinct localized vibrational responses, significantly altering spectral features at the defect core, which return to bulk-like behavior beyond the core. This spatially resolved vibrational mapping directly links lattice topology to phonon dynamics, confirmed by large-scale machine-learned molecular dynamics simulations that reproduce both the frequency shifts and vortex-induced vibrational symmetry breaking. Our findings show that ferroelectric topologies can impose symmetry-selective control over phonons and realize dynamic modulation of thermal, electronic, and phonon-mediated properties through lattice design and topological manipulation.

Future Work

Proximity-Modulated Excitonic and Topological States in Moiré Heterostructures. We will explore vdW moiré heterostructures, such as MoTe_2 paired with $1\text{T}'\text{-WTe}_2$, a quantum spin Hall insulator with strong spin-orbit coupling and in-plane anisotropy, to investigate proximity-induced modulation of excitonic and topological states across the moiré interface. MoTe_2 offers a tunable

excitonic landscape, while WTe_2 introduces strong correlations and edge-state physics. We hypothesize that interfacial hybridization in twist-controlled heterostructures will enable control over interlayer excitons, valley polarization, and possibly topological edge modes. Using cryogenic, liquid helium-cooled monochromated STEM-EELS, we aim to directly probe these effects and gain new insights into exciton-topology coupling in 2D moiré systems.

Toward Predictive Modeling of Phonon Scattering in q-EELS. As q-EELS becomes more widely used for phonon studies, a deeper understanding of the scattering mechanisms that govern phonon visibility is needed. Selection rules and coherence effects across the crystal basis can obscure specific phonon branches and alter the effective Brillouin zone. We aim to develop a predictive framework that incorporates these effects into efficient modeling strategies, enhancing the accuracy, interpretability, and experimental guidance of q-EELS measurements in complex materials.

Probing Quantum Critical Phonon and Electronic Excitations via High-Momentum EELS. We plan to leverage our advancements in high-momentum-resolution EELS and inelastic electron scattering selection rules to investigate phonon modes that carry angular momentum, as well as electronic signatures of 2D quantum materials at finite momentum. Phonons with angular momentum play a key role in quantum phenomena such as the anomalous Hall effect and ultrafast demagnetization; however, their study has been limited by the lack of techniques capable of probing excitations at finite momentum. As quantum materials approach critical transitions, their many-body electronic states are expected to exhibit characteristic softening behaviors, reflecting underlying changes in electronic structure. Our work will focus on capturing these signatures, advancing our ability to probe quantum critical behavior in both phononic and electronic systems.

References

- [1]. May, A. F.; Du, M.-H.; Cooper, V. R.; McGuire, M. A. Tuning Magnetic Order in the van Der Waals Metal Fe_5GeTe_2 by Cobalt Substitution. *Phys. Rev. Mater.* 4, 074008 (2020).
- [2]. H. Ni, A. F. May, J. Zuo and M. Chi, Probing Structural and Chemical Short-Range Ordering in $\text{Fe}_5\text{-xGeTe}_2$ Using 4D-STEM and EELS, in revision (2025).
- [3]. E. Thompson, K.T. Chu, F. Mesple, X.-W. Zhang, C. Hu, Y. Zhao, H. Park, J. Cai, E. Anderson, K. Watanabe, T. Taniguchi, J. Yang, J.-H. Chu, X. Xu, T. Cao, D. Xiao, M. Yankowitz, Microscopic signatures of topology in twisted MoTe_2 , *Nat. Phys.* 1–7 (2025).
- [4]. E. R. Hoglund, H. A. Walker, K. Hussain, D. Bao, H. Ni, A. Mamun, J. Baxter, J. D. Caldwell, A. Khan, S. T. Pantelides, P. E. Hopkins and J. A. Hachtel, Nonequivalent Atomic Vibrations at Interfaces in a Polar Superlattice, *Advanced Materials* 36, 2402925 (2024).

Publications

1. H. Ni, A. F. May, J. Zuo and M. Chi, Probing Structural and Chemical Short-Range Ordering in $\text{Fe}_5\text{-xGeTe}_2$ Using 4D-STEM and EELS, in revision (2025).
2. J. Smith, H. Tran, K. M. Roccapiore, Z. Shen, G. Zhang and M. Chi, Advanced Compressive Sensing and Dynamic Sampling for 4D-STEM Imaging of Interfaces, *Small Methods* 9, 2400742 (2025).

3. T. W. Pfeifer, H. A. Walker, H. T. Aller, S. Graham, S. Pantelides, J. A. Hachtel, P. E. Hopkins and E. R. Hoglund, Understanding Phonon Selection and Interference in Momentum-Resolved Electron Energy Loss Spectroscopy, arXiv, in revision (2025).
4. E. R. Hoglund and A. R. Lupini, Multidimensional Images and Aberrations in STEM, *Chinese Physics B* **33**, 096807 (2024).
5. Kumar, E. Tiukalova, K. Venkatraman, A. Lupini, J. A. Hachtel and M. Chi, Calibrating Cryogenic Temperature of TEM Specimens Using EELS, *Ultramicroscopy* **265**, 114008 (2024).
6. E. R. Hoglund, H. A. Walker, K. Hussain, D. Bao, H. Ni, A. Mamun, J. Baxter, J. D. Caldwell, A. Khan, S. T. Pantelides, P. E. Hopkins and J. A. Hachtel, Nonequivalent Atomic Vibrations at Interfaces in a Polar Superlattice, *Advanced Materials* **36**, 2402925 (2024).
7. H. Zhang, M. A. McGuire, A. F. May, H.-Y. Chao, Q. Zheng, M. Chi, B. C. Sales, D. G. Mandrus, S. E. Nagler, H. Miao, F. Ye and J. Yan, Stacking Disorder and Thermal Transport Properties of RuCl₃, *Phys. Rev. Mater.* **8**, 014402 (2024).
8. Z. Huang, T. Li, B. Li, Q. Dong, J. Smith, S. Li, L. Xu, G. Wang, L. Hu and M. Chi, Tailoring Local Chemical Ordering via Elemental Tuning in High-Entropy Alloys, *J. Am. Chem. Soc.* **146**, 2167 (2024).
9. H. Ni, W. R. Meier, H. Miao, A. F. May, B. C. Sales, J.-M. Zuo and M. Chi, Real-Space Visualization of Atomic Displacements in a Long-Wavelength Charge Density Wave Using Cryogenic 4D-STEM, *Phys. Rev. Mater.* **8**, 104414 (2024).

Advancements in Cryogenic and Monochromated STEM-EELS Experimentation for Quantum Materials

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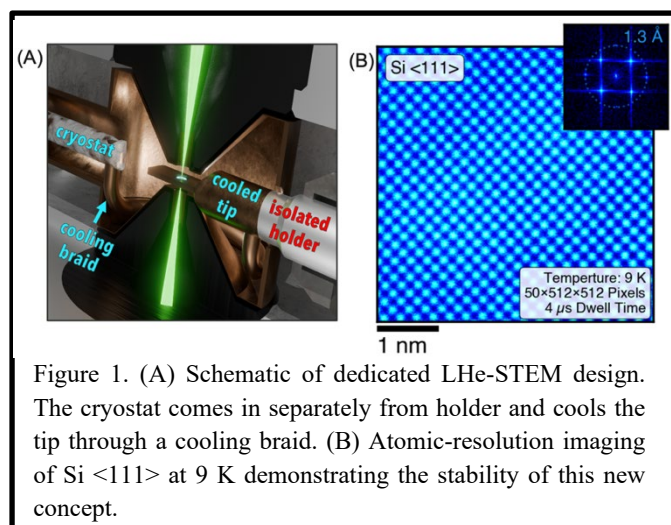
Keywords: cryogenic STEM, monochromated EELS, quantum materials

Research Scope

Understanding of both the atomic-structure and the low-energy excitations—including excitons, phonons, and charge orderings—in quantum materials is critical to unlocking their potential. However, this goal needs experimental techniques that can probe these samples with high spatial and spectral resolution directly at the critical temperatures where the emergent quantum properties appear. Our team has a unique combination of both instrumentation and expertise in cryogenic scanning transmission electron microscopy (cryo-STEM) and monochromated electron energy-loss spectroscopy (EELS), which situates us optimally to probe fragile quantum materials with atomic spatial resolution and sub-10 meV energy precision, both at liquid nitrogen (LN, ~100 K) and liquid helium (LHe, ~10 K) temperatures. Our focus is high spatial/spectral resolution monochromated EELS experiments at cryogenic temperatures to explore the emergent properties of two-dimensional (2D) van der Waals (vdW) heterostructures and correlated quantum phases.

Recent Progress

We have developed several key strategies to enhance our experimental studies of low-dimensional quantum materials leveraging cryogenic cooling and electron spectroscopy. These cutting-edge experimental developments provide unprecedented insight into these systems.



First Experiments with Atomic-Resolution Imaging on a Dedicated LHe-STEM: Quantum materials can host a wide range of fascinating properties but their behavior at LHe temperatures is critical for their interaction with other quantum phenomena (like superconductivity or topologically protected states). Our group is receiving the first-of-a-kind STEM featuring a dedicated LHe cooling stage, and this year we conducted initial experiments on an advanced prototype at the Bruker Production Facility. Shown in Figure 1a, is a schematic of the design. Here, the polepiece of the instrument is shown with the

cryostat coming in from the side, as opposed to directly through the rod itself. This design helps isolate the

rod from the helium bubbling vibrations that have, until now, prevented clear imaging of atomic-structure with active LHe cooling in STEM-mode. There are several key milestones that were achieved. Figure 1b shows a Si $\langle 111 \rangle$ atomic resolution image conducted at 9 K, from the Bruker prototype, demonstrating the extreme stability of the instrument.

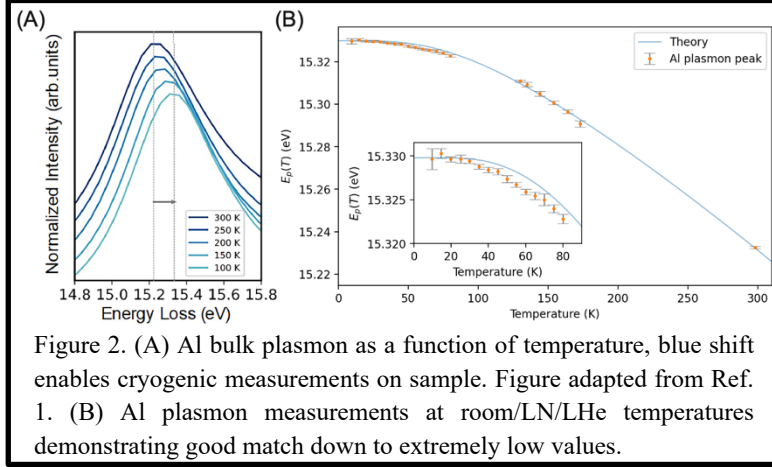


Figure 2. (A) Al bulk plasmon as a function of temperature, blue shift enables cryogenic measurements on sample. Figure adapted from Ref. 1. (B) Al plasmon measurements at room/LN/LHe temperatures demonstrating good match down to extremely low values.

high-temperatures². Initially validated at LN₂ temperatures, we extended this method to the LHe regime by integrating it with an advanced condenZero cryogenic system on a JEOL (S)TEM as well as on the dedicated LHe instrument at Bruker. The results demonstrate that the temperatures reached by the sample are consistent with the sub-10 K temperatures reported by the resistance thermometers³, thereby verifying that the deep cryogenic temperatures extend to the sample.

Identification of unique excitonic response at 9 K with Monochromated EELS: Having a comprehensive understanding of the thermal and spectral response of a sample are particularly impactful for studying moiré-engineered quantum states. During our test run, we examined a WS₂/1T-TaS₂ system, the 1T-TaS₂ undergoes temperature-dependent CDW transitions that induce strain and dielectric modulation in the adjacent WS₂ layer. Monochromated EELS at 9 K reveals a ~ 44 meV splitting of the WS₂ A-exciton, observable only below the CDW transition temperature. This splitting provides a direct spectroscopic fingerprint of interfacial coupling between excitons and CDW order, which can only be observed through combining the high energy resolution of monochromated EELS and the low-temperatures of LHe cryogenic cooling.

Balancing Spatial-Resolution and Momentum-Resolution in Monochromated EELS: Momentum-resolution is fundamentally challenging to add to the spatial/spectral-resolution of monochromated EELS because the momentum-resolution and spatial-resolution conflict with each other due to the fundamental limitations of quantum mechanics (i.e. Heisenberg uncertainty). As a result, conducting experiments with controlled degrees of spatial/momentum-resolution (at high spectral resolution) requires a deep understanding of the desired properties to extract from the system as well as the electron optics of the instrument. The STEM-FWP is one of the world leaders in momentum-resolved electron energy-loss spectroscopy (qEELS) and

Temperature Measurements Ready for Quantum: The instrument measures temperatures on resistance thermometers embedded in the holder itself, meaning the actual temperature at the sample might be different. We have developed¹ a direct on-sample calibration measurement for cryogenic STEM based on the temperature-dependent energy shift of the bulk aluminum (Al) plasmon peak in EELS pioneered by Mecklenburg *et al.* for

have developed multiple strategies to extract the emergent response from quantum materials leveraging qEELS.

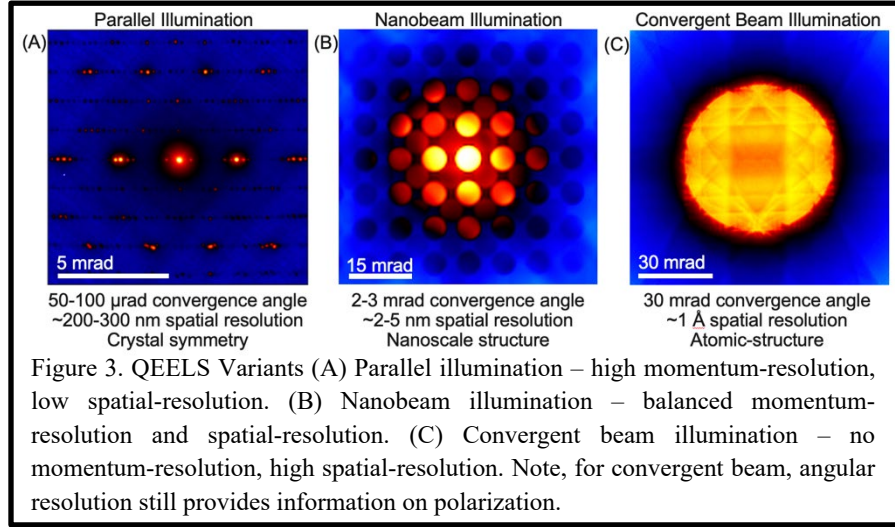


Figure 3 demonstrates the classes of qEELS that are investigated in this FWP. Figure 3A shows parallel illumination, meaning a large area of sample is simultaneously probed, allowing for the dispersion of a mode over that entire region to be probed efficiently, while still maintaining better spatial resolution than beam-line techniques like neutron

scattering. Figure 3B shows a nanobeam illumination mode, where the probe is converged but only to a small angle. Here, spatial resolution on the scale of a few nm is maintained along with the momentum-resolution of the materials Brillouin zone. Such modes are highly sensitive to local distortions such as polarization, strain, and CDW reconstructions, allowing us to directly map these effects surrounding nanoscale heterogeneities. Finally, Figure 3C shows a convergent beam-illumination. This is the conventional atomic-resolution STEM imaging mode that maximizes spatial-resolution, but at the cost of integrating all the momentum information at each point in angular space. However, by collecting EELS away from the optic axis critical polarization-sensitivity is still achieved granting a flavor of momentum-resolution, even in a momentum-integrated mode⁴. The dichroic measurements are highlighted in Figure 4 and demonstrate that not only do the vibrations modulate with the same periodicity of the ferroelectric vortex polarization in the samples, but an asymmetric vibrational response also emerges that shares the dichroic signal from Friedel symmetry breaking.

Developing New Theoretical Tools for QEELS: We have been working with theorists to develop new ways to simulate the complex physics that dominates quantum materials. One of the key techniques has been to develop software that utilizes machine-learning molecular dynamics (MLMD) simulations with vibrational EELS simulations to understand realistic physical models of extremely complex systems. For instance, in a polarized vortex topology, as found in PbTiO_3 superlattices, literally millions of atoms are needed to replicate the behavior observed in the experiment. While this is impossible to treat directly with DFT, MLMD that is trained on DFT, can be applied to these massive systems while retaining DFT accuracy. Figure 4 shows the application of MLMD to the polarization vortex system. In Figure 4A, the polarizations directly mapped from the MLMD supercell are shown, demonstrating the alternating vortices that define

the system. Through these simulations, we can examine the localizations of various modes (Figure 4B) or examine the way the PbTiO_3 dispersion has been altered by the formation of the vortices (Figure 4C). Such simulations present a critical path to understanding the complex measurements observed in monochromated qEELS. Especially for qEELS, the simulations can be computationally expensive. Ergo, we have also developed a code for simulations to generate qEELS dispersions at different levels of accuracy/efficiency while still maintaining the correct selection rules for the measured EELS signal⁵. This will enable the utilization of these techniques for large-scale materials exploration in complex systems and predictions of the vibrational responses.

Future Plans

Together, these developments in cryogenic cooling and monochromated EELS define a new paradigm in electron microscopy of quantum materials. By integrating precise temperature calibration, LHe-cooled low-drift operation, high-resolution EELS, and atomic-scale imaging, our development in cryo-STEM/EELS enables systematic exploration of structure–property relationships in low-dimensional quantum materials. By accessing <10 K temperatures with <10 meV energy resolution, we can observe quantum phase transitions, proximity effects, and excitonic phenomena that are inaccessible under conventional conditions, laying the foundation for the discovery and design of next-generation quantum and optoelectronic systems. Having the ability to measure types of phonons will allow us to better understand their influence, for example in chiral charge density wave transitions. To verify our understanding of these modes we are currently pursuing new high-momentum resolution EELS methods to measure the phonon angular momentum in hexagonal 2D materials. We plan to extend our current efforts to understand phonon and free carrier behavior in charge density wave transitions.

References

1. Kumar, A. *et al.* Calibrating cryogenic temperature of TEM specimens using EELS. *Ultramicroscopy* **265**, 114008 (2024).
2. Mecklenburg, M. *et al.* Nanoscale temperature mapping in operating microelectronic devices. *Science* **347**, 629–632 (2015).
3. Johnson, C. W. *et al.* High-Resolution Imaging and Spectroscopy in STEM Below 10 Kelvin. *Microscopy and Microanalysis* **31**, oza048.713 (2025).
4. Hoglund, E. R. *et al.* Nonequivalent Atomic Vibrations at Interfaces in a Polar Superlattice. *Advanced Materials* **36**, 2402925 (2024).
5. Pfeifer, T. W. *et al.* Understanding phonon selection and interference in momentum-resolved electron energy loss spectroscopy. Preprint at <https://doi.org/10.48550/arXiv.2503.09792> (2025).

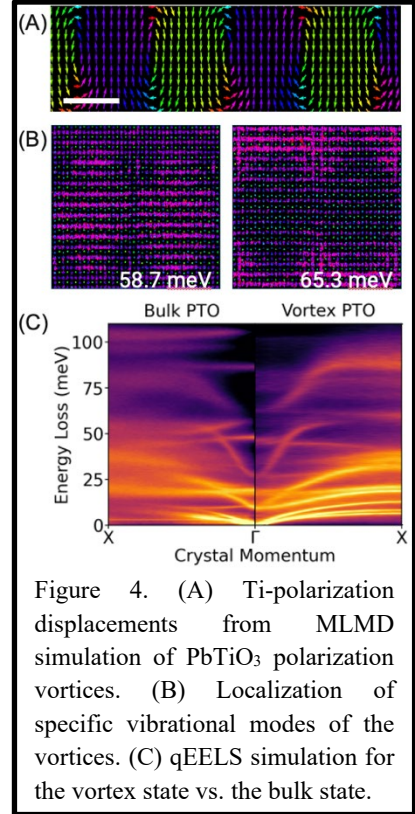


Figure 4. (A) Ti-polarization displacements from MLMD simulation of PbTiO_3 polarization vortices. (B) Localization of specific vibrational modes of the vortices. (C) qEELS simulation for the vortex state vs. the bulk state.

Publications (10)

1. H. Ni, A. F. May, J. Zuo and M. Chi, Probing Structural and Chemical Short-Range Ordering in Fe_{5-x}GeTe₂ Using 4D-STEM and EELS, in revision (2025).
2. J. Smith, H. Tran, K. M. Roccapriore, Z. Shen, G. Zhang and M. Chi, Advanced Compressive Sensing and Dynamic Sampling for 4D-STEM Imaging of Interfaces, *Small Methods* **9**, 2400742 (2025).
3. T. W. Pfeifer, H. A. Walker, H. T. Aller, S. Graham, S. Pantelides, J. A. Hachtel, P. E. Hopkins and E. R. Hoglund, Understanding Phonon Selection and Interference in Momentum-Resolved Electron Energy Loss Spectroscopy, arXiv, in revision (2025).
4. E. R. Hoglund and A. R. Lupini, Multidimensional Images and Aberrations in STEM, *Chinese Physics B* **33**, 096807 (2024).
5. Kumar, E. Tiukalova, K. Venkatraman, A. Lupini, J. A. Hachtel and M. Chi, Calibrating Cryogenic Temperature of TEM Specimens Using EELS, *Ultramicroscopy* **265**, 114008 (2024).
6. E. R. Hoglund, H. A. Walker, K. Hussain, D. Bao, H. Ni, A. Mamun, J. Baxter, J. D. Caldwell, A. Khan, S. T. Pantelides, P. E. Hopkins and J. A. Hachtel, Nonequivalent Atomic Vibrations at Interfaces in a Polar Superlattice, *Advanced Materials* **36**, 2402925 (2024).
7. H. Zhang, M. A. McGuire, A. F. May, H.-Y. Chao, Q. Zheng, M. Chi, B. C. Sales, D. G. Mandrus, S. E. Nagler, H. Miao, F. Ye and J. Yan, Stacking Disorder and Thermal Transport Properties of RuCl₃, *Phys. Rev. Mater.* **8**, 014402 (2024).
8. Z. Huang, T. Li, B. Li, Q. Dong, J. Smith, S. Li, L. Xu, G. Wang, L. Hu and M. Chi, Tailoring Local Chemical Ordering via Elemental Tuning in High-Entropy Alloys, *J. Am. Chem. Soc.* **146**, 2167 (2024).
9. H. Ni, W. R. Meier, H. Miao, A. F. May, B. C. Sales, J.-M. Zuo and M. Chi, Real-Space Visualization of Atomic Displacements in a Long-Wavelength Charge Density Wave Using Cryogenic 4D-STEM, *Phys. Rev. Mater.* **8**, 104414 (2024).
10. G. Ren, G. Y. Jung, H. Chen, C. Wang, B. Zhao, R. K. Vasudevan, J. A. Hachtel, A. R. Lupini, M. Chi, D. Xiao, J. Ravichandran and R. Mishra, Strain-Driven Stabilization of a Room-Temperature Chiral Multiferroic with Coupled Ferroaxial and Ferroelectric Order, *Advanced Functional Materials* **35**, 2416560 (2025).

Cryogenic Electron Microscopy for Electrochemical Energy Materials

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Keywords: CryoEM, tomography, operando, energy, electrochemistry

Research Scope

The research theme of this proposal is to establish an integrated research program (Fig. 1) to explore the use of cryoEM and cryoET to characterize the spatial organization of atoms and molecules and the compositional and structural variations underlying dynamic chemical processes in an exciting family of electrochemical energy materials relevant to DOE missioned research. We hypothesize that the ability to freeze materials' authentic dynamic structural and chemical configuration under cryo conditions will reveal unprecedented knowledge about the electrochemical processes. We propose to enable this ability by developing cryogenic preservation techniques to freeze materials in operando under voltage bias. We also hypothesize that the 3D structure and chemical mapping of their constituents with unprecedented spatial and temporal resolution will provide a more complete understanding of these electrochemical materials. We will explore state of the art image processing methods for CryoET. Our long-term vision is to build a world-leading research program for discovering and understanding fundamental aspects of electrochemical energy materials and devices by advancing and establishing cryoEM as a foundational technique.

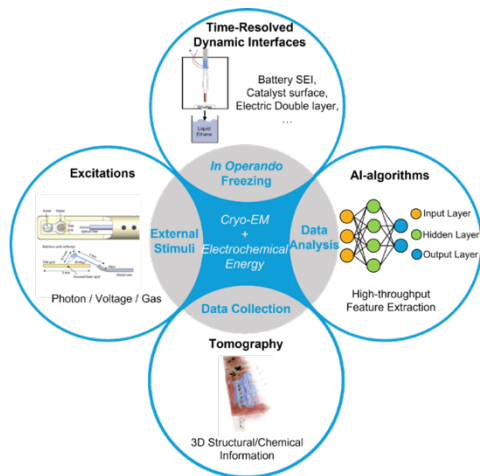


Figure 1. Our proposal is centered on the development of the cryogenic electron microscopy methodology from sample preparation to data collection and image processing to retrieve unprecedented structural and chemical information to understand the properties of electrochemical energy materials under different environmental conditions in its operational conditions.

Recent Progress

We organize our research program into three thrusts and summarize key scientific achievements below. This work has resulted in 17 published papers, with 5 papers jointly between the co-PIs.

Thrust 1. CryoEM of in operando frozen solid-liquid interfaces

Thrust 2. CryoEM tomography over multiple length scales

Thrust 3. Frozen electrochemical energy materials in response to external stimuli (gas, photon)

Progress 1: CryoEM of in operando frozen solid-liquid interfaces

The ability to freeze and stabilize reaction intermediates in their metastable states and obtain their structural and chemical information with high spatial resolution is critical to advance materials technologies such as catalysis and batteries.¹⁻³ We developed an electrified operando-freezing methodology to preserve these metastable states under electrochemical reaction conditions for cryogenic electron microscopy (cryo-EM) imaging and spectroscopy.⁴ Using Cu catalysts for CO₂ reduction as a model system, we observe restructuring of the Cu catalyst in a CO₂ atmosphere while the same catalyst remains intact in air at the nanometer scale. Furthermore, we discover the existence of a single valence Cu (1+) state and C–O bonding at the electrified liquid–solid interface of the operando-frozen samples, which are key reaction intermediates that traditional ex situ measurements fail to detect. This work highlights our novel technique to study the local structure and chemistry of electrified liquid–solid interfaces, with broad impact beyond catalysis (Fig. 2).

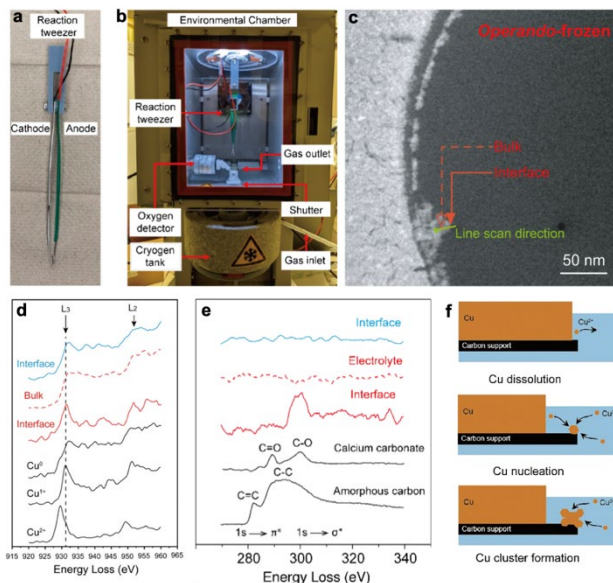


Figure 2. (a) Digital image of reaction tweezer. (b) Digital image of environmental chamber for the plunge freezing method, showing all parts of this chamber including tweezer, gas outlet, shutter, gas inlet, oxygen detector and cryogen tank. (c) The cryo-STEM-ADF images of an operando-frozen sample. Showing the sample at the edge of the copper grid. (d, e) EELS signal taken from the line scan in (c), showing the intermediate Cu (+1) state. (f) The schematic of Cu, showing the dissolution and redeposition process during electrochemical CO₂RR.

Progress 2: Capturing the swelling of solid-electrolyte interphase in lithium batteries

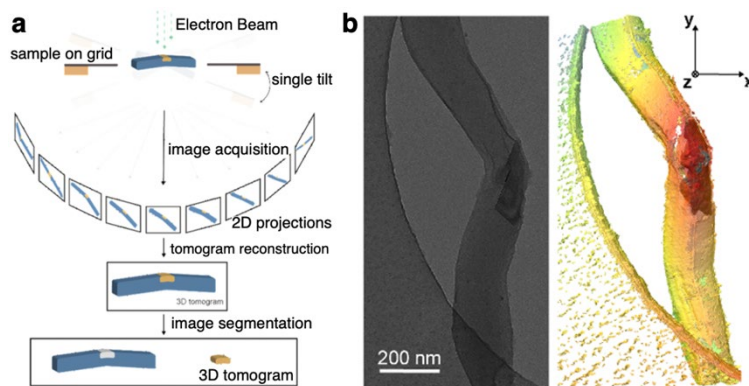
Although liquid-solid interfaces are foundational in broad areas of science, characterizing this delicate interface remains inherently difficult because of shortcomings in existing tools to access liquid and solid phases simultaneously at the nanoscale. This leads to substantial gaps in our understanding of the structure and chemistry of key interfaces in battery systems. In this work, which was published in *Science*, we adopted and modified a thin film vitrification method to preserve the sensitive yet critical interfaces in batteries at native liquid electrolyte environments to enable cryoEM and spectroscopy (Fig. 3). We report substantial swelling of the solid-electrolyte interphase (SEI) on lithium metal anode in various electrolytes. The swelling behavior is

dependent on electrolyte chemistry and is highly correlated to battery performance. Higher degrees of SEI swelling tend to exhibit poor electrochemical cycling.

Progress 3: CryoEM tomography over multiple length scales

We developed a cryoET and high-resolution cryoEM imaging approach to investigate nanoscale heterogeneity in lithium metal dendrites in 3D. Through this approach, we discovered that formation of extended solid electrolyte interface (extended SEI) is spatially and temporally distinct from LiH, decoupling the formation of these two important processes which contribute to capacity decay during lithium metal battery cycling (Fig. 4). Based on the finding of spatial and temporal separation of LiH growth with the extended SEI, we proposed that the region of the lithium metal dendrite far from the initial LiH nucleation and growth site formed a thick extended SEI through

reactions with the surrounding electrolyte, which prevented hydrogen species from diffusing through the thick SEI and reacting with the Li metal surface to form LiH. Therefore, the formation of extended SEI and LiH are spatially distinct from each other. Our study not only provided a 3D characterization of nanoscale heterogeneities in lithium metal dendrites, but also discovered a spatial separation between LiH and extended SEI growth and proposed a mechanism for this spatial separation. Overall, this study provides a detailed understanding of LiH and extended SEI



batteries.

Future Plans

Visualizing and understanding transient states provides tremendous insight into how any reaction proceeds. Some stable intermediate states in batteries (e.g. phase change, alloying) may exist

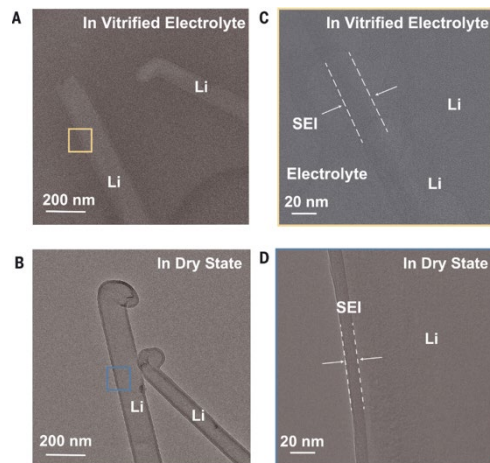


Figure 3. SEI on Li dendrite in dry state and vitrified organic electrolyte imaged with cryo-TEM. (A and B) Li metal dendrites in vitrified electrolyte and in dry state. (C and D) HRTEM of SEI on Li metal dendrite in vitrified electrolyte and in dry state.

formation, both of which contribute to capacity loss in lithium metal

Figure 4. (a) The schematic of cryo-ET data collection and image processing procedures. (b) A single image from the tilt series of Li metal dendrite (left panel) and the corresponding 3D representation of reconstructed calendar aged Li metal dendrite (right panel). The darker contrast region in the cryo-EM image corresponds to LiH.

within a time scale of minutes to hours, which allows them to be characterized with the cryoEM methods we developed in previous studies. *Here we **hypothesize** that we could capture these metastable intermediates by directly plunge-freezing the entire device during its operation without shutting off the applied current or voltage.* Success in kinetically trapping metastable intermediates will largely be determined by the freezing rate, which can vary depending on several parameters (e.g., sample thickness, cryogen, plunging speed, etc.). The main goal of Thrust 1 is to understand the structural and chemical information of electrochemical materials/liquid interfaces at the in-operando frozen states. We will design, engineer, and build an electrochemical plunge-freezing apparatus with optimized freezing protocols that can capture short-lived intermediates present during electrochemical device operation. We will extend these protocols to oxidation experiments including oxygen evolution reaction (OER) catalysts to capture active and degrading morphologies under OER conditions, to better understand the mechanisms of catalyst degradation. We expect the results of Thrust 1 to bring significant new insights towards dynamic electrochemical processes occurring at the nanoscale.

Combined with the operando freezing technique developed in Thrust 1, we will establish how electrochemical energy systems operate across multiple length scales, from the individual particle to full device level. Current direct observation of sensitive battery materials, including lithium metal anode and zinc anode for aqueous battery, relies on two-dimensional (2D) imaging, leaving out their three-dimensional (3D) relationship. We plan to use cryo-ET to visualize the lithium metal, zinc metal as well as their SEI, in 3D at nanometer resolution and cryo-EM to reveal atomic details in local regions.

In Thrust 3, we propose to study the response of electrochemical energy materials to external stimuli, particularly gases and light. Understanding the interaction of these materials with gases is crucial as it directly impacts their performance and efficiency in energy conversion and storage applications. Gases such as methane and carbon dioxide, as two greenhouse gas, are of significant interest in clean energy transition. They can be transformed into valuable energy resources or chemicals through processes like steam reforming or photocatalytic conversion. Cryo-EM can be utilized to study these processes at the nanoscale, providing detailed insights into the structural and compositional changes of materials under different gas and light stimuli.

References

1. K. Xu, *Electrolytes and interphases in Li-ion batteries and beyond*. Chem. Rev. **114**, 11503-11618 (2014).
2. A. Sood, et al. *Electrochemical ion insertion from the atomic to the device scale*. Nat. Rev. Mater. **6**, 847-867 (2021).
3. M. Z. Bazant, K. Thornton, and A. Ajdari, *Diffuse-charge dynamics in electrochemical systems*. Phys. Rev. E **70**, 021506 (2004).
4. Y. Li, et al. *Electrified operando-freezing of electrocatalytic CO₂ reduction cells for cryogenic electron microscopy*. Nano Lett. **24**, 10409-10417 (2024).

Publications

1. Q. Fan, et al. *Phase segregation dynamics in mixed-halide perovskites revealed by cryogenic electron microscopy*. Cell Rep. Phys. Sci. **6**, 102653 (2025).
2. Z. Zhang, et al. *Resolving three-dimensional nanoscale heterogeneities in lithium metal batteries with cryogenic electron tomography*. Matter **8**, 102266 (2025).
3. W. Yu, et al. *Electrochemical formation of bis(fluorosulfonyl)imide-derived solid-electrolyte interphase at Li-metal potential*. Nat. Chem., **17**, 246-255 (2025).
4. Y. Li, et al. *Electrified operando-freezing of electrocatalytic CO₂ reduction cells for cryogenic electron microscopy*. Nano Lett. **24**, 10409-10417 (2024).
5. Y. Yang, et al. *Capacity recovery by transient voltage pulse in silicon anode batteries*. Science **386**, 322-327 (2024).
6. Y. Li, et al. *In-situ formation of liquid crystal interphase in electrolytes with soft templating effects for aqueous dual-electrode-free batteries*. Nat. Energy **9**, 1350-1359 (2024).
7. S. Peng, et al. *Kinetics and Mechanism of Light-Induced Phase Separation in a Mixed- Halide Perovskite*. Matter **6**, 1-14 (2023).
8. R. A. Vilá, et al. *LiH formation and its impact on Li batteries revealed by cryogenic electron microscopy*. Sci. Adv. **9**, eadf3609 (2023).
9. Z. Zhang, et al. *Capturing the swelling of solid-electrolyte interphase in lithium metal batteries*. Science **375**, 66-70 (2022).

Visualization of the finite-momentum pairing state in EuRbFe₄As₄

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Keywords: Unconventional Superconductivity, magnetic order, Pair Density Wave, Finite-momentum pairing, Doppler shift

Research Scope

The pair density wave (PDW) is a novel superconducting state in which Cooper pairs carry center-of-mass momentum in equilibrium, leading to the breaking of translational symmetry [1]. Experimental evidence for such a state exists in high magnetic field and in some materials that feature density wave orders that explicitly break translational symmetry. However, evidence for a zero-field PDW state that exists independent of other spatially ordered states has so far been elusive. Here, we show that such a state exists in the iron pnictide superconductor EuRbFe₄As₄ (Eu-1144), a material that features coexisting superconductivity ($T_c \sim 37$ K) and magnetism ($T_m \sim 15$ K) [2]. We show from the Spectroscopic Imaging Scanning Tunneling Microscopy (SI-STM) measurements that the superconducting gap at low temperature has long-range, unidirectional spatial modulations with an incommensurate period of ~ 8 unit cells. Upon raising the temperature above T_m , the modulated superconductor disappears, but a uniform superconducting gap survives to T_c . When an external magnetic field is applied, gap modulations disappear inside the vortex halo. The SI-STM and bulk measurements show the absence of other density wave orders, showing that the PDW state is a primary, zero-field superconducting state in this compound. Both four-fold rotational symmetry and translation symmetry are recovered above T_m , indicating that the PDW is a smectic order.

In addition, we performed a doping dependent study of the Eu-1144 system, and we show evidence from SI-STM that a phase-modulated superconducting order parameter exists in the ground state of Eu-1144, which is another form of the PDW. By utilizing the quasiparticle interference (QPI) imaging technique, we reveal that the magnetic superconducting state features gapless excitations of a residual Fermi surface, which break the four-fold rotational (C_4) symmetry of the crystal lattice. The C_4 symmetry can be restored by temperatures and magnetic fields that change magnetic ordering, demonstrating that the anisotropic residual Fermi surface is closely tied to the crystal's magnetic order. The observed anisotropy can be naturally explained by the unidirectional Doppler shift in the quasiparticle energies that is inherent to a phase-modulated superconductor. By investigating a theoretical model that accounts for the simultaneous presence of superconductivity and helical magnetic order, we show that such a modulated state is symmetry required and generated by a combination of local time-reversal and inversion symmetry breaking.

Recent Progress

Doping dependent study of magnetic superconductor Eu-1144 has revealed highly distinct properties of the modulated superconductivity. The topograph shown in Fig. 1a shows relatively less number dopants as indicated by red crosses in Fig. 1b. In this FOV, an amplitude modulation of the superconducting order parameter is observed such that the coherence peak positions are spatially modulated as shown in Fig. 1c. In the overdoped sample (Fig. 1d) in which more dopants are found as indicated by red crosses in Fig. 1e, no amplitude modulation of the superconducting order parameter is observed. However, as we shall discuss later, a signature of the phase modulated superconductivity was observed as a C_2 symmetric residual Fermi surface.

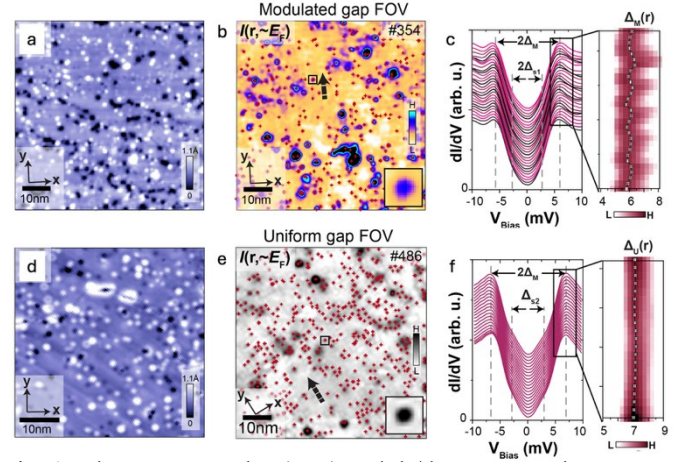


Fig. 1 a, b, c Topograph, $I(r, E_F)$ and dI/dV spectra where amplitude gap modulation is present. a, e, f, same as a, b, c, but in the overdoped region where amplitude modulation is absent.

We next proceed to measure the local spectroscopic properties of Eu-1144. Shown in Fig. 1a is a map of the local values of the gap $|\Delta(\mathbf{r})|$ measured at each point within a $\sim 30\text{nm} \times \sim 30\text{nm}$ FOV. Remarkably, a unidirectionally modulated $|\Delta(\mathbf{r})|$ along the Fe-Fe direction is clearly resolved. The spatial variation of $|\Delta(\mathbf{r})|$ is well described by the form $|\Delta(\mathbf{r})| = |\Delta_0| + |\Delta_1|\cos(\mathbf{Q}_{PDW} \cdot \mathbf{r})$, with $|\Delta_0| = 6\text{ mV}$ and $|\Delta_1| = 0.6\text{ mV}$. We see clearly from this image that the unidirectional modulations in $|\Delta(\mathbf{r})|$ persist across the image with a uniform period. The FT of Fig. 1a is shown in Fig. 1b, that exhibits clear $\mathbf{Q}_{PDW}$ peaks (circled) corresponding to the modulation of $|\Delta(\mathbf{r})|$ seen in Fig. 1a. The observed incommensurate wavelength is about eight unit-cells. Direct inspection of the modulations in Fig. 2a as well as the sharpness of the $\mathbf{Q}_{PDW}$ peak in Fig. 2b indicates that the coherence length of the $|\Delta(\mathbf{r})|$ modulations is larger than 30 nm. Our observation of the spatially modulated energy gaps is our primary result and indicates the presence of electron pairs with a finite center-of-mass momentum, as we explain below.

We next study the temperature dependence of the phenomena observed in Figure 2a. Shown in Figs. 2c is a $|\Delta(\mathbf{r})|$ measured in the same FOV as Fig. 2a at 16K. It is obvious that with increasing temperature the modulations

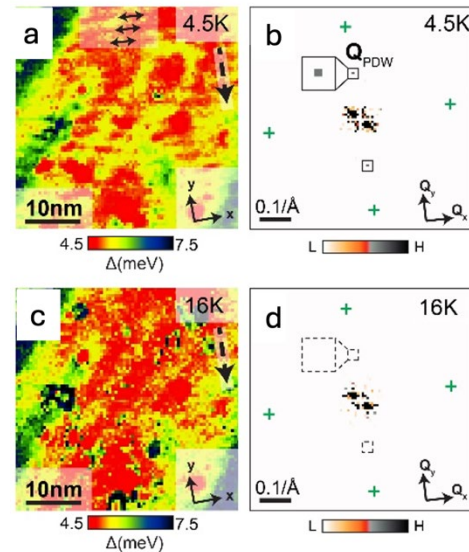


Fig. 2 a, gapmap measured at 4.5K below T_m and T_c . B, Fast Fourier transform of a. b, gapmap measured at 16K above T_m

disappear around the magnetic transition temperature T_m . Our conclusion is that the modulated part of the superconducting gap $|\Delta_1|$ disappears precisely when magnetism of the Eu plane is lost.

In the overdoped regime of Eu-1144, where amplitude modulations are absent, we performed QPI measurements to explore the properties of the finite-momentum superconducting state at $T = 4.5\text{K}$. Shown in Fig. 3a is a real space differential conductance image $g(r,0\text{mV})$ acquired at the Fermi level. Remarkably, this image shows the presence of pronounced scattering interference, indicating the presence of quasiparticles even at the Fermi level in the magnetic superconducting state – i.e., the superconducting state features gapless excitations. This can be understood as a residual Fermi surface arising from the Bogoliubov quasiparticle excitations, sometimes referred to

as a Bogoliubov Fermi surface. A Fourier transform (FT) of this image, shown in Fig. 3d, reveals clearly the presence of several scattering wavevectors. These wavevectors include $\mathbf{Q}_{x,y}$ aligned with the Fe-Fe lattice directions and wavevectors $\mathbf{Q}_{a,b}$ that are at approximately from the Fe-Fe direction. A second remarkable observation from this image is that it clearly shows the absence of the four-fold rotational symmetry that the material otherwise possesses. This is seen both by the different intensity of the features along the $\mathbf{Q}_x$ and $\mathbf{Q}_y$ directions, as well as the length of the scattering wavevectors $|\mathbf{Q}_x|$ and $|\mathbf{Q}_y|$. Having established that the magnetic superconducting state features quasiparticles at the Fermi level, we now show that these features are intimately related to the presence of magnetic order in the sample. To accomplish this, we raise the temperature to $T = 18\text{K}$ across the magnetic transition. In a standard superconductor, the main consequence of increasing the temperature is the enhancement of the DOS at low energy due to thermal broadening. Thus, we would expect from thermal broadening alone to see QPI signals at the Fermi level at higher temperature. Shown in Fig. 3c is the $g(r,0\text{mV})$ map at the Fermi level taken at 18K in the same area of the sample. In contrast to the expectation from thermal broadening, this image and its FT show that all periodic modulations associated with scattering, and thus with QPI, are absent in the nonmagnetic state, with only randomly distributed signals due to defect states present in real space (Fig. 3c). Thus, our temperature-dependent QPI measurements clearly show that the presence of the residual Fermi surface arises from the interplay between superconductivity and magnetism. We next consider the breaking of C_4 symmetry seen in the Bogoliubov QPI (BQPI) spectrum in the magnetic superconducting state. One possibility for this breaking of C_4 symmetry is the direction of the in-plane magnetic moments in the Eu^{2+} layer closest to the STM tip. Recall that the magnetically ordered state consists of aligned Eu moments in a given Eu^{2+} layer, whose in-plane orientation rotates by 90° between consecutive Eu^{2+} layers. While the structure of the

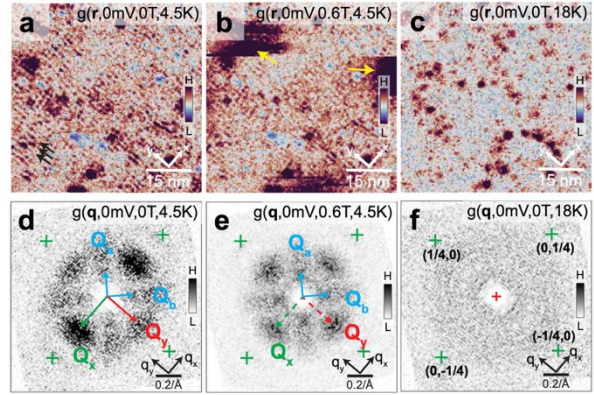


Fig. 3 a, $g(r,0\text{mV})$ map measured at 4.5K. b, $g(r,0\text{mV})$ map measured at 0.6T along c-axis that is greater than saturation field. c, $g(r,0\text{mV})$ measured at 18K that is above T_m below T_c . d, e, f, Fourier transforms of a, b, c, respectively.

material as a whole retains C_4 symmetry in the magnetic state, each individual FeAs layer does not have this symmetry since the Eu^{2+} moments select an in-plane direction. Importantly, the application of a modest out-of-plane magnetic field (0.6 T) is sufficient to polarize the Eu^{2+} moments out of the plane, which approximately restores the C_4 symmetry in every individual FeAs layer. Shown in Fig. 3b is a $g(\mathbf{r}, 0\text{mV})$ image obtained at a 0.6 T external field along the c-axis. This image shows Abrikosov vortices together with QPI modulations. A FT of the real-space image in Fig. 3e, shows that C_4 symmetry is restored both in the intensity of the features along the q_x and q_y axes and in the length of the scattering wavevectors $|\mathbf{Q}_{x,y}|$. This indicates that the anisotropy of the QPI is closely related to the orientation of the Eu^{2+} magnetic order. We now proceed to investigate the shape of the detected residual Fermi surface in the magnetic superconducting state. Previous ARPES measurements on ER-1144 show a normal-state Fermi surface that consists of three concentric hole pockets at and two electron pockets at the M point [3]. We find that the magnitudes of our scattering wavevectors $\mathbf{Q}_x$ and $\mathbf{Q}_y$ are reproduced well by a backscattering vector associated with only one of the hole pockets. The QPI patterns seen in Fig. 3d and e show high-intensity spots that are isolated in the reciprocal lattice space. Such discrete spots arise naturally in superconducting materials at low energies when the superconducting gap has significant momentum space anisotropy. For example, in the case of the cuprates, the constant energy contours at low energies are banana-shaped, reflecting the underlying d-wave nature of the superconducting gap together with the nearly circular hole pocket. All these observations are consistent with signatures of the phase modulated superconductivity at the wavevector $\mathbf{Q}$ - the Bogoliubov quasiparticle dispersion $E(\mathbf{k})$ is modified by having an offset term (dubbed Doppler shift) $\delta E(\mathbf{k}) = \frac{1}{2}\hbar v_{\mathbf{k}} \cdot \mathbf{Q}$ where $v_{\mathbf{k}}$ the velocity at momentum $\mathbf{k}$. For a unidirectional wavevector $\mathbf{Q}$, such a Doppler shift breaks spatial symmetries of the quasiparticle's wavefunction in reciprocal space. Moreover, a sufficiently large Doppler shift is generally expected to result in a residual Fermi surface of Bogoliubov quasiparticles inside the superconducting state.

Future Plans

We plan to continue doping dependent studies of the finite momentum pairing state in $\text{EuRbFe}_4\text{As}_4$ and construct a phase diagram.

References

1. Daniel F. Agterberg, J.C. Séamus Davis, Stephen D. Edkins, Eduardo Fradkin, Dale J. Van Harlingen, Steven A. Kivelson, Patrick A. Lee, Leo Radzihovsky, John M. Tranquada, and Yuxuan Wang, *The Physics of Pair-Density Waves: Cuprate Superconductors and Beyond*, *Annu. Rev. Condens. Matter Phys.* **11**, 231–270 (2020).
2. K. Iida, Y. Nagai, S. Ishida, M. Ishikado, N. Murai, A. D. Christianson, H. Yoshida, Y. Inamura, H. Nakamura, A. Nakao, K. Munakata, D. Kagerbauer, M. Eisterer, K. Kawashima, Y. Yoshida, H. Eisaki, and A. Iyo, *Coexisting spin resonance and long-range magnetic order of Eu in $\text{EuRb-Fe}_4\text{As}_4$* , *Phys. Rev. B* **100**, 014506 (2019)
3. T. K. Kim, K. S. Pervakov, D. V. Evtushinsky, S. W. Jung, G. Poelchen, K. Kummer, V. A. Vlasenko, A. V. Sadakov, A. S. Usoltsev, V. M. Pudalov, D. Roditchev, V. S. Stolyarov, D. V. Vyalikh, V. Borisov, R. Valentí, A. Ernst, S. V. Eremin, and E. V. Chulkov, *Electronic structure and coexistence of superconductivity with magnetism in $\text{RbEuFe}_4\text{As}_4$* , *Phys. Rev. B* **103**, 174517 (2021)

Publications

1. He Zhao, Raymond Blackwell, Morgan Thinel, Taketo Handa, Shigeyuki Ishida, Xiaoyang Zhu, Akira Iyo, Hiroshi Eisaki, Abhay N. Pasupathy and Kazuhiro Fujita, *Smectic pair-density-wave order in $\text{EuRbFe}_4\text{As}_4$* , *Nature* **618**, 940 (2023).
2. He Zhao, Raymond Blackwell, Shigeyuki Ishida, Akira Iyo, Hiroshi Eisaki, Roland Willa, Yue Yu, Daniel F. Agterberg, Rafael M. Fernandes, Joërg Schmalian, Abhay N. Pasupathy, and Kazuhiro Fujita, *Visualizing the finite-momentum pairing state in $\text{EuRbFe}_4\text{As}_4$ via quasiparticle interference*, Under review (2025).

Direct Probing Polarization and Magnetization Behaviors in Ferroics by In Situ Cryogenic-(S)TEM

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Keywords: Multiferroics, Topological defects, Skyrmions, *in situ* cryo-TEM, Domain switching dynamics

Research Scope

This research task, under the FWP Number MA-015-MACA, aims to investigate the ordering of charge and spin degrees of freedom – particularly those associated with topological defects such as ferroic domain walls, vortices, and chiral textures in ferroics and quantum materials – under external stimuli, to unveil the underlying physical principles governing macroscopic functionalities. We utilize *in situ* electron microscopy to investigate the dynamics and functionalities of topological defects across phase transitions in response to external electric and magnetic fields. This is performed under precisely controlled thermal environments, with particular emphasis on cooling down to liquid helium temperatures (~ 10 K), to access low-energy states and unveil emergent phenomena that are otherwise masked at higher temperatures.

Recent Progress

In the last two years, our research focused mainly on understanding and manipulation of magnetic spin textures and ferroelectric domain structures in ferroic systems using cryogenic (S)TEM and *in situ* electric/magnetic fields.

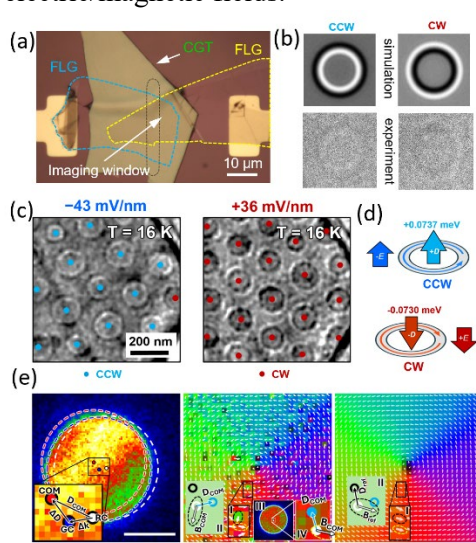


Fig. 1. Electric-field control of spin helicity in skyrmionic bubbles. (a) Optical image of FLG (a few layers of graphene)/CGT/FLG on a custom silicon nitride membrane for *in situ* biasing cryo-TEM experiments. (b) Simulated and experimental LTEM images of counterclockwise (CCW) and clockwise (CW) bubbles. (c) LTEM images obtained after negative and positive electric field and a constant magnetic field (50 mT) cooling. The CW (CCW) bubbles are marked with red (blue) dots. (d) Schematics of in-plane spins within the Bloch domain walls under negative (left) and positive (right) electric fields. Electric-field-induced Dzyaloshinskii–Moriya interactions (d) are indicated with the blue and red arrows. (e) A new 4D-STEM method we developed via circular Hough transform and refinement for spin mapping with an order of magnitude improvement in measurement accuracy. Spin-vector map of permalloy near the vortex core based on the traditional COM method (middle), our method (right). The experimental intensity distribution within the center disk is shown on the left [3].

Deterministic electric-field control of spin helicity in skyrmionic bubbles in 2D vdW magnet

Electric field-control of magnetic skyrmions is a key capability to realize skyrmion-based qubit for quantum computing [1]. We show that the skyrmion chirality in the insulating centrosymmetric 2D vdW magnet $\text{Cr}_2\text{Ge}_2\text{Te}_6$ can be controlled by the direction of the external electric field applied during the magnetic field cooling process. The electric-field-tuned chirality remains stable despite variations in magnetic and electric fields. Our theoretical investigation reveals that nonzero Dzyaloshinskii-Moriya interactions between

nearest neighbors, induced by the external electric field, change sign upon reversing the field direction, thereby facilitating chirality selection. Our results demonstrate that electric fields can effectively control the stability and chirality of magnetic skyrmions in insulating systems, providing a crucial foundation for designing skyrmion-based spintronic and quantum computing devices [2].

On the methodology side, we developed a new iteration procedure for magnetic imaging based on Lorentz 4D-STEM through the refinement of peak shapes and positions in circular Hough transformation filtered central diffraction disks (Fig. 1e). The refinement is based on nonlinear trust-region algorithm in two-dimensional space with combined elliptical Gaussian and Lorentzian functions. The accuracy in the disk position measurement can achieve sub- μrad , about one to two orders improvement comparing to the traditional COM based method when the intensity distribution inside the disk is considerably uneven and when the rigid-body-shift model breaks down [3].

Topological ferroelectric domain structures and domain switching in $\text{SrBi}_2\text{Ta}_2\text{O}_9$

Lead-free $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) is a promising ferroelectric material due to its high fatigue endurance and low leakage current [4]. However, the atomic-scale domain structure and switching dynamics have not been reported. Our study shows that spontaneous polarization arises from canted bismuth-cation displacements, forming 90° and Ising-type 180° domain walls. We found topological pairs of vortex and antivortex where three domain walls converge. Our in situ electrical biasing experiments show the dominance of 180° polarization switching over 90° , where oxygen octahedral connectivity is protected by ferroelastic energy in the 90° domain wall, consequently removing all (anti)vortices in the poled states. Our study demonstrates that the outstanding ferroelectric properties arise from the interplay of structural order parameters and intriguing domain wall networks consisting of vortices and antivortices, providing an ideal testbed to explore topological defect phenomena [5].

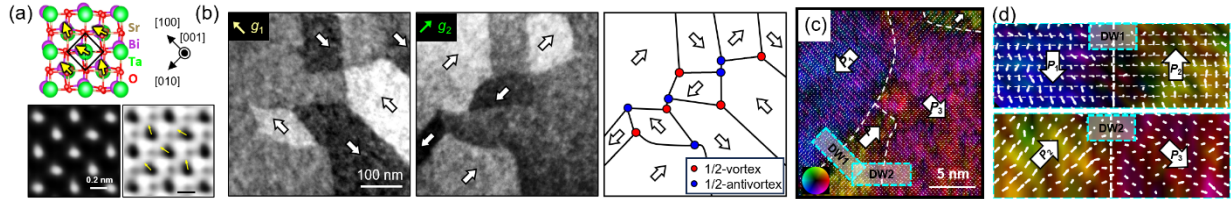


Fig. 2. Topological ferroelectric domain structures in $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBTO) and electric-field-induced domain switching. (a) Crystal structure of SBTO. The dipole moments are mainly generated by the displacement between the center of mass of the oxygen octahedra and the positions of bismuth atoms. HAADF and ADF STEM images below the atomic model. The yellow arrows indicate dipole moments within the unit cell. (b) SAED pattern and dark-field (DF) images showing four equivalently degenerate ferroelectric domains along the $[001]$ zone axis. Based on bright/dark/gray contrasts in the DF images, polarization orientation is indicated by the white arrows. (c) Schematics of ferroelectric domain structures under zero bias (middle), positive (left), and negative (right) electric fields. The blue and red dots are $1/2$ -vortex and $1/2$ -antivortex, respectively. The 180° domain walls that disappeared due to domain switching are indicated with dotted lines, and the remaining 90° walls are indicated with solid lines. (d) Atomic-resolution polarization map (top), color-coded according to the color-wheel in the inset and zoomed-in maps of 180° (middle) and 90° (bottom) domain wall areas.

Future Plans

Building on our expertise in cryogenic electron microscopy and atomic scale characterization, we propose future studies that explore emergent domain phenomena and orbital-driven phase behavior in complex oxides and spinel compounds. These investigations aim to uncover new mechanisms for electronic and spin control at the nanoscale, for next-generation microelectronics and quantum computing.

Ferro-rotational phase transition and domain structures

Ferro-rotational order, marked by rotating structural units and a coupled electric dipole moment, has drawn attention for its interplay with magnetic chirality and polarization—offering new avenues for studying domain behavior and magnetoelectric control [6]. Our preliminary study reveals highly anisotropic nanoscale ferro-rotational domains in $\text{RbFe}(\text{MoO}_4)_2$ through cryogenic TEM imaging and diffraction, showing plate-like features and sharp $\{001\}$ domain walls where rotational moments flip across Rb planes [7]. If these walls persist below the Néel temperature, they may give rise to charged ferroelectric-domain-wall configurations with emergent properties. Such domain configurations could represent a universal motif across ferro-rotational systems, offering a new framework for tuning electronic and spin functionalities at the nanoscale, paving the way for domain-wall-based nanoelectronics.

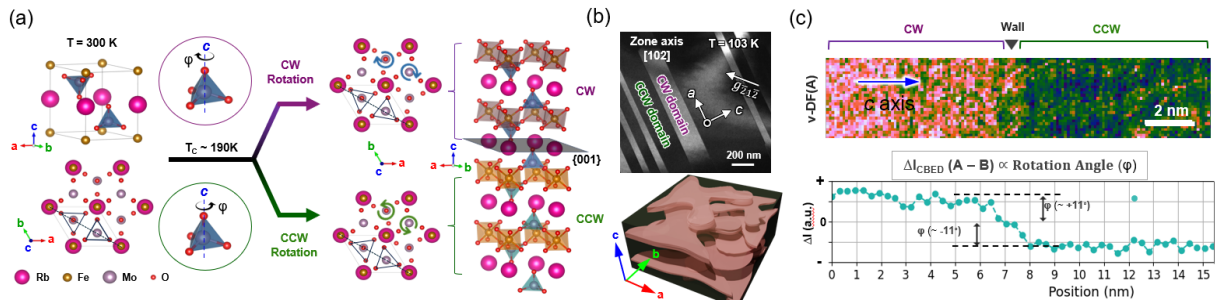


Fig. 3. Ferro-rotational phase transition in $\text{RbFe}(\text{MoO}_4)_2$ (RFMO) and domain structures. (a) schematic of RFMO crystal structures from space group $P3m1$ to $P3$ with two structural variants: clockwise (CW) and counterclockwise (CCW) rotation domains, as identified by the rotation of MoO_4 tetrahedra. (b) dark-field (DF) TEM image imaged along the $[102]$ zone axis with $(2\bar{1}2)$ reflection at 103 K (top panel) and a schematic of three-dimensional domain structure (bottom panel). (c) Virtual-DF (v-DF) image (top panel) obtained from 4D STEM data acquired at 100 K . (e) line profile of average intensity (bottom panel) obtained from the v-DF image, showing $\sim 1.5 \text{ nm}$ domain wall width.

Orbital-selective Peierls metal-insulator transitions

Transition-metal spinel compounds have been widely studied because they exhibit various exotic magnetic and electronic ground states [8]. Leveraging our in situ cryogenic electron microscopy capabilities—including electrical biasing and atomic-resolution STEM imaging—we will investigate orbital-driven oligomerization phenomena in mixed-valence CuIr_2S_4 , characterized by an average iridium valence of $\text{Ir}^{3.5+}$. We will fabricate microdevice TEM samples using focused ion beam (FIB) to directly probe transport properties while structural characterization is being performed for direct structure-property correlation. Our preliminary results in Fig. 4 show transport data, electron diffraction patterns, DF TEM images, and atomic resolution STEM images, successfully acquired such correlative experiments. Our data shows two separate phase transitions with $T_{C1} \sim 190$ K and $T_{C2} \sim 60$ K, showing $[111]$ and $[110]$ superlattice reflections, respectively. We also observe the formation of quasi-2D nanoplate-like domains below T_{C1} and T_{C2} , which indicates the long-range order along the $[111]$ direction when $T_{C1} > T > T_{C2}$ and short-range order along the $[110]$ when $T < T_{C2}$. We will further explore the underlying electronic structures in terms of direct d-d hopping, for the two insulating states observed. This approach will establish a powerful framework for directly correlating electronic transport with nanoscale structural transitions, advancing the understanding of orbital-driven phase behavior in strongly correlated systems.

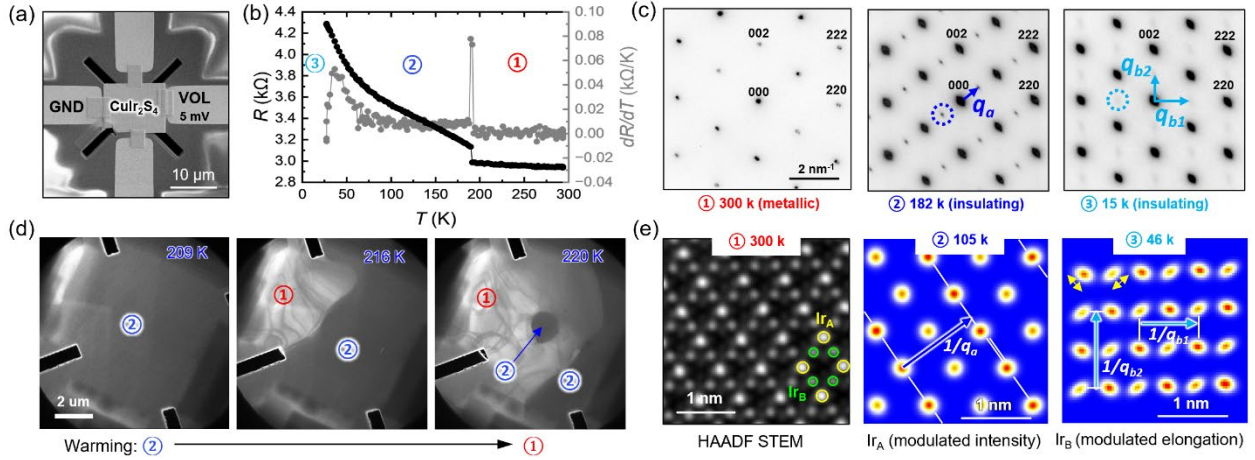


Fig. 4. Orbital-driven Peierls metal-insulator transition in CuIr_2S_4 by microelectronics-integrated cryogenic TEM. (a) Scanning electron microscopy image of the FIB-fabricated microdevice showing electrically connected CuIr_2S_4 lamella. (b) Resistance – temperature (R - T) curves and first derivative of resistance with respect to temperature (dR/dT) obtained from the device TEM sample shown in (a) during cooling experiment in TEM. (c) Selected-area electron diffraction (SAED) patterns along the $[1-10]$ zone axis at different temperatures. (d) DF TEM images obtained upon warming the TEM device sample, showing insulator (2)-metal (1) transition. (e) Atomic resolution HAADF STEM image at 300 K (left), 105 K (middle), and 46 K (right). The image at 105 K only shows the Ir_A columns, while the image at 46 K only shows Ir_B columns. Two low-temperature images show structural modulations, consistent with the SAED patterns in (d).

References

- [1] C. Psaroudaki and C. Panagopoulos, *Skyrmion Qubits: A New Class of Quantum Logic Elements Based on Nanoscale Magnetization*, Phys. Rev. Lett. **127**, 067201 (2021).
- [2] M.-G. Han, J. D. Thomsen, J. P. Philbin, J. Mun, E. Park, F. Camino, L. Děkanovský, C. Liu, Z. Sofer, P. Narang, F. M. Ross and Y. Zhu, *Electric field control of magnetic skyrmion helicity in a centrosymmetric 2D van der Waals magnet*, Nano Lett. **25**, 13, 5174-5180 (2025).
- [3] L. Wu, M.-G. Han and Y. Zhu, *Toward accurate measurement of electromagnetic field by retrieving and refining the center position of non-uniform diffraction disks in Lorentz 4D-STEM*, Ultramicroscopy **250**, 113745, (2023).
- [4] C. A. P. de Araujo, J. D. Cuchiaro, L. D. McMillan, M. C. Scott and J. F. Scott, *Fatigue-free ferroelectric capacitors with platinum electrodes*, Nature **374**, 627-629 (1995).
- [5] J. Mun, F.-T. Huang, Y. Pivak, X. Fang, F. Camino, S.-W. Cheong, Y. Zhu and M.-G. Han, *Probing ferroelectric domain structures and their switching dynamics in SrBi₂Ta₂O₉ by in-situ biasing in transmission electron microscopy*, Commun. Mater. **5**, 1, 145 (2024).
- [6] S.-W. Cheong, D. Talbayev, V. Kiryukhin and A. Saxena, *Broken symmetries, non-reciprocity, and multiferroicity*, npj Quantum Mater. **3**, 19 (2018).
- [7] B. Gil, M.-G. Han, F.-T. Huang, S.-W. Cheong, M. Kim and Y. Zhu, *Nanoscale plate-like domain structures in ferro-rotational RbFe(MoO₄)₂*, under review
- [8] D. I. Khomskii and S. V. Streltsov, *Orbital effects in solids: Basics, recent progress, and opportunities*, Chem. Rev. **121**, 2992-3030 (2021).

Publications

(10 most relevant papers out of total 25 articles from this research task, Jan. 2023 - July. 2025)

1. Jang, J.; Jin, Y.; Nam, Y.-S.; Park, H.-S.; Kim, J.; Kang, K.T.; So, Y.; Choi, J.; Choi, Y.; Shim, J.; Sriboriboon, P.; Lee, D.K.; Go, K.-J.; Kim, G.-Y.; Hong, S.; Lee, J.H.; Lee, D.; Han, M.-G.; Son, J.; Kim, Y.; Taniguchi, H.; Kang, S.; Lee, J.-S.; Tian, H.; Yang, C.-H.; Zhu, Y.; Cheong, S.-W.; Choi, W.S.; Lee, J.; Choi, S.-Y. “Sub-unit-cell-segmented ferroelectricity in brownmillerite oxides by phonon decoupling”, Nat. Mater. 1-8 (2025).
2. Han, M.-G.*; Thomsen, J.D.; Philbin, J.P.; Mun, J.; Park, E.; Camino, F.; Dekannovsky, L.; Liu, C.; Sofer, Z.; Narang, P.; Ross, F.M.; Zhu, Y. “Electric field control of magnetic skyrmion helicity in a centrosymmetric 2D van der Waals magnet”, Nano Lett. (2025).
3. Liu, C.; Ai, F.; Reisbick, S.; Zong, A.; Pofelski, A.; Han, M.-G.; Camino, F.; Jing, C.; Lomakin, V.; Zhu, Y. “Correlated spin-wave generation and domain-wall oscillation in a topologically textured magnetic film”, Nat. Mater. 24, 3, 406-413 (2025).
4. Mun, J.; Potemkin, D.; Jang, H.; Park, S.; Mick, S.; Petrovic, C.; Cheong, S.-W.; Han, M.-G.*; Zhu, Y. “Atomic resolution scanning transmission electron microscopy at liquid helium temperatures for quantum materials”, Ultramicroscopy 267, 114039 (2024).
5. Mun, J.; Huang, F.-T.; Pivak, Y.; Fang, X.; Camino, F.; Cheong, S.-W.; Zhu, Y.; Han, M.-G.* “Probing ferroelectric domain structures and their switching dynamics in SrBi₂Ta₂O₉ by in-situ electric biasing in transmission electron microscopy”, Communications Materials 5, 1, 145 (2024).
6. Thomsen, J.D.; Han, M.-G.*; Penn, A.N.; Foucher, A.C.; Geiwitz, M.; Burch, K.S.; Dekanovsky, L.; Sofer, Z.; Liu, Y.; Petrovic, C.; Ross, F.M.; Zhu, Y.; Narang, P. “Effect of surface oxidation and

crystal thickness on the magnetic properties and magnetic domain structures of $\text{Cr}_2\text{Ge}_2\text{Te}_6$ ”, ACS Nano 18, 21, 13458-13467 (2024).

7. Hao, Y.; Chen, X.; Zhang, L.; Han, M.-G.; Wang, W.; Fang, Y.-W.; Chen, H.; Zhu, Y.; Hong, X. “Record high room temperature resistance switching in ferroelectric-gated Mott transistors unlocked by interfacial charge engineering” Nat. Commun. 14, 1, 8247 (2023).
8. Han, M.-G.*; Camino, F.; Vorobyev, P.A.; Garlow, J.; Rov, R.; Sohnle, T.; Seidel, J.; Mostovoy, M.; Tretiakov, O.A.; Zhu, Y. "Hysteretic responses of skyrmion lattices to electric fields in magnetoelectric Cu_2OSeO_3 ", Nano Lett. 23, 7143-7149 (2023).
9. Han, M.-G.*; Garlow, J.; Du, K.; Cheong, S.-W.; Zhu, Y. "Chirality reversal of magnetic solitons in chiral $\text{Cr}_{1/3}\text{TaS}_2$ ", Appl. Phys. Lett. 123, 022405 (2023).
10. Wu, L.; Han, M.-G.; Zhu, Y. “Toward accurate measurement of electromagnetic field by retrieving and refining the center position of non-uniform diffraction disks in Lorentz 4D-STEM”, Ultramicroscopy 250, 113745 (2023).

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Towards Universal Hall Transport Mapping at the Nanoscale in the Electron Microscope

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Research Scope

This project aims to achieve a mechanistic understanding of energy and angular momentum transport phenomena underpinning charge-neutral Hall effects, with the goal of enabling their quantitative characterization and control at the atomic scale. We focus on how quantum behaviors—such as spin, orbital, valley, exciton, and phonon Hall effects—can be harnessed through compositional and structural inhomogeneities in materials, including defects, interfaces, and reduced dimensionality. Our approach integrates monochromated aberration-corrected electron microscopy with in-situ biasing and gating liquid-helium cryogenic capabilities, combined with theoretical modeling and advanced materials synthesis to study epitaxial thin films and two-dimensional materials engineered via strategic interface modifications. Using these model systems, we aim to unravel the interplay between *d*-shell electron configurations and spin–orbit coupling, clarify how atomic-scale heterogeneities shape a family of Hall transport phenomena, identify the factors governing orbital angular momentum transmission across interfaces, and directly detect multiple charge-neutral Hall effects with nanometer-scale spatial resolution.

The spin Hall effect (SHE) has become a central mechanism in spin-based electronics, converting charge currents into transverse spin currents via spin–orbit coupling, with heavy 5d metals such as W and Pt providing strong spin–orbit torques. In parallel, theoretical predictions indicate the existence of an orbital Hall effect (OHE), potentially much larger than the SHE in light 3d-transition metals and not requiring spin–orbit coupling [1]. While optical and transport-based techniques such as magneto-optical Kerr effect and Hanle magnetoresistance have provided evidence for the OHE [1], key questions remain about its microscopic origins, nanometer-scale spin and orbital accumulation, and the magnitude of the orbital diffusion length, which has been reported with widely varying values. By exploiting the high spatial and spectral resolution of advanced electron microscopy, our work will directly probe OHE-related phenomena at the nanometer scale, distinguish spin from orbital contributions, and establish quantitative links between structural inhomogeneities and Hall transport mechanisms in quantum materials.

Recent Progress

Over the past fiscal year, in collaboration with Uppsala University, we investigated the spatial variation of the energy-loss magnetic circular dichroism (EMCD) signal in alumina-coated titanium thin films patterned into suspended bridge geometries. Titanium has recently been proposed to exhibit a sizable OHE, as evidenced by magneto-optical Kerr effect (MOKE) measurements in similar thin-film systems [1]. Building on these findings, we are now probing the same phenomenon using electron energy-loss spectroscopy (EELS) to achieve nanometer-

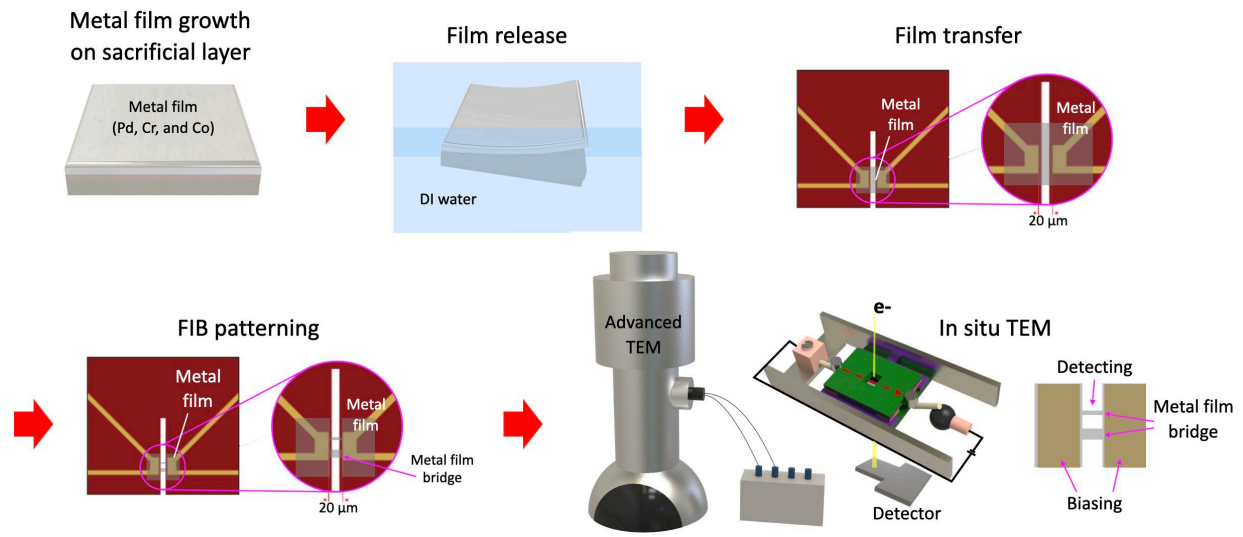


Figure 2. Workflow for creating suspended metal film bridges for in situ TEM studies. Metal films (Pd, Cr, and Co) are grown on a sacrificial layer, released in deionized water, and transferred onto pre-patterned substrates. Focused ion beam patterning defines suspended bridge structures ($\sim 20\ \mu\text{m}$ wide), enabling in situ TEM measurements of electrically biased films with nanometer-scale resolution.

scale spatial resolution. Our EMCD maps in a Ti sample revealed a dichroic signal localized at transverse edges of the sample with opposite magnitudes in the different edges. In contrast, the central region of the film exhibited no detectable EMCD signal above the noise level.

Parallel with the sample preparation method using electron-beam evaporation on SiNx substrates, we developed advanced preparation methods based on pulsed laser deposition (PLD) and molecular beam epitaxy (MBE) for making high quality self-supported devices. This is central to this program as it allows to study the different Hall effect signals as a function of various types of defects. Here, the films are grown on a sacrificial SrO layer, which is then dissolved, releasing the film and allowing transfer onto TEM chip. The final shape of the device is achieved with P/FIB. The schematic of the steps involved in the newly developed preparation process is shown in Fig.1.

While these methods allow precise microstructural control, it also introduces new challenges, particularly for a reliable transfer of high-quality metal thin films onto biasing-ready TEM devices suitable for EELS/EMCD measurements. We have successfully optimized this procedure and fabricated Cr and Pd thin films on SrO/LSAT(100) and SrO/LSAT(001) substrates,

respectively. Fig. 2 shows a representative Cr films after transfer and FIB fabrication. The process can introduce porosity, tearing, and other structural imperfections, as seen in Figs. 2a and 2b. The key is to keep this damage away from the TEM analyzed areas. Recent improvements to our growth/transfer protocol have reliably yielded high-quality samples, such as the one shown in the Figs. 3c 3d that suitable for in situ TEM Hall effect measurements.

In addition, we collaborated with Protochips to design new TEM devices with integrated electrical contacts capable of isolating different Hall contributions. This capability is essential, as metals such as Co, Cr, and Pd can exhibit conventional Hall effects arising from either hole or electron carriers [2]. The newly developed devices will allow us to distinguish and quantify these various Hall components.

Future Plans

We will exploit our improved transfer protocols to perform in situ EELS/EMCD measurements on high-quality Pd, Cr, Co, and Ti films using multi-contact TEM devices, enabling separation of conventional, spin, and orbital Hall contributions. Variable-temperature studies down to liquid-helium conditions will probe the temperature dependence of orbital accumulation and its underlying scattering mechanisms.

In parallel, PLD and MBE growth will be used to precisely control microstructure and interfaces, allowing us to systematically link defect type and density to Hall responses. By integrating advanced synthesis, in situ microscopy, and modeling, we aim to establish atomic-scale design rules for engineering charge-neutral Hall effects in quantum materials.

References

- [1] Y.-G. Choi, D. Jo, K.-H. Ko, D. Go, K.-H. Kim, H. G. Park, C. Kim, B.-C. Min, G.-M. Choi, and H.-W. Lee, *Observation of the orbital Hall effect in a light metal Ti*. *Nature* **619**, 52-56 (2023).
- [2] S. Foner, *Hall effect in Titanium, Vanadium, Chromium and Manganese**, *Physical Review* **107**, 1513 (1957).

Publications

J.C. Idrobo, *Technicolor at the Nanoscale is Heating Up: How Monochromation and Liquid He/N₂ Cryogenic Holders are Revolutionizing STEM*, *Microscopy and Microanalysis* **34**, DOI:10.1093/mam/ozaf048.001, Presented as a Conference Plenary Talk (2025)

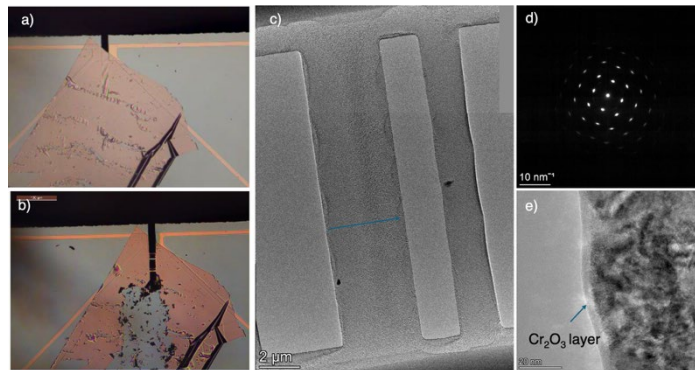


Figure 2. Fabrication and structural characterization of Cr thin-film biasing devices. a, Optical micrograph of the Cr film after initial deposition onto the biasing chip. b, Same device following plasma-focused ion beam (PFIB) shaping and isolation of electrical contacts to the electron-transparent bridges. c, TEM image of the fabricated electron-transparent bridges. d, Selected-area electron diffraction pattern from the synthesized device, revealing crystalline ordering. e, High-resolution TEM image showing the formation of a 2–4 nm Cr₂O₃ protective layer at the film surface.

Emergent Behavior in Nanoscale Functional Heterostructures

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Keywords: Magnetic nanostructures, van der Waals materials, topological structures, microscopy

Research Scope

Our vision is to develop a framework to design, explore and control emergent behavior in functional nanoscale heterostructures and deepen our understanding of the complex energy landscape that governs such behavior. We will focus on confined heterostructures of nanomagnetic materials comprising of ferromagnets (FM) and antiferromagnets (AF). The scientific challenges that we seek to address include understanding and controlling topologically non-trivial spin textures via geometric confinement, in addition to their transport behavior and driven dynamics. Our use-inspired research will focus on exploring the parameter space in two broad categories, (1) intrinsic such as composition, crystal structure and (2) extrinsic such as interfaces, geometric effects, and the presence of defects. Our approach will use 2D and 3D aberration-corrected Lorentz transmission electron microscopy (LTEM), and advanced scanning probe microscopy combined with simulations and machine-learning methods. Our work will lead to strategies to create and design nanoscale heterostructures that will exhibit desired spin textures and novel phenomena enabling transformational functionality for microelectronics and quantum relevant technologies.

Recent Progress

Ferromagnetic van der Waals (vdW) materials: vdW material ferromagnet $\text{Fe}_{5-x}\text{GeTe}_2$ has layered centrosymmetric structure which shows topological Hall effect (THE) over a wide range of temperatures, from room temperature down to 2 K. Additionally, temperature-dependent unconventional THE can be divided into three temperature regions. We unveiled the interplay between topological spin

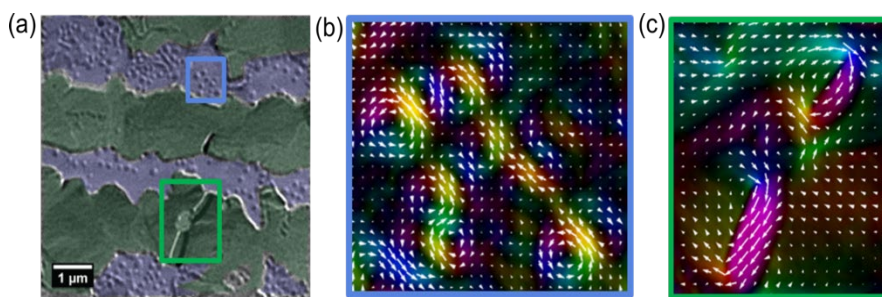


Figure 1. (a) LTEM image and corresponding magnetic induction maps at 100 K showing coexistence of (b) skyrmions and (c) merons.

textures and THE using LTEM. The high-temperature (> 170 K) THE is attributed to the formation of meron-antimeron pairs. When temperature is lower than 170 K, the skyrmions and merons coexist (Figure 4). We further found that the formation of merons or skyrmions is governed by the local magnetocrystalline anisotropy. We showed that the spatial variations in local magnetic

anisotropy are attributed to subtle fluctuations in Fe content. This work demonstrates that vdW magnetic materials could be promising candidates for the applications in skyrmionics/meronics.

Curved 3D Nanohelices: Curved 3D nanostructures provide a unique platform to explore the interplay between geometry topology and magnetic spin topology leading to unique magnetic states such as double-helix ground state. We explored the magnetic behavior of interwoven 3D Cobalt nanohelices fabricated using electron-beam induced deposition (Fig 2(a)). The magnetic state of these nanostructures was observed using off-axis electron holography and compared with micromagnetic simulations. We demonstrated that by applying specific global external magnetic fields, we can reconfigure the distribution of magnetic charges in the same nanostructure and create complex localized magnetic fields such as multipole field cusps, antivortices, and skyrmions. Our work provides insights into the effect of 3D curvature on the creation of topologically non-trivial field distributions that can be harnessed for proximity effects in various use-inspired applications.

Figure 2. (a) SEM image of an interwoven 3D printed magnetic nanostructure; (b) Simulated topological magnetic field arising from controlled distribution of magnetic charges in the 3D nanostructure.

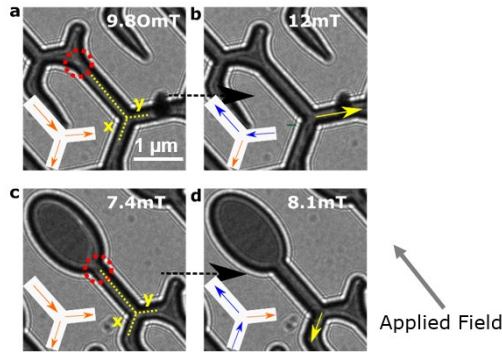


Figure 3. LTEM images of vortex domain walls observing path selectivity arising from domain wall chirality. (a-b) A bright region corresponding to a vortex of one chirality moves to the Y branch under an applied field. (c-d) a dark region corresponding to a vortex of opposite chirality to that of (a) moves along the X branch..

Nanomagnetic Galton boards: Domain wall propagation in nanomagnetic networks can strongly depend on the local spin texture as well as geometry. We have directly imaged the stochastic decision-making processes in nanomagnetic Galton boards fabricated from Permalloy using LTEM. We have uncovered that the randomness, essential to many types of neuromorphic computing, arises from a combination of factors: (1) the chirality of injected domain walls, which leads to a topologically dictated path selection at Y-shaped bifurcations, (2) asymmetry in the sizes of the bifurcated vertices within each honeycomb structure, results in a complex magnetic energy landscape, and (3) the strength of the applied magnetic field, leads to domain wall transformations.

By identifying these key mechanisms contributing to stochasticity, we have expanded our understanding of domain wall behavior in nanomagnetic

networks. Additionally, the gained insights offer a promising route toward neuromorphic computing applications.

Rich Spin Textures in Ferrimagnets:

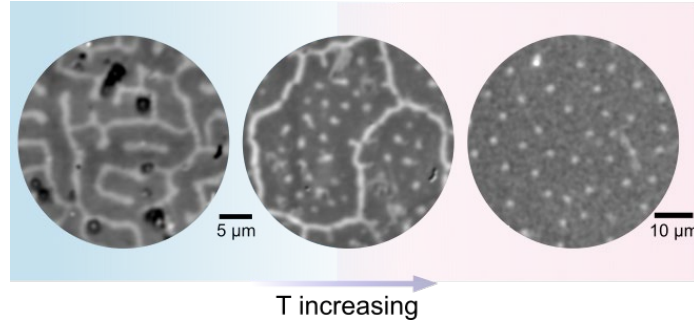


Figure 4. MOKE images of $\text{Mn}_{1.15}\text{Zn}_{0.85}\text{Sb}$ crystal showing rich spin textures as a function of applied magnetic field and temperature.

Ferrimagnets have both ferromagnetic and antiferromagnetic coupling. The difference in magnetic behavior of the two inequivalent sublattices results in exotic and diverse temperature-dependent spin texture. We investigated the field- and temperature-dependent behavior of spin textures in ferrimagnetic $\text{Mn}_{2-x}\text{Zn}_x\text{Sb}$ using magneto-optical Kerr effect microscopy and showed the formation of rich spin textures including stripes, high-charge-order skyrmion bags, and

skyrmion lattices. The nature of these spin textures was determined to be chiral Néel-type using LTEM. The atomically resolved STEM images showed a slight displacement of the Mn ions toward Sb sites thereby breaking local inversion symmetry. This work provides a pathway to use heterogeneity in a ferrimagnet to control and generate chiral nontrivial topological spin textures.

We also recently installed the BES-funded room temperature scanning NV microscope that we are now using for imaging magnetic domains in ferrimagnetic and antiferromagnetic materials under applied magnetic fields.

Machine learning and Automated microscopy: In order to obtain quantitative information on magnetic induction of the sample, it is essential to retrieve the phase shift of electron wave after it interacts with the sample in LTEM. In in-situ LTEM experiments, it is often not possible to acquire through-focus series of images for phase retrieval using methods such as TIE. We have developed a machine learning method, SIPRAD, based on automatic differentiation combined with deep-image-priors that enables magnetic phase retrieval from a single out-of-focus LTEM image. Our method enables qualitatively superior and quantitatively accurate phase reconstructions of time-resolved or in-situ LTEM data, and the method is available in the open-source software package PyLorentz developed by our group.

We also developed an automated method for imaging of in-situ magnetic domain behavior with sub-millisecond time resolution using the IDES Relativity system. Using this capability, we revealed the annihilation process of a transverse domain wall under applied transverse magnetic field through generation of an antivortex-vortex pair. Our work provides insights into design of future domain wall mediated spintronic applications.

Future Plans

Topological Excitations in Ferromagnetic van der Waals materials: We are exploring ways to control the formation of novel topological excitations such as skyrmions or spin textures with higher winding numbers and their behavior in van der Waals (vdW) ferromagnets. We will explore the role of local heterogeneities such as compositional variations, microstructural defects on the behavior of skyrmions and their nature (Bloch-type or Néel-type) in Fe-Ge-Te family. We will use high resolution TEM combined with in-situ field cooling protocols to understand their formation, and stability. We will elucidate the role of strain on skyrmion behavior by exfoliating flakes of vdW material on pre-patterned substrates consisting of nanopillars and nanoridges. Additionally, we will also study the role of local order/disorder as well as nanoscale strain on the magnetic behavior by combining in-situ X-ray nanodiffraction and X-ray photo correlation spectroscopy with LTEM imaging.

Curvature effects in magnetic nanostructures: We are exploring novel curved 3D geometries where the interplay between geometric topology and magnetic spin topology can lead to stabilization of new non-trivial spin textures and unique transport properties. In particular, we will understand the nucleation and propagation of domain walls during magnetization reversal of extended arrays of interwoven 3D nanohelices. We will correlate the geometric chirality of the nanohelices with the nature of the domain walls formed and their relationship with distribution of magnetic charges. We will also explore magnetic helicoidal nanotubes. By tuning the winding of the helicoid, we will influence the local magnetostatic interactions that lead to pinning of domain walls. Additionally, we will also explore the effect of a right-handed or a left-handed helicoid on the chirality and motion of domain walls in these nanostructures. We will use off-axis electron holography to map the local magnetic induction in 3D using vector field tomography. The experimental results will be combined with our micromagnetic simulations to elucidate the relative strengths of the contributing energy terms such as magnetostatic energy, exchange energy, and Zeeman energy.

Magnetic solitons in nanopatterned networks: We are advancing our understanding of domain wall motion in connected nanowire networks. Building on our earlier work, we are now exploring how topology and local energetics influence domain wall behavior in complex configurations. Additionally, we will study how local changes to magnetic anisotropy affect magnetic domain wall evolution in both static and dynamics scenarios. The changes to local anisotropy could be brought upon electrically, or chemically. We will also perform electrical transport measurements in-situ in LTEM which will enable us to correlate the magnetoresistance of these networks with the presence of magnetic solitons, and provide insight into their memrisive behavior. We will also explore the energetics of magnetic solitons in dipolar coupled nanopatterned networks, with a focus on magnetically frustrated artificial spin ice structures. Specifically, we aim to understand how geometry affects energy relaxation pathways in finite-sized structures. We will achieve this

through direct in-situ imaging under field-induced relaxation as well as thermal relaxation of the magnetic islands in artificial spin ice structures.

Publications

- [1] A.R.C. McCray, Y. Li, E. Qian, Y. Li, W. Wang, Z. Huang, X. Ma, Y. Liu, D.Y. Chung, M.G. Kanatzidis, A.K. Petford-Long, and C. Phatak, “Direct Observation of Magnetic Bubble Lattices and Magnetoelastic Effects in van der Waals $\text{Cr}_2\text{Ge}_2\text{Te}_6$,” *Adv Funct Materials*, **33**, 2214203 (2023).
- [2] Y. Li, X. Hu, A. Fereidouni, R. Basnet, K. Pandey, J. Wen, Y. Liu, H. Zheng, H.O.H. Churchill, J. Hu, A.K. Petford-Long, and C. Phatak, “Visualizing the Effect of Oxidation on Magnetic Domain Behavior of Nanoscale Fe_3GeTe_2 for Applications in Spintronics,” *ACS Appl. Nano Mater.* **6**, 4390–4397 (2023).
- [3] B. W. Casas*, Y. Li*, A. Moon, Y. Xin, C. McKeever, J. Macy, A. K. Petford-Long, C. M. Phatak, E. J. G. Santos, E. S. Choi and L. Balicas. Coexistence of Merons with Skyrmions in the Centrosymmetric van der Waals Ferromagnet $\text{Fe}_{5-x}\text{GeTe}_2$, *Adv. Mater.* **35**, 2212087 (2023). (*co-first author)
- [4] J. Fullerton, A.R.C. McCray, A.K. Petford-Long, and C. Phatak, “Understanding the Effect of Curvature on the Magnetization Reversal of Three-Dimensional Nanohelices,” *Nano Lett.* **24**, 2481–2487 (2024).
- [5] A.R.C. McCray, A. Bender, A. Petford-Long, and C. Phatak, “Simulation-trained machine learning models for Lorentz transmission electron microscopy,” *APL Machine Learning* **2**, 026120 (2024).
- [6] A.R.C. McCray, T. Zhou, S. Kandel, A. Petford-Long, M.J. Cherukara, and C. Phatak, “AI-enabled Lorentz microscopy for quantitative imaging of nanoscale magnetic spin textures,” *Npj Comput Mater* **10**, 1–10 (2024).
- [7] J. Fullerton, and C. Phatak, “Design and Control of Three-Dimensional Topological Magnetic Fields Using Interwoven Helical Nanostructures,” *Nano Lett.* **25**, 5148–5155 (2025).
- [8] Y. Li, M.R.U. Nabi, H. Park, Y. Liu, S. Rosenkranz, A.K. Petford-Long, J. Hu, S.G.E.T. Velthuis, and C. Phatak, “Observation of Topological Spin Textures in Ferrimagnetic $\text{Mn}_{2-x}\text{Zn}_x\text{Sb}$,” *Small*, **21**, 2406299 (2025).
- [9] K.L. Mendoza, H. Ni, G. Varnavides, M. Chi, C. Ophus, A. Petford-Long, and C. Phatak, “Quantitative phase retrieval and characterization of magnetic nanostructures via Lorentz (scanning) transmission electron microscopy,” *J. Phys.: Condens. Matter* **37**(20), 205301 (2025).
- [10] H. Arava, D. Sanz-Hernandez, J. Grollier, A. K. Petford-Long, “Real Space Imaging of Field-Driven Decision-Making in Nanomagnetic Galton Boards”, *Phys. Rev. Lett.*, **134**, 086704 (2025).

Liquid Cell Electron Microscopy: Heterogeneity and Fluctuations at Solid-Liquid Interfaces

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Keywords: Liquid cell electron microscopy, nucleation and growth, nanoscale materials transformations, non-equilibrium processes, solid-liquid interfaces

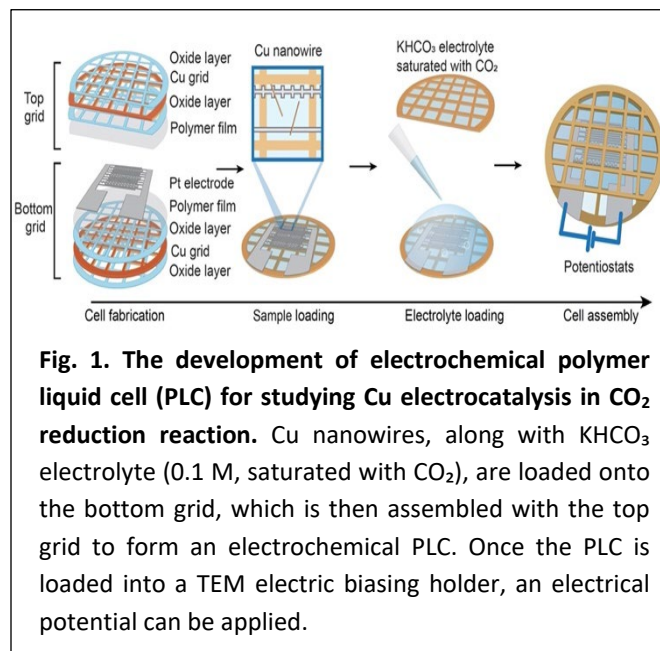
Research Scope

The overarching goal of this program is to develop and advance a state-of-the-art liquid cell transmission electron microscopy (TEM) platform to reveal how atomic-level heterogeneity and fluctuations at solid-liquid interfaces govern the physical and chemical processes of materials, with a primary focus on nucleation and nanoscale materials transformations. We are advancing this capability through the development of high-resolution liquid cells, fast imaging with high quantum efficiency, low-dose techniques to minimize electron beam damage, and machine learning-based image analysis. Using this platform, we investigate non-conventional nucleation and growth pathways, along with nanoscale materials transformations involving non-equilibrium processes and complex solid-liquid interfaces at the atomic level. Mechanistic insights are obtained through an integrated experimental-theoretical approach. The success of this program will address critical scientific challenges at the frontiers of basic energy sciences, enabling transformative advances in understanding materials behavior under realistic conditions and offering novel insights and strategies for materials discovery and applications.

Recent Progress

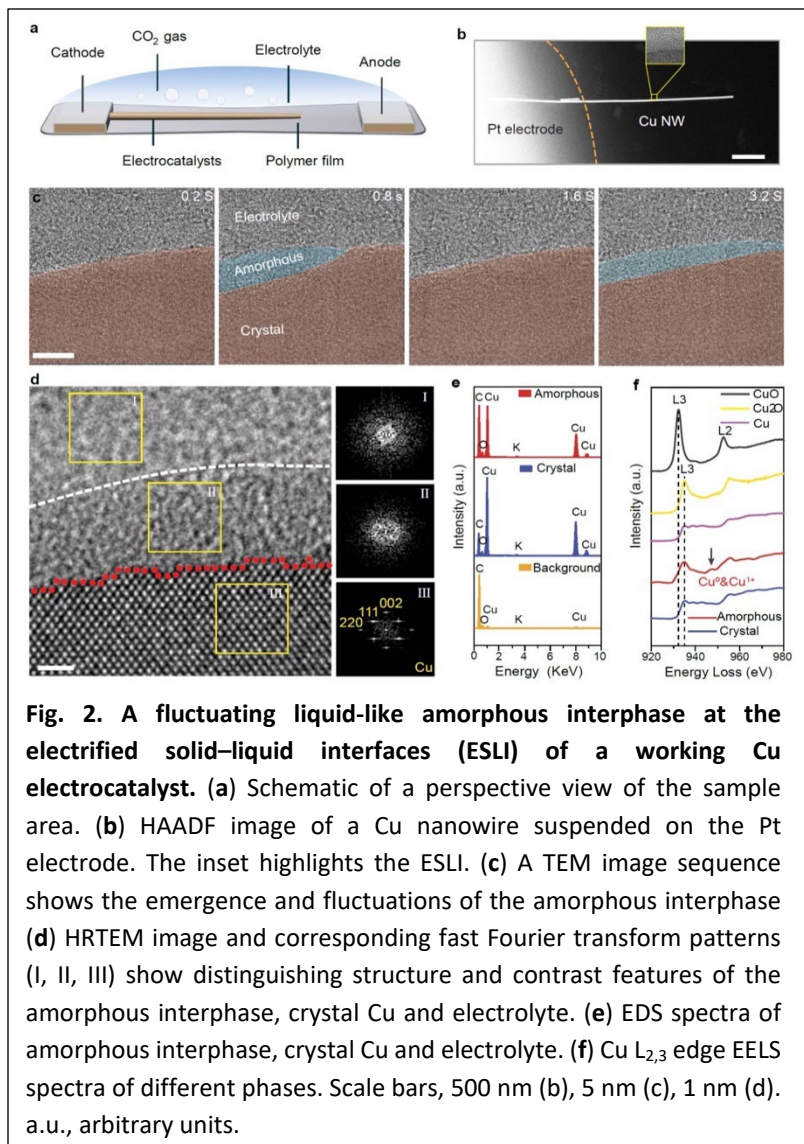
1. Atomic dynamics of solid-liquid interfaces

Solid-liquid interfaces play a pivotal role in a wide range of electrochemical processes relevant to energy, biology, and geochemistry. Electron and mass transport at electrified interfaces can induce structural modifications that significantly influence reaction pathways. Despite their importance, directly probing the atomic dynamics of solid-liquid interfaces under electric bias remains challenging,



owing to their being buried in liquid electrolytes and the limited spatial resolution of current *in situ* imaging techniques through liquids. With our development of novel polymer electrochemical liquid cells (PLCs) for TEM (Fig. 1), we directly monitored the atomic dynamics of copper (Cu) catalysts during CO₂ electroreduction reactions (CO₂ERs)¹. As shown in Fig. 2, a Cu nanowire was connected to a Pt cathode in electrolyte within a PLC, enabling real-time observation of the Cu–electrolyte interfaces under operating electrochemical conditions. Upon applying an electrochemical potential, we observed a fluctuating, liquid-like amorphous structure on the Cu nanowire surface, which cyclically appeared and disappeared (Fig. 2c–d). This amorphous interphase exhibited two distinct dynamic behaviors: (1) flowing along the crystalline Cu surfaces, and (2) interconverting with crystalline Cu, resulting in the originally smooth Cu surfaces becoming rough. Composition and valence-state analyses of the frozen amorphous interphase, using energy-dispersive X-ray spectroscopy (EDS) and electron energy-loss spectroscopy (EELS) (Fig. 2e–f), revealed Cu, C, H, and O, with Cu present in both Cu⁰ and Cu⁺ states. These findings were further validated by control experiments. Further studies showed that crystalline surfaces covered by the amorphous interphase experienced more severe Cu dissolution than bare surfaces, indicating that the amorphous interphase mediates catalyst dissolution and thus impacts catalyst stability.

This study demonstrates that the atomic dynamics of solid–liquid interfaces under electrocatalytic reactions provide new insights into intermediate formation and catalyst surface restructuring. Our PLC-TEM development opens new avenues for probing the atomic mechanisms of electrocatalysis across a wide range of material systems.² These advances enable a deeper understanding of dynamic atomic structure–function relationships and lay the foundation for



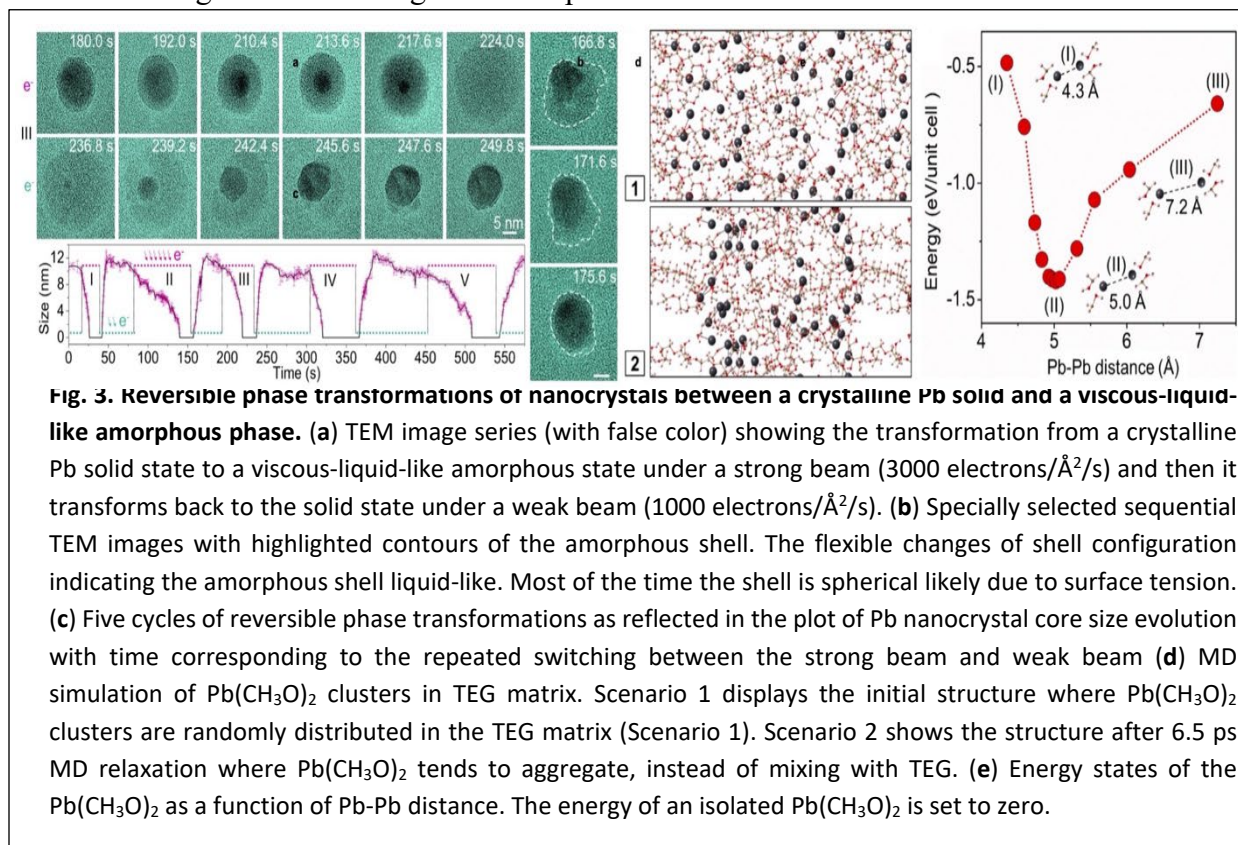
controlling diverse electrochemical reactions through the deliberate tuning of solid–liquid interfaces.

2. Unveiling nanoscale materials transformations

2.1 Reversible phase transformations between Pb nanocrystals and a viscous-liquid-like phase

Phase transformations play a critical role across science and technology, as they are often accompanied by property changes that enable applications ranging from sensing and energy storage to thermal energy conversion, drug delivery, and biotechnology. Extensive studies have been conducted to resolve the structural changes in materials undergoing phase transformations under various stimuli, including temperature variations, applied electric fields, light, electron beams, and more.

Many solid–solid phase transformations occur through local atomic rearrangements within the solid and are typically reversible. In contrast, structural transformations driven by solid–liquid chemical reactions are often irreversible, due to structural and chemical heterogeneity at solid–liquid interfaces or mass loss from reactants diffusing away. The resulting structures from solid–liquid reactions can be complex and challenging to resolve. Exploring reversible solid–liquid phase transformations and developing a fundamental understanding of their mechanisms are essential for advancing future technologies. However, directly observing such reversible transformations remains a significant challenge due to experimental limitations.



We recently reported reversible phase transformations between Pb metal nanocrystals and a unique viscous, liquid-like phase, discovered through *in situ* liquid cell TEM.³ The Pb nanocrystals were prepared *in situ* in a liquid cell under TEM, using a precursor solution of lead(II) acetylacetonate mixed with triethylene glycol (TEG). By modulating the electron current density (e.g., between 1000 and 3000 electrons/Å²/s), we observed remarkable reversible transformations of the Pb nanocrystals. As shown in **Fig. 3**, when the electron beam is focused on an as-synthesized Pb nanocrystal in the liquid cell, the nanocrystal expands and transforms into an amorphous phase, identified as a metal–organic, viscous, liquid-like phase exhibiting short-range ordering with a preferred Pb–Pb distance of 0.5 nm. When the beam is spread, the nanocrystal immediately regains its original crystallinity, size, and shape. Density functional theory (DFT) and molecular dynamics (MD) calculations indicate that this viscous, liquid-like phase forms through reactions between Pb and CH₃O fragments generated from the triethylene glycol (TEG) solution under electron beam irradiation.

We also observed similar structures in other metal nanoparticle systems (e.g., Bi) under electron beam irradiation or during electrochemical reactions, suggesting that the reversible transformations identified in this study may have broad applicability. The insights gained here could inform future applications of metal nanoparticles in sensing, drug delivery, and other technologies.

2.2 Understanding materials corrosion pathways

Unveiling materials' corrosion pathways is essential for understanding corrosion mechanisms and guiding the design of corrosion-resistant materials. We investigated the corrosion behavior of Sn@Ni₃Sn₄ and Sn nanocrystals in aqueous solution in real time using high-resolution liquid cell TEM. Our observations revealed unprecedented detail on the corrosion of Sn metal, with and without a Ni₃Sn₄ coating, at both nanometric and atomic scales.

The Sn@Ni₃Sn₄ nanocrystals exhibit pitting corrosion initiated at defect sites in the Ni₃Sn₄ protective layer. The initial isotropic etching evolves into facet-dependent etching, producing cavities terminated by low-index facets. Sn nanocrystals with fast etching kinetics undergo uniform corrosion, yielding smooth surfaces, whereas slower etching results in “creeping-like” behavior and rough surfaces. This study provides critical insights into the roles of coatings, defects, and ion diffusion in controlling corrosion kinetics and shaping final morphologies.

Future Plans

Development of liquid cell TEM platform. The advanced liquid cell TEM platform forms the foundation for numerous unique scientific discoveries that would be difficult to achieve by other means. We plan to further advance this platform by developing high-resolution, functional liquid cells and expanding its applications to unique systems that align with the program's scope.

Developing new methods for imaging of beam-sensitive materials. The team is developing advanced techniques to mitigate beam-induced damage—a critical need for this program, as many

material systems, including solvents and liquids, are highly susceptible to degradation under electron beam irradiation. Led by Co-PIs Chan and Ercius, this effort will make a significant contribution to the program's objectives and broaden its overall impact.

The study of PdH_x system. Using cutting-edge *in situ* liquid cell TEM, we investigated hydrogen desorption processes in hydrogen-rich β -PdH_x nanocubes with face-centered cubic (fcc) structures, achieving outstanding preliminary results on hydrogen intercalation dynamics. Building on these findings, we developed an atomistic model to elucidate the formation and structural transformation mechanisms of unconventional PdH_x structures. This modeling effort, led by co-PI Limmer, together with our experimental studies, will enable timely publication of our results and guide the batch synthesis of metastable PdH_x nanocrystals as well as other novel crystalline structures in intercalation-mediated materials. This work also highlights the effective use of electron beam interactions with liquids and the application of liquid cell TEM for studying complex reactions involving solid–liquid–gas interfaces⁵, which we will further explore.

Innovations inspired by liquid cell TEM discoveries. In recent years, this program has advanced the understanding of nucleation, growth, and dynamic transformation of materials at the nanoscale, with a strong emphasis on uncovering synthesis mechanisms through real-time liquid cell TEM studies. These efforts have elucidated formation pathways for numerous reported syntheses.

Leveraging insights from *in situ* liquid cell TEM, we developed a patented method for synthesizing high-entropy alloys via an isothermal solidification strategy. This approach enables the low-temperature (near room temperature) production of high-entropy alloys with precisely controlled morphology, crystallinity, and composition—capabilities unmatched by other methods. Moving forward, we will further expand the potential of this method and deepen our understanding of its underlying mechanisms.

References

1. Q. Zhang, Z. Song, X. Sun, Y. Liu, J. Wan, S. B. Betzler, Q. Zheng, J. Shangguan, K. C. Bustillo, P. Ercius, P. Narang, Y. Huang, and H. Zheng, *Atomic dynamics of electrified solid–liquid interfaces in liquid-cell TEM*, *Nature* **630**, 643–647 (2024).
2. J. Wan, Q. Zhang, E. Liu, Y. Chen, J. Zheng, A. Ren, W. Drisdell, and H. Zheng, *In-situ/operando study of Cu-based nanocrystals for CO₂ electroreduction using electrochemical liquid cell TEM*, *Frontiers in Chemistry* **13**, 1525245 (2025).
3. W. Zheng, J. Kang, K. Niu, C. Ophus, E. M. Chan, P. Ercius, L.-W. Wang, J. Wu, and H. Zheng, *Reversible phase transformations between Pb nanocrystals and a viscous liquid-like phase*, *Science Advances* **10**, eadn6426 (2024).
4. X. Peng, J. Shangguan, Q. Zhang, M. Hauwiller, H. Yu, Y. Nie, K. C. Bustillo, A. P. Alivisatos, M. Asta, and H. Zheng, *Unveiling corrosion pathways of Sn nanocrystals through high-resolution liquid cell electron microscopy*, *Nano Letters* **24**, 1168–1175 (2024).
5. W. Zheng, D. Lee, and H. Zheng, *Strategies to overcome electron beam issues in liquid phase TEM study of chemical processes*, *MRS Bulletin* **49**, 205–213 (2024).

Publications

1. X. Peng, J. Shangguan, Q. Zhang, M. Hauwiller, H. Yu, Y. Nie, K. C. Bustillo, A. P. Alivisatos, M. Asta, and H.

- Zheng, *Unveiling corrosion pathways of Sn nanocrystals through high-resolution liquid cell electron microscopy*, Nano Letters **24**, 1168-1175 (2024).
2. J. Wan, Q. Zhang, J. Liang, K. C. Bustillo, Z. Y. Al Balushi, M. Asta, and H. Zheng, *Visualizing facets asymmetry induced directional movement of cadmium chloride nanomotor*, Nano Letters **23**, 10132-10139 (2023).
 3. Q. Zhang, D. Lee and H. Zheng, *Nanoscale materials transformations revealed by liquid phase TEM*, Nano Research **17**, 9152-9165 (2024).
 4. Q. Zhang, Z. Song, X. Sun, Y. Liu, J. Wan, S. B. Betzler, Q. Zheng, J. Shangguan, K. C. Bustillo, P. Ercius, P. Narang, Y. Huang, and H. Zheng, *Atomic dynamics of electrified solid-liquid interfaces in liquid-cell TEM*, Nature **630**, 643-647 (2024).
 5. W. Zheng, J. Kang, K. Niu, C. Ophus, E. M. Chan, P. Ercius, L.-W. Wang, J. Wu, and H. Zheng, *Reversible phase transformations between Pb nanocrystals and a viscous liquid-like phase*, Science Advances **10**, eadn6426 (2024).
 6. Q. Zheng, A. Ren, A. Zagalskaya, H. Mao, D. Lee, C. Yang, K. C. Bustillo, L. F. Wan, T. A. Pham, J. A. Reimer, J. Zhang, Y. Liu, and H. Zheng, *Multistep growth pathway of covalent organic framework onion nanostructures*, Journal of the American Chemical Society **146**, 34167-34175 (2024).
 7. J. Wan, Q. Zhang, E. Liu, Y. Chen, J. Zheng, A. Ren, W. Drisdell, and H. Zheng, *In-situ/operando study of Cu-based nanocrystals for CO₂ electroreduction using electrochemical liquid cell TEM*, Frontiers in Chemistry **13**, 1525245 (2025).
 8. Q. Zhang, H. Dong, A. Ren, Y. Nie, and H. Zheng, *In situ atomic observation of transformation twinning in nanocrystals*, Nano Today **60**, 102547 (2025).
 9. D. Cheng, J. Hong, D. Lee, S. Y. Lee, and H. Zheng, *In situ TEM characterization of battery materials*, Chemical Reviews **125**, 1840-1896 (2025).
 10. Q. Zhang, M. C. Gallant, Z. Song, Y. Chen, Y. Liu, Q. Zheng, K. C. Bustillo, Y. Huang, K. A. Persson, and H. Zheng, *Isothermal solidification for high-entropy alloy synthesis*, Nature **accepted** (2025).

Exploring Charge and Lattice Correlations and Dynamics in Quantum Materials

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Keywords: Electron microscopy instrumentation, Electron-spin-lattice correlation, Electronic heterogeneities, Ultrafast and non-equilibrium, and Quantum materials

Research Scope

The goal of this FWP (MA-015-MACA) is to investigate property-sensitive nanoscale structure, defects, and interfaces in advanced materials, including correlated electron systems, transition-metal oxides, ferroelectric and spintronic films. We develop and implement advanced electron microscopy methods and instrumentation with the necessary spatiotemporal resolutions to uncover atomic disorder, electronic inhomogeneity, transient phenomena, and coupled charge-spin-lattice behaviors. Our research is organized around three central themes: (1) Heterogeneities, (2) non-equilibrium dynamics, and (3) Development of advanced tools to enable investigation under themes (1) and (2). Related studies on ferroelectric and ferromagnetic materials, including charge and spin ordering and switching in theme (1) are also addressed on a separate abstract.

Recent Progress

Over the past two years, we have made great strides in materials research, unraveling several long-standing puzzles regarding charge-orbital-spin-lattice correlations and the roles of defects. We have also made significant progress in advancing the frontier of electron microscopy instrumentation and methods, notably through the development of a laser-free electron pulser enabling microwave excitation and imaging, and a liquid-He-free, closed-cycle cryogenic sample holder that can reach 5.6K. We refer to our research outcomes to the publications listed at the end of this abstract.

Heterogeneities. Our research in this area focuses on understanding how defects and disorders give rise to emergent phenomena. For example, we demonstrate the ability to fine-tune the electronic structure and Fermi level in a topological Weyl semimetal (TaP) [1] and a Mott insulator (VO_2) [2] through hydrogen implantation and doping. A major challenge in microscopy is visualizing hydrogen, the lightest element, due to its extremely low scattering cross-section. This challenge is even more pronounced in EELS, as the core electron in hydrogen merges with the valence band in solids, eliminating its ionization edge. In Fig. 1, we demonstrate atomic imaging of hydrogen-implantation-induced stacking faults and associated lattice distortions and near-

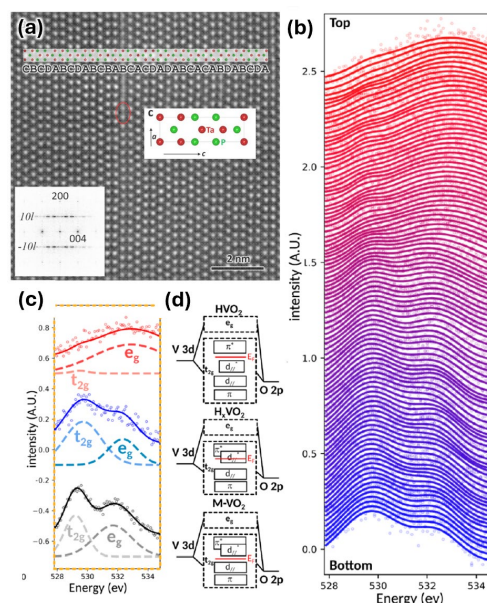


Fig.1. STEM-HAADF image of stacking faults (area marked by the red circle) induced by hydrogen implantation in topological Weyl semimetals TaP [1]. (b) EELS depth profile of O-K edge (after PCA denoising) from hydrogen-implanted VO_2 to reveal the effects of proton on metal-insulator transition. (c) the corresponding t_{2g} and e_g features (red: top, blue: bottom, black: without H^+ implantation). (d) Schematic of the molecular orbital energy levels near the Fermi level for the three situations: HVO_2 , H_xVO_2 ($0.2 < x < 0.5$) and pristine monoclinic VO_2 [2].

atomic resolution EELS mapping of the t_{2g}/e_g fine structure from the O-K-edge, capturing changes in hybridization, electronic localization and orbital reordering induced by H^+ incorporation. By combining advanced microscopy with DFT calculations, we reveal detailed insights into local electronic structure modifications driven by the nonuniform distribution of protons. These results open new pathways for high-resolution imaging and dopant profiling in next-generation microelectronic and quantum information devices.

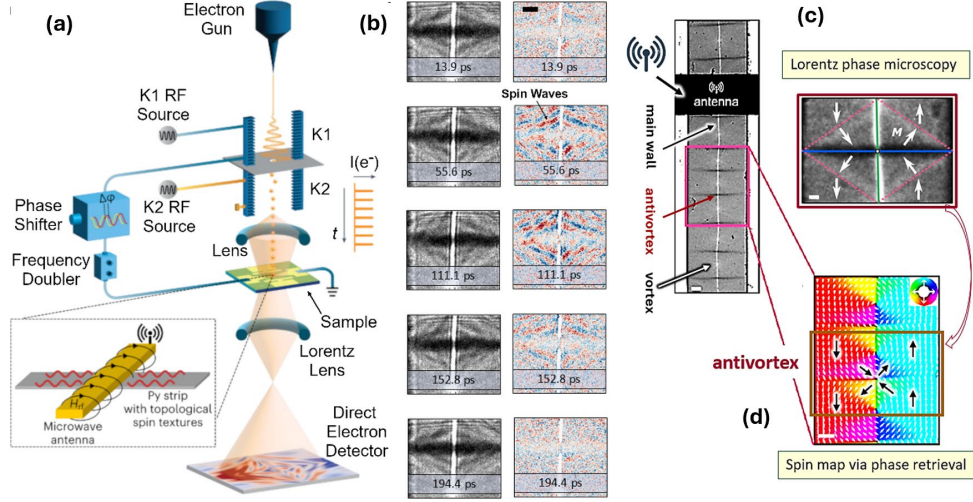


Fig.2. (a) Schematic of the microwave UEM system we developed. The electric signals are sent to the RF cavity, which chops the electron beam into electron pulses. The RF signals then exit the cavity and are sent into the sample via a phase shifter, where the delay between the RF pump and the electron pulses are synchronized and controlled. (b) Time resolved LTEM images near the antivortex core showing magnon generation and propagation dynamics using 0 ps delay as reference (right column). Scale bar: 500 nm. (c) LTEM image of a crosstic magnetic structure in the permalloy strip with three types of domain walls, and two types of topological spin singularities (vortex and antivortex pairs). (d) The enlarged color panel is the magnetic induction map of the crosstic, experimentally reconstructed via a phase retrieval method [3]. In a crosstic spin structure, the vortex and antivortex pairs may act as localized, nonlinear dynamic elements, analogous to neurons in brain, while the connecting domain walls can serve as synapses for signal transmission via spin waves.

Non-equilibrium and ultrafast phenomena. A major accomplishment in this area is the direct visualization of spin-wave (magnon) initiation and propagation, which are essential for energy-efficient spintronics and magnonic device applications. Nanoscale observation of these dynamics at microwave frequencies has long been hindered by the lack of spin-sensitive, time-resolved microscopy. We overcame this by developing an electrically driven, GHz ultrafast Lorentz electron microscopy technique with high spatiotemporal resolution, enabling direct imaging of spin-wave behavior (Fig. 2). Using microwave stabilized topological spin textures with vortex-antivortex pairs and domain walls in permalloy, we observed and quantified spin-wave emission, propagation, reflection, and interference under RF excitation. Our results reveal that spin waves emerge from antivortices and are driven by the oscillatory motion of specific domain walls, providing unprecedented insights into spinwave dynamics in TEM [3]. In parallel, our ultrafast electron diffraction combined with quantitative diffuse scattering simulations and analysis reveals the dynamics of charge and lattice correlations (Fig. 3) during photoinduced 2D-CDW evolution in 1T-TiSe₂. We find that one-dimensional domain walls form less than 1 ps after photoexcitation, driven not by the amplitude of the order parameter, but by a non-thermal population of longitudinal optical phonons. This work [4] establishes a framework for ultrafast engineering of topological defects and dynamic control of non-equilibrium phases in correlated materials.

Advanced tools. During the funding period, we achieved several major instrumentation and methodology advances. We designed and constructed a novel liquid-helium-free cryogenic TEM sample holder that integrates a cryocooler, a superconductor-based temperature stabilizer, and a vibration damping system. This closed-cycle system operates between 5.6 K - 300 K with stability down to 1 mK, and extremely long hold times and virtually zero

helium consumption, eliminating the need for He refills [5]. In ultrafast electron microscopy (UEM), we extended the experimental capabilities down to 1 Hz for AC and DC excitation. We also developed a methodology to extract time-resolved signals from highly noisy data sets using a randomized acquisition process combined with a statistically guided AI algorithm (Fig. 4e). This overcomes a critical limitation in conventional UEM, where long acquisition times make experiments vulnerable to environmental instability and high probability of failure [6]. Together, these developments significantly expand our capabilities for probing quantum phenomena with unprecedented precision and success rates.

Future Plans

We will continue to focus on our three research themes: Heterogeneities, Non-equilibrium/ultrafast-phenomena and Advanced characterization tools, to understand electron-spin-lattice correlations in quantum materials. Below are some proposed activities.

AI-assisted analysis for mapping orbital electrons Valence electrons (VE), though few in number, are crucial for chemical bonding and material functionality. Quantitative convergent beam electron diffraction (CBED) can map VE by refining low-order structure factors, but traditional refinement is complex and time-consuming, involving nonlinear optimization of multiple parameters such as crystal structure, thermal vibrations, multipole density functions, orientation, and thickness, limiting its use to small-unit-cell crystals. We propose a machine-learning approach to replace this manual process. By generating a large synthetic CBED dataset (millions of images) via Bloch-wave simulations, we will train a deep neural network to rapidly extract crystal parameters and VE distributions from experimental data. This AI-assisted method is ideal for high-throughput, in-situ experiments, including those under GHz electrical excitation.

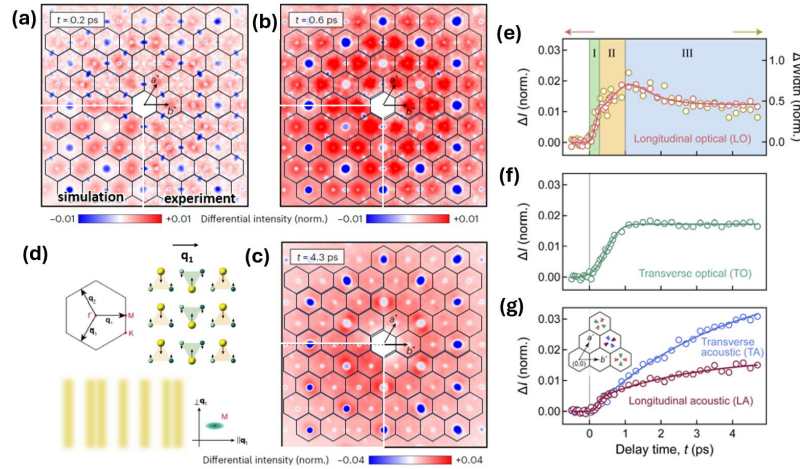


Fig.3. (a–c), Experimental differential electron diffraction intensity taken at 210 K at three time-delays after photoexcitation in CDW 1T-TiSe₂. The lower-left quadrant shows the simulations. (d) Projected Brillouin zone with three equivalent CDW wavevectors and one of the corresponding atomic displacements (yellow: Ti, green: Se). The bottom panel shows the CDW peak at the M point and the associated 1D domain walls, highlighting their role in the photoinduced CDW evolution. (e–g) Color coded time evolution of diffuse intensities for different phonon branches (LO, TO, TA and LA (see the inset of (g))). Note, LO phonon population show three-stage dynamics, which are distinct from TO, TA and LA phonons [4].

Elucidating field-induced CDW evolution and sliding in layered materials While photoinduced CDW dynamics are well studied, the response of CDWs to electric fields remains poorly understood. We propose to investigate RF-induced CDW dynamics in TaS₂ to determine whether reordering occurs via growth from favorable nucleation sites or through stochastic transformations.

This will involve time-resolved structural analysis following ultrashort voltage pulses that melt CDW order, using real-space and reciprocal-space coupled techniques. In parallel, we will study CDW sliding in TbTe₃ via *in situ* electrical biasing and RF excitation. Our approach enables real-time imaging of CDW dynamics with sub-nanometer and sub-nanosecond resolution, essential for elucidating their onset, pinning, and depinning under high-frequency fields. The insights will deepen our understanding of non-equilibrium correlated electron behavior and guide the development of ultrafast, low-power CDW-based devices.

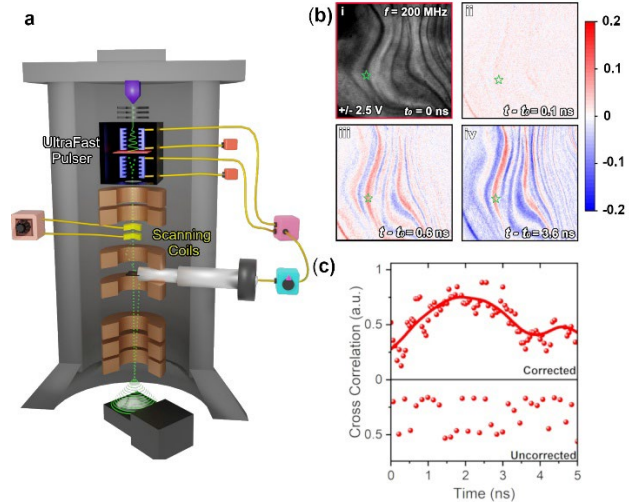


Fig.4. (a) Developing 5D-STEM capabilities. (b) Probing dynamics of surface acoustic wave in piezoelectrics. Diffraction contrast of bend contours (i-iv) revealing wave propagation under electric excitation. (c) Wave dynamics retrieved after being corrected by a statistical-based AI model from noisy data sets.

Probing speed limits in electrically driven Mott switching Mott materials are key quantum systems with potential applications in non-Von Neumann computing, robotics, energy storage, and photonic/microwave technologies. VO₂ and V₂O₃ are among the most studied due to their sharp insulator-to-metal transitions (IMT). Driven by electric fields, the systems can rapidly switch states, enabling information encoding and dynamic modulation of optical and dielectric properties. We propose to use our frequency-tunable, microwave-driven pulsed electron microscope to directly image the ultrafast formation and dissolution of metallic phases in real and reciprocal space under MHz–GHz electrical excitation—conditions relevant to modern wireless and qubit devices. This will reveal not only electric-field-driven IMT dynamics but also the fundamental limits of reversible switching speed.

Exploring 5D-STEM capabilities for electrically excited dynamics We propose to develop ultrafast, time-resolved 4D-STEM, a reciprocal- and real-space coupled diffraction technique, to investigate material dynamics under electrical excitation. On the instrumentation side, we will install a high-speed scanning unit covering a broad frequency range, improve microwave impedance matching and waveform control, and implement AI-assisted analysis to eliminate experimental artifacts (Fig. 4). These advancements are essential for probing the functional behavior of microelectronic devices under in-operando conditions.

References - Publications (I) cited in the abstract and supported by this FWP (past two years).

1. Mandal, M., Chotrattanapituk, A., Woller, K., Wu, L., Xu, H., Mao, N., Okabe, R., Boonkird, A., Nguyen, T., Drucker, N.C.; Momiki, T., Li, J., Kong, J., Zhu, Y., Li, M., "Precise Fermi-level engineering in a topological Weyl semimetal via fast ion implantation", *Appl. Phys. Rev.* 11, 021429 (2024).
2. Pofelski, A., Jia, H., Deng, S., Yu, H., Park, T.J., Manna, S., Chan, M.K.Y., Sankaranarayanan, S.K.R.S., Ramanathan, S., and Zhu, Y., "Sub-nanometer Scale Mapping of Hydrogen Doping in Vanadium Dioxide", *Nano letters*, 24, 6, 1974-1980, (2024)
3. Liu, C., Ai, F., Reisbick, S., Zong, A., Pofelski, A., Han, M.-G., Camino, F., Jing, C., Lomakin, V., and Zhu, Y., "Correlated spin wave generation and domain-wall oscillation in a topologically textured magnetic film", *Nature Materials*, 24, 406-413 (2025).
4. Cheng, Y., Zong, A., Wu, L., Meng, Q., Xia, W., Qi, F., Zhu, P., Zou, X., Jiang, T., Guo, Y., van Wezel, J., Kogar, A., Zuerch, M.W., Zhang, J., Zhu, Y., Dao X., "Ultrafast formation of topological defects in a two-dimensional charge density wave". *Nature Physics*, 20, 54-60 (2024).
5. He, X., Kostin, R., Knight, E., Han, M.-G., Mun, J., Bozovic, I., Jing, C., and Zhu, Y., "Development of a liquid-helium free cryogenic sample holder with mK temperature control for autonomous electron microscopy" *Ultramicroscopy* 267 114037 (2024).
6. Reisbick, S., et al "Statistically elucidated responses from low-signal contrast mechanisms in ultrafast electron microscopy", *Structural Dynamics*, 12, 34302 (2025).

Publications (II) additional 10 most relevant and supported by this FWP (2023-2025).

For full list of publications (total 81), see <https://www.bnl.gov/cmpmsd/tem/publications/>

1. Cheng, S., Navarro, H., Wang, Z., Li, X., Kaur, J., Pofelski, A., Chen, C., Dean, M.P., Meng, Q., Zhou, C., Liu, M., Basaran, A.C., Rozenberg, M., Ong, S.P., Schuller, I.K., Zhu, Y., "Purely electronic insulator-metal transition in rutile VO₂", *Nat. Comm.*, 16:5444 (2025).
2. Hwang, S., Wu, L., Kisslinger, K., Yang, J., Egerton, R., Zhu, Y., "Secondary-electron imaging of bulk crystalline specimens in an aberration corrected STEM", *Ultramicroscopy* 261, 113967 (2024).
3. Li, Z., Zhang, H., Li, G., Guo, J., Wang, Q., Deng, Y., Hu, Y., Hu, X., Liu, C., Qin, M., Shen, X., Yu, R., Gao, X., Liao, Z., Liu, J., Hou, Z., Zhu, Y., and Fu, X., "Room-temperature sub-100nm Néel-type skyrmions in non-stoichiometric van der Waals ferromagnet Fe₃-xGaTe₂ with ultrafast laser writability", *Nat. Comm.*, 15:1017 (2024).
4. Mun, J., Zhou, C., Kisslinger, K., Liu, M., and Zhu, Y., "Comparative S/TEM study of superconducting Ta quantum resonators by wet and dry etching types", *Appl. Phys. Lett.* 125, 164002 (2024), Editor's Pick.
5. Yang, X., Wang, L., Maxson, J., Christopher B.A., Kaemingk, M., Wan, W., Cultrera, L., Wu, L., Smaluk, V., Shafit, T., McSweeney, S., Jing, C., Kostin, R., and Zhu, Y., "Towards Construction of a Novel Nanometer-Resolution MeV-STEM for Imaging Thick Frozen Biological Samples", *Photonics*, 11, 252 (2024).
6. Egerton, R.F., and Zhu, Y., "Spatial resolution in secondary-electron microscopy", *Microscopy*, 72(2), 66-77 (2023).
7. Han, M.-G., Garlow, J., Du, K., Cheong, S.-W., and Zhu, Y., "Chirality reversal of magnetic solitons in chiral Cr_{1/3}TaS₂", *Appl. Phys. Lett.* 123, 022405 (2023).
8. Mun, J., Sushko, P.V., Brass, E., Zhou, C., Kisslinger, K., Qu, X., Liu, M., and Zhu, Y., "Probing Oxidation-Driven Amorphized Surfaces in a Ta (110) Film for Superconducting Qubit", *ACS Nano*, 18, 1126 (2023).
9. Reisbick, S.A.; Pofelski, A.; Han, M.-G.; Liu, C.; Montgomery, E.; Jing, C.; Sawada, H.; Zhu, Y., "Characterization of transverse electron pulse trains using RF powered traveling wave metallic comb striplines". *Ultramicroscopy*, 249, 113733 (2023).
10. Wang, W.; Li, J.; Liang, Z.; Wu, L.; Lozano, P.M.; Komarek, A.C.; Shen, X.; Reid, A.H.; Wang, X.; Li, Q.; Yin, W.; Sun, K.; Robinson, I.K.; Zhu, Y.; Dean, M.P.M.; Tao, J., "Verwey transition as evolution from electronic nematicity to trimerons via electron-phonon coupling", *Sci. Adv.* 9, eadf8220 (2023).

Additional publications are also listed in a separate abstract as part of this FWP (MA-015-MACA), entitled "Direct Probing Polarization and Magnetization Behaviors in Ferroics by In Situ Cryogenic-(S)TEM", by M.-G. Han, L. Wu and Y. Zhu

*University
Abstracts*

Studying moiré quantum phases with *in situ* sliding tip galvanometry

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Keywords: Moiré materials, quantum sensing, correlated electrons, scanning probe microscopy, topological physics

Research Scope:

Two-dimensional quantum materials are ultimately thin materials with outstanding performance in terms of their electronic, optical and mechanical properties. It was recently discovered that the twisting between two-dimensional materials offers further control over their band structures and many-body correlations via moiré effects, which allows the creation of a plethora of exotic quantum states, including unconventional superconductivity, strongly correlated phases, and fractional quantum states. Studying these quantum phases with novel scanning microscopy techniques can further elucidate fundamental questions about these quantum states and open new paths to tailor these states for quantum applications. This research project will use novel scanning microscopy techniques to study emerging quantum phenomena that exist in moiré matter beyond twisting. This research will use recently developed microelectron-mechanical system (MEMS)-based manipulators to develop a novel scanning microscopy approach called sliding tip galvanometry (STG) that enables *in situ* study of electromechanical behaviors in moiré materials with high spatial resolution and unprecedented degree of control, both electrically and mechanically. STG will be used to investigate quantum phenomena in graphene and transitional metal dichalcogenide heterostructures.

The research will first explore novel electromechanical transduction mechanisms based on topological charge pumping effect, which is a process where electronic charges are transported across insulators in a quantized manner. Using this quantization, the goal of this research is to further study the spin and charge orders in the correlated energy gaps of twisted moiré materials to gain insight into their underlying mechanism. STG will also be used to study ferroelectric

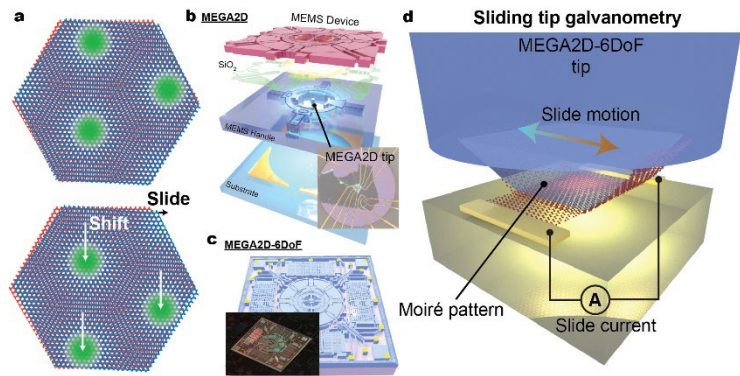


Figure 1. (a) A small interlayer slide creates a large perpendicular shift in moiré patterns. (b) MEMS-based platform (MEGA2D) for *in situ* twisting & pressurizing. Inset shows an *in situ* transport device we fabricated with a Hall bar at the center. (c) Proposed MEGA2D-6DoF with additional translational capability. (d) We propose to use sliding tip galvanometry to measure sliding quantum number in moiré systems.

two-dimensional materials to understand nano-actuation and to further tailor moiré quantum materials. The results from these studies will answer fundamental questions about moiré physics and give new insight into the electromechanical coupling at two-dimensional interfaces, which is highly relevant to quantum technologies and energy science.

References

1. Yuan Cao, Valla Fatemi, Shiang Fang, Kenji Watanabe, Takashi Taniguchi, Efthimios Kaxiras, Pablo Jarillo-Herrero. *Unconventional superconductivity in magic-angle graphene superlattices*. Nature **556**, 43–50 (2018).
2. Haoning Tang, Yiting Wang, Xueqi Ni, Kenji Watanabe, Takashi Taniguchi, Pablo Jarillo-Herrero, Shanhui Fan, Eric Mazur, Amir Yacoby and Yuan Cao. *On-chip multi-degree-of-freedom control of two-dimensional materials*. Nature **632**, 1038–1044 (2024).
3. A. Inbar, J. Birkbeck, J. Xiao, T. Taniguchi, K. Watanabe, B. Yan, Y. Oreg, Ady Stern, E. Berg and S. Ilani. *The quantum twisting microscope*. Nature **614**, 682–687 (2023).
4. Y. Zhang, Y. Gao, Y. and D. Xiao. *Topological charge pumping in twisted bilayer graphene*. Phys. Rev. B **101**, 041410 (2020).
5. M. Wu and J. Li, *Sliding ferroelectricity in 2D van der Waals materials: Related physics and future opportunities*. Proc. Natl. Acad. Sci. **118**, e2115703118 (2021).

4D-STEM Based Electron Diffraction Contrast Tomography of Charge-Lattice Coupled Materials

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Keywords: Electron Microscopy, 4D-STEM, Tomography, Heterogeneity, Defect

Research Scope

Our goal is to understand atomic and nanoscale mechanisms underpinning charge-lattice coupling—the interactions of charges (ions, electrons) with lattices—occurred in materials that are widely relevant to ion separation, energy storage, and catalysis as well as to quantum behaviors such as magnetoresistance, multiferroicity, and topological protection. We propose to establish and implement the principles of four-dimensional scanning transmission electron microscopy (4D-STEM) based electron diffraction contrast tomography (EDCT) and related techniques for understanding structurally complex and heterogeneous charge-lattice coupled materials. The 4D-STEM platform utilizes a nanometer (nm)-sized electron probe raster-scans a sample region of interest in the (x,y) plane to collect a large set of electron diffraction patterns (DPs) using a pixelated detector. We incorporated advancements in electron beam instrumentation and data-mining—from precisely analyzing Bragg diffraction spots for the averaged, ordered lattice to quantify diffuse scattering to identify the types and spatial distribution of defects. Simultaneously, our EDCT method goes beyond current practices of 4D-STEM by fundamentally extending from two-dimensional (2D) structural feature extraction to three-dimensional (3D) reconstruction of structure, defect, and strain in the (x,y,z) space, as well from immutable samples to samples evolving under operando conditions. Separately, we have developed the large-angle rocking beam electron diffraction (LARBED) technique to collect 4D diffraction datasets in reciprocal space as function of beam tilt. We have explored this technique for the study of charge density wave materials with promising results.

Recent Progress

1) Unveiling pseudosymmetry at nano-to-bulk crossover of gold decahedral NP

In nanomaterials, five-fold multi-twinned structures are widely used to introduce symmetry-breaking and anisotropy that render superior properties. To fulfill the five-fold symmetry not existing in nature, the crystal lattice must

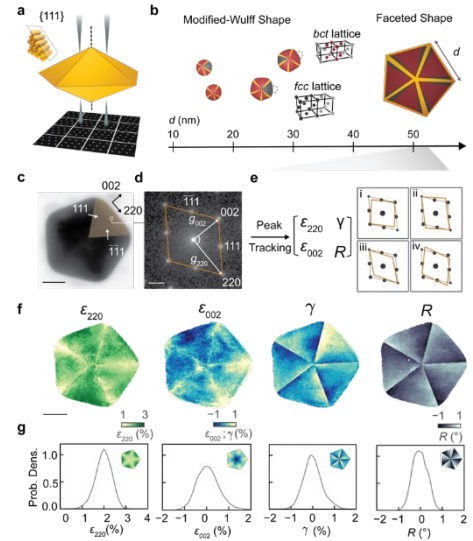


Figure 1. Strain mapping in decahedral Au NPs.

overcome a geometric misfit through straining. While nanoparticles (NPs) of five-fold symmetry are synthesized with sizes in nano- to mesoscale (nm to sub- μm), currently there is a lack of nanoscale understanding of how they can do so with such intrinsic strain. We performed 4D-STEM strain mapping on decahedral Au NP to answer the question (Fig. 1). Using diffraction disc tracking algorithm (developed by Zuo), we comprehensively mapped strain components (ϵ_{xx} , ϵ_{xy} , ϵ_{yy}) and lattice rotation (R) at 2-nm spatial resolution in two dimensions across the entire NP for the first time. Results from intermediate sized NPs reveal the mechanism of the size-dependent lattice deformation being closely related to particle morphology across the “nano-to-bulk” transition.

2) Correlative imaging of crystal defects and their impact on NP electrodes

We have previously shown for the first time that charge insertion induces oriented phase domains in $\lambda\text{-MnO}_2$, a model system for understanding the multivalent ion transport and structural stability in cathode materials—an intrinsic challenge due to the strong charge-lattice interactions.^{1–2} In this work, we propose a novel approach to address these challenges by introducing abundant planar defects—stacking faults (SFs)—via controlled thermal treatment. Through collocated atomic resolution high-angle annular dark-field imaging (HAADF) and 4D-STEM, we reveal that SFs are the intermediate state in this transition pathway. The distribution of each phase across entire particles is quantitatively mapped at nanometer resolution through cepstral analysis³ of the 4D-STEM data (Fig. 2a–b). By correlating 4D-STEM strain mapping with Zn-ion insertion profiles derived from electron energy loss spectroscopy (EELS), we show that Zn-ion insertion in the spinel lattice induces strong tensile strain (Fig. 2c,d). This strain drives a local cubic-to-tetragonal phase transformation that limits further Zn migration, impeding ion extraction during charging. The incorporation of SFs significantly enhances the cycling stability of $\lambda\text{-MnO}_2$ cathodes in Zn-ion batteries. The same principle also robustly extends to other metal ion systems, including Mg^{2+} , Li^+ and Na^+ . Our findings thus introduce a generalizable pathway for enhancing metal-ion diffusion kinetics in earth-abundant MnO_2 -based cathodes.

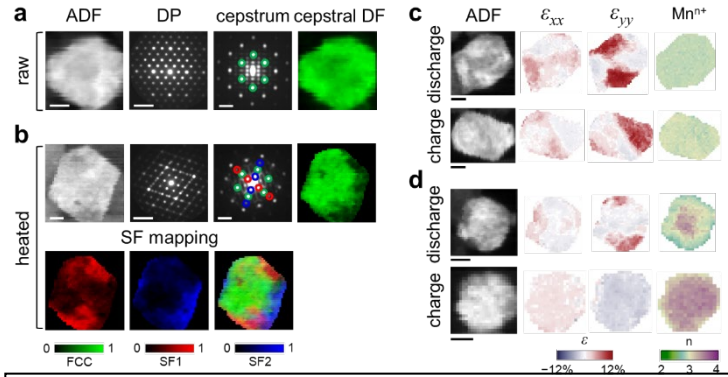


Figure 2. a–b 4D-STEM data and analysis of a raw (a) and heated (b) $\lambda\text{-MnO}_2$ NP. (c–d) Virtual ADF, 4D-STEM strain mapping along $(2\bar{2}0)$ (ϵ_{xx}) and (002) (ϵ_{yy}) directions and Mn valence map of raw (c) and heated (d) particles in Zn-ion batteries.

3) Resolving the three-dimensional nanoscopic strain field in lattice mismatched nanomaterials using 4D-STEM EDCT

We have established an EDCT tomography technique (Fig. 3). In short, we acquire a series of ADF images and a series of arrays of DPs at each tilt angle simultaneously, which allow us to reconstruct the 3D lattice spacing and strain. We have achieved a voxel resolution of $(2\text{ nm})^3$, and lattice spacing accuracy of ~ 5 picometer. We applied the technique to metallic core-shell NPs. Our method maps the elemental distribution with EDS (Fig. 3b), defects distribution in ADF (Fig. 3c), lattice spacing and strain distributions across of surfaces, interfaces, and defects (Fig. 3d–e) in complex 3D geometries. We uncover a hierarchy of strain relaxation mechanisms governed by lattice mismatch and composition: surface-dominated relaxation for single component NPs, stacking fault and dislocation formation at medium mismatch, and dislocation aggregation into small-angle domain boundaries at highly lattice-mismatched heterogeneous interfaces.

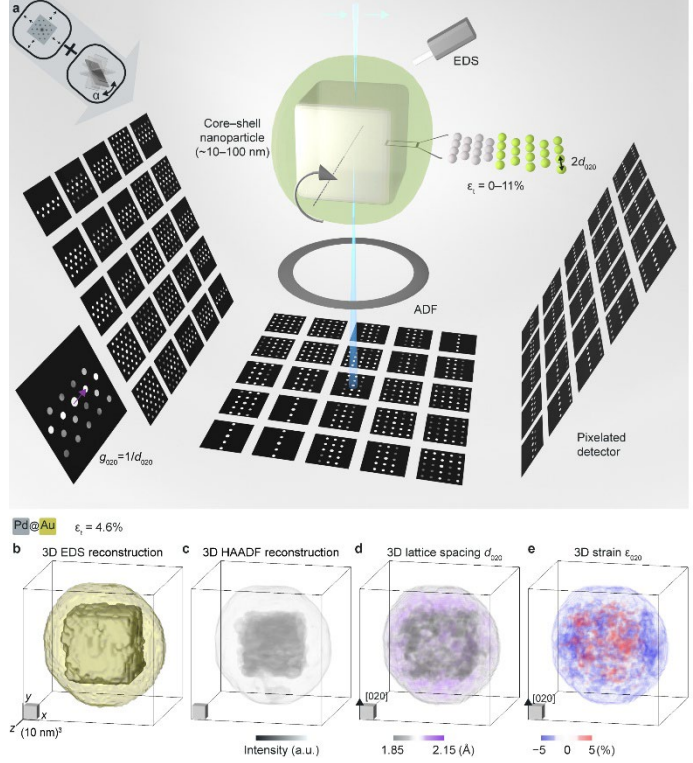


Fig. 3. 4D-STEM strain tomography scheme of nanomaterials. **a** Schematic diagram of 4D-STEM strain tomography of a core-shell NP. **b** 3D rendering of the EDS, ADF, lattice spacing, and strain reconstruction of a Pd@Au NP. Scale box: $(10\text{ nm})^3$.

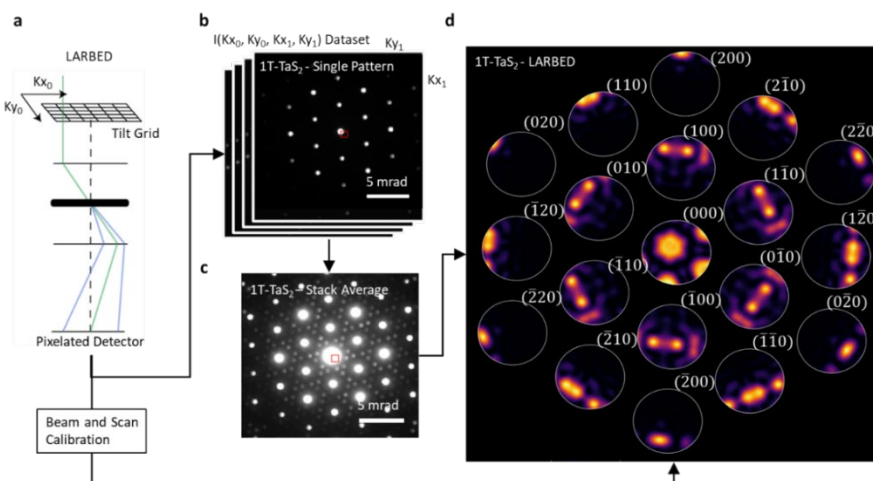
4) LARBED for Quantum material analysis

We probe the crystal potential using LARBED that allows access to dose-sensitive, large unit-cell crystals, typical for many complex quantum materials, overcoming limitations in convergent beam electron diffraction (CBED). Specifically, we implemented for the first time LARBED utilizing high-throughput electron direct detectors to provide high fidelity electron diffraction rocking curves. Experimentally, this is effectively a k -space 4D-STEM method allowing for downstream data processing (Fig. 4a). High-throughput data collection provides access to rocking curve analysis and established quantitative electron diffraction techniques for more complicated structures. We demonstrate LARBED on 1T-TaS₂ in the [001] orientation on the nearly commensurate charge density wave (NC-CDW) at room temperature using an 8 nm probe. Fig. 4b–c shows the single pattern and tilt-averaged electron diffraction pattern over the LARBED sampled space. The LARBED intensity profiles (Fig. 4d) show approximately 6-fold rotational and mirror symmetry expected from the projected trigonal planar structure. represents a major advancement in quantitative electron diffraction as profiles from these quantum materials were previously inaccessible.

Future Plans

We aim to further apply the 4D-STEM EDCT technique to energy storage material system and obtain the evolution of 3D lattice strain and composition during electrochemical cycles by combining the 4D-STEM EDCT with identical location TEM technique. This will allow us to correlate lattice structural with charge insertion processes. Although ultra-high spatial resolution can be achieved with 4D-STEM, the dynamics of phase transitions are still missing with only ex-situ characterizations, which are crucial for the design of next-generation electrode materials. Therefore, we plan to combine

Fig. 4. Simplified overview describing the LARBED data and resultant curves for [001] 1T-TaS₂ at Room Temperature in the NC-CDW state.



4D-STEM with in-situ heating TEM to obtain rich temporal information. We will also initiate efforts to quantitatively analyze electron DPs for paradigm quantum systems (1T-TaS₂). This represents a major advancement in quantitative electron diffraction as profiles from these quantum materials of this quality were previously inaccessible. The continued study of 1T-TaS₂ as a prototypical CDW material using LARBED will provide critical experimental results for validating theory of CDW formation and has the potential to offer new insights into our understanding of phase transitions and nucleation of CDWs. With the LARBED experimental methodology in place at room temperature, we will expand our testing to varied temperatures allowing us to directly observe phase transitions in these materials.

References

1. Z. Tang, W. Chen, Z. Lyu, and Q. Chen, *Size-dependent reaction mechanism of λ -MnO₂ particles as cathodes in aqueous zinc-ion batteries*. Energy Material Advances **2022**, doi:10.34133/2022/9765710 (2022).
2. W. Chen, X. Zhan, R. Yuan, S. Pidaparthi, A. X. B. Yong, H. An, Z. Tang, K. Yin, A. Patra, H. Jeong, C. Zhang, K. Ta, Z. W. Riedel, R. M. Stephens, D. P. Shoemaker, H. Yang, A. A. Gewirth, P. V. Braun, E. Ertekin, J. Zuo, and Q. Chen, *Formation and impact of nanoscopic oriented phase domains in electrochemical crystalline electrodes*. Nat. Mater. **22**, 92–99, (2023).

3. Y. Shao, R. Yuan, H. Hsiao, Q. Yang, Y. Hu, and J. Zuo, *Cepstral scanning transmission electron microscopy imaging of severe lattice distortions*. *Ultramicroscopy* **231**, 113252, (2021).

Publications

1. R. Busch, H.C. Ni, Y.T. Shao, J.M. Zuo*. (2025). Large-Angle Rocking Beam Electron Diffraction of Large Unit Cell Crystals Using Direct Electron Detector. *Microscopy and Microanalysis*, 31(1), ozae088.
2. R. Busch, H.C. Ni, Y.T. Shao, J.M. Zuo*. (2025). Large Angle Rocking Beam Electron Diffraction Utilizing Electron Direct Detector, *Microscopy and Microanalysis*, 30(Supplement_1), ozae044.943.
3. R. Busch, H.C. Ni, J.M. Zuo*. (2024). Quantification of Dynamic Scattering Effects in Molecular Crystals using Large Angle Rocking Beam Electron Diffraction. *BIO Web of Conferences* 129, 07007.
4. O. Lin, Z. Lyu, H.C. Ni, Y. Jia, K. Zhao, J.M. Zuo, Q. Chen*. (2024). Unveiling Structural Heterogeneity and Imbalance of Gold Decahedral Nanoparticles using Four-dimensional Scanning Transmission Electron Microscopy. *BIO Web of Conferences* 129, 07002.
5. H. Ni, W. R. Meier, H. Miao, A.F. May, B.C. Sales, J.M. Zuo*, M. Chi*. (2024). Real-space visualization of atomic displacements in a long-wavelength charge density wave using cryogenic 4D-STEM. *Physical Review Materials*, 8(10), 104414.
6. Z. Ye, J. Zhao, K. Kang, S.J. McCormack, Y. T. Shao, M.Y. Efremov, A. Schleife, W.M. Kriven, J.M. Zuo, L. H. Allen*. (2025). Birefringent Color Filter by Layered Metal-Organic Chalcogenides: In-Plane Anisotropy and Odd/Even Effect. *Advanced Optical Materials*, 13(9), 2402159.
7. J. Han, N. Sharma, K. Zhao. Computational modeling of coupled mechanical damage and electrochemistry in ternary oxide composite electrodes. *Journal of Power Sources*, 595, 234034 (2024)
8. C. Liu, O. Lin, S. Pidaparthi, H. Ni, Z. Lyu, J.-M. Zuo, Q. Chen. 4D-STEM mapping of nanocrystal dynamics and heterogeneity in a graphene liquid cell. *Nano Letters*, 24(13), 3890-3897 (2024)
9. H.-C. Ni, R. Yuan, J. Zhang, J.-M. Zuo. Framework of compressive sensing and data compression for 4D-STEM. *Ultramicroscopy* 259, 113938 (2024).
10. O. Lin, Z. Lyu, H.-C. Ni, X. Wang, Y. Jia, C.-Y. Hwang, L. Yao, J.-M. Zuo, Q. Chen. Size-Dependent Lattice Pseudosymmetry for Frustrated Decahedral Nanoparticles. <https://doi.org/10.48550/arXiv.2507.14781>

Visualizing interactions and inhomogeneity in magnetic van der Waals materials

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Keywords: Scanning Tunneling Spectroscopy, van der Waals magnets, RKKY interactions.

Research Scope

Magnetic materials are essential for various modern technologies. Recently, metallic van der Waals (vdW) magnets have gained significant attention as they can be easily engineered into thin crystals, facilitating their integration into devices and switches. Because these materials are also metallic, itinerant conduction electrons play a pivotal role in mediating magnetic interactions within these systems. Indeed, the interplay between metallicity and magnetism enables the electrical control of the magnetic structure, which is a cornerstone for future spintronic technologies. Yet, the fundamental mechanisms by which itinerant electrons interact with spins and influence magnetic structures are not yet fully understood.

This project is dedicated to understanding the local charge, spin, and structural properties of metallic van der Waals magnetic compounds, along with the interactions that dictate their magnetic behavior. It specifically focuses on the spatial variations of these properties within inhomogeneous materials. Utilizing Scanning Tunneling Microscopy (STM) combined with Spectroscopy (STS) and extended to include spin-polarized measurements (SP-STM/S). The initial proposed focus is on three classes of metallic van der Waals magnetic materials: $(\text{Fe}_{1-x}\text{Ni}_x)_5\text{GeTe}_2$ (Ni-FGT), $(\text{Fe}_{1-x}\text{Co}_x)_5\text{GeTe}_2$ (Co-FGT) and Fe_xNbS_2 near $x=1/3$ (FNS). Key objectives include: (i) Investigating the microscopic mechanisms and the role of phase separation in enhancing the ferromagnetic transition temperature and magnetic ground state tunability in Ni- and Co-FGT [1,2]. (ii) Visualizing the interactions between Fe atoms in Fe_xNbS_2 and the spin glass phase that are key for the materials resistive switching behavior [3].

Recent Progress

Through the early stages of this project, we have focused on establishing the basic framework and methodologies for the study of FNS with various STM/S measurements at 4.2K.

Accessible surface morphologies: Based on the crystal structure (Fig. 1a) different surface terminations are expected from the cleaving process. We observed ordered Fe surfaces (Figs. 1b-c), and we also found disordered Fe regions (Fig. 1d-f). Within those surfaces, we identified regions where the underlying NbS_2 could be observed (Figs. 2a-c). Importantly, in those terminations, Fe atoms separated by different distances (Figs. 2b) can be observed.

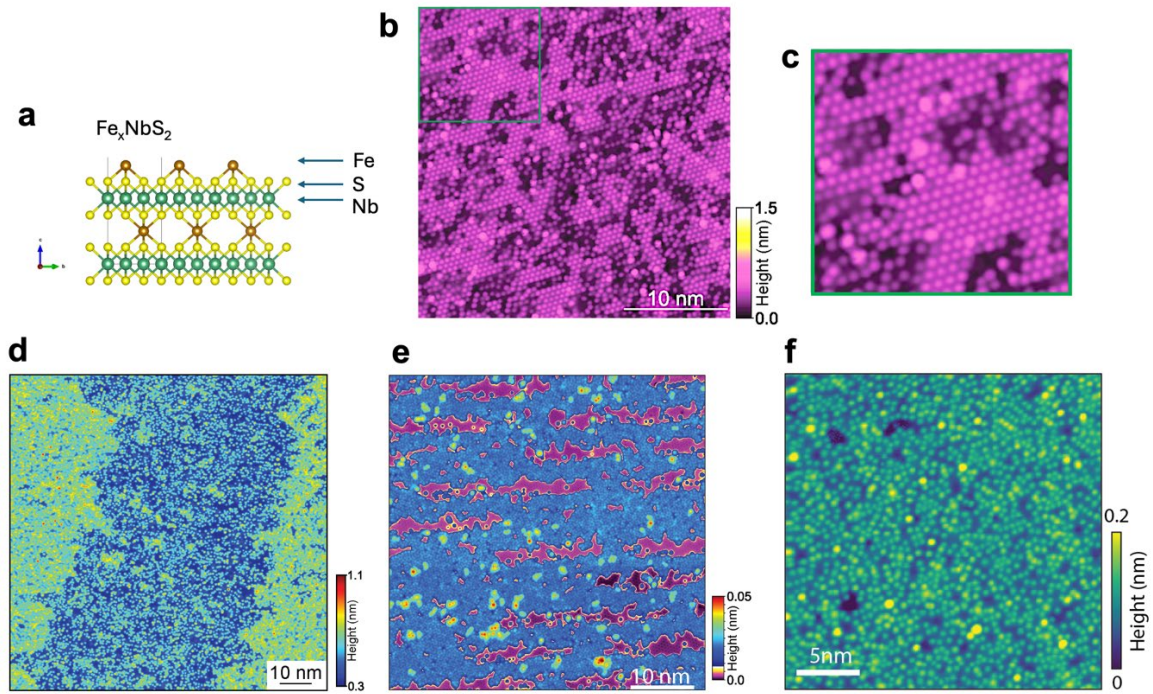


Figure 1: Multiple surface terminations obtained from the cleaving process in Fe_xNbS_2 . From the crystal structure in (a) the weakest bond is between Fe and S, which could result in an ordered Fe-covered surface, in a NbS₂ terminated surface or regions partially covered with Fe. (b,c) Areas of partial Fe coverage. Notice the Fe is not periodically ordered in these areas. (d) Areas of nearly full Fe-coverage. (e) Zoom-in of the area marked in (d) showing Fe atoms forming an ordered lattice.

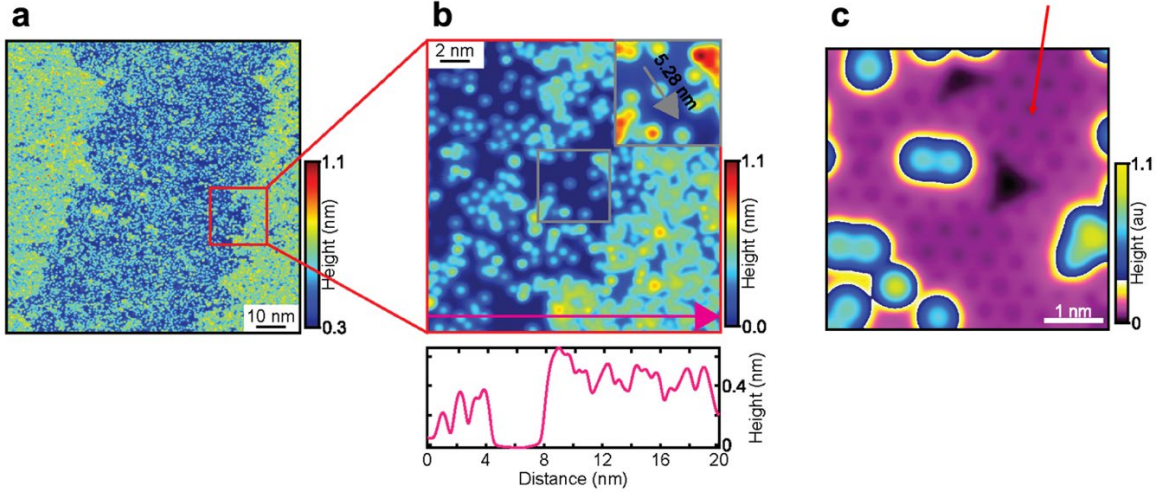


Figure 2: (a) Same as in Figure 1. (b) Zoom-in of the topography in (a) showing a region of sparsely distributed Fe atoms. Inset shows a region with an isolated Fe atom. The bottom plot shows a linecut of the topography, indicated by the pink arrow. (c) A nearby region showing an isolated Fe-Fe dimer, the underlying NbS₂ termination and triangular defects on that termination.

Local density of states: We obtained local density of states (LDOS) measurements on various regions with different Fe coverages (i.e. regions with Fe atoms at various Fe-Fe distances, in hexagonal patterns or random distributions). For example, there are clear differences between the LDOS on isolated Fe atoms, dimers or when on lattice ordered regions.

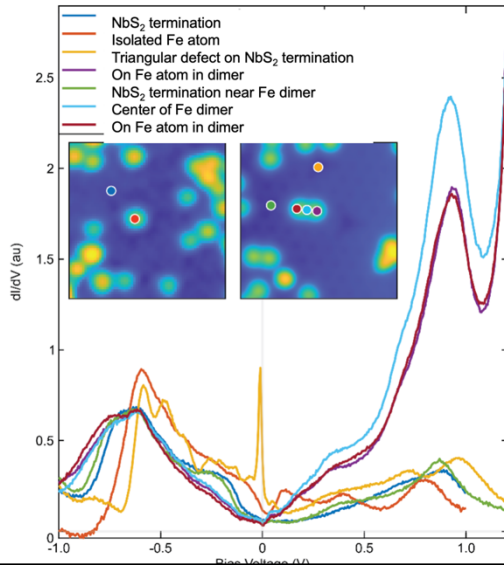


Figure 3: Examples of measured LDOS. Notice the substantial modifications for the spectra acquired between Fe dimers and isolated atoms. The colored dots in the inset indicate the locations where the spectra were acquired.

Teasing out interactions from the various distributions of Fe atoms: We are comprehensively measuring the LDOS for various arrangements of Fe atoms. In principle, these measurements allow us to glean insight into the magnetic interactions between Fe atoms. For example, Ruderman–Kittel–Kasuya–Yosida (RKKY) interactions have been teased out from LDOS measurements of dimers and trimers of magnetic atoms on metals, as a function of distance between the constituent atoms [4]. There are three main steps in our methodology. First, acquiring comprehensive LDOS maps over different arrangements of Fe atoms. The second step is to categorize the different LDOS spectra corresponding to different Fe structures (e.g., isolated atoms, dimers and trimers, one-dimensional structures, and 2D lattices). To achieve this, we are investigating the applicability of machine learning algorithms. Third

we need to model the LDOS. To understand the large energy range spectra, we are performing DFT calculations to simulate the DOS of various Fe atom configurations in the -1 to +1 eV range. At the same time, we are investigating phenomenological models that can be applied to understand the -50 to 50 meV spectral range.

Future Plans

The immediate plan is to perform similar measurements on FNS at temperatures above 50 K, i.e., above the spin-glass transition, followed by systematic measurements for different intercalation levels. These will then be followed by initial attempts to perform spin-polarized STM (SP-STM) on these materials to investigate the magnetic interactions more directly.

References

1. X. Chen, Y.-T. Shao, R. Chen, S. Susarla, T. Hogan, Y. He, H. Zhang, S. Wang, J. Yao, P. Ercius, D. A. Muller, R. Ramesh, & R. J. Birgeneau, *Pervasive beyond Room-Temperature Ferromagnetism in a Doped van der Waals Magnet*, Phys. Rev. Lett. **128**, 217203 (2022).
2. A. F. May, M.-H. Du, V. R. Cooper, & M. A. McGuire, *Tuning magnetic order in the van der Waals metal Fe_5GeTe_2 by cobalt substitution*, Phys. Rev. Mater. **4**, 074008 (2020).
3. N. L. Nair, E. Maniv, C. John, S. Doyle, J. Orenstein, & J. G. Analytis, *Electrical switching in a magnetically intercalated transition metal dichalcogenide*, Nature Materials **19**, 153–157 (2020).
4. P. Wahl, P. Simon, L. Diekhöner, V. S. Stepanyuk, P. Bruno, M. A. Schneider, & K. Kern, *Exchange Interaction between Single Magnetic Adatoms*, Phys. Rev. Lett. **98**, 056601 (2007).

Nanoscale Imaging of Correlations, Topology, and Magnetism in WSe₂ Layers

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Keywords: topology, phase transitions, Hofstadter's butterfly, magnetism, single-electron transistor

Research Scope

Moiré materials formed by stacking van der Waals layers have emerged as a highly flexible platform to engineer strong electronic interactions, topologically nontrivial phases, and—most excitingly—both simultaneously. Their combination can generate fundamentally new phases of matter of potential technological importance. The overarching goal of this project is to utilize single-electron transistor (SET) microscopy to image and study the resulting emergent quantum ground states, their low-energy excitations, and their responses to external stimuli. SET measurements yield thermodynamic electronic properties down to nanoscale spatial resolution. Moreover, other properties such as magnetism can also be deduced from the response to applied electromagnetic fields and electrostatic gating. We have utilized these capabilities to reveal and better understand correlated topological phases as well as transitions between distinct states in transition metal dichalcogenide (TMD) systems. We are also developing novel scanned probe techniques and instrumentation to extend our measurement capabilities.

Recent Progress

1. Mapping twist-tuned multiband topology in bilayer WSe₂

Twisted semiconducting TMD homobilayers were theoretically proposed as an excellent platform to realize flat topological energy bands that can host interaction-induced topological states with nontrivial twist angle dependence. However, prior study of these phenomena was hindered by difficulty achieving a homogeneous system with the requisite low twist angles (i.e. long moiré wavelength), as well as challenges of making good electrical contact due to the presence of Schottky barriers. The high spatial resolution of the SET and its capacitive measurement approach are ideal for overcoming both challenges.

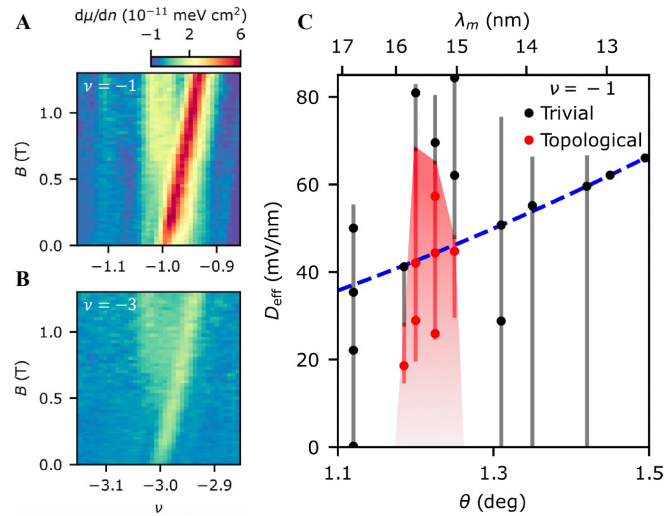


Figure 1. A-B, Inverse electronic compressibility of twisted bilayer WSe₂ showing QAH states at moiré filling factors $\nu = -1, -3$. C, Topological phase diagram at $\nu = -1$ as a function of twist angle and displacement field.

We used a scanning SET to image twisted bilayer WSe₂ (tWSe₂) at much lower angles than previously investigated. Our measurements revealed multiple topological bands and quantum anomalous Hall (QAH) insulators at moiré filling factors $\nu = -1$ and -3 at zero magnetic field (Fig. 1A-B). Using the scanning capability to probe different regions of the device with different local twist angles, we demonstrated that while correlated states persist in all areas, topological states are only present within a narrow window around a “magic angle” of 1.23°. In addition, we developed a new method that uses the SET tip to apply a local electric field, through which we were able to induce a topological quantum phase transition at $\nu = -1$. Together, these advances allowed us to map out the phase diagram of topological and trivial insulators (Fig. 1C). Our work represents experimental quantum simulation of a generalized Kane-Mele-Hubbard model on a tunable real-space lattice. It has inspired new theoretical investigation and understanding of the microscopic parameters that dictate which ground states are favored in different regimes.

2. Anomalous gaps and magnetic transitions in monolayer and bilayer WSe₂

Twisting two layers can induce flat electronic bands, but even TMD monolayers exhibit rich physics due to their unique hierarchy of energy scales and relatively strong interactions. Their large effective mass, together with additive orbital and Berry curvature effects, lead to a single-particle Zeeman splitting between spin-valley flavors which is large compared to the cyclotron energy scale. Electronic interactions further enhance the splitting so that the system is fully spin polarized at low densities and high magnetic fields but exhibits spin transitions as density is increased. Through SET measurements, we were able to significantly extend the understanding of the resulting magnetic phase diagram of monolayer and (untwisted) bilayer WSe₂.

We observed an intriguing pattern of first order magnetic phase transitions, indicated by abrupt changes in Landau level (LL) gaps and adjacent regions of negative compressibility (Fig. 2A). Prior work had also resolved

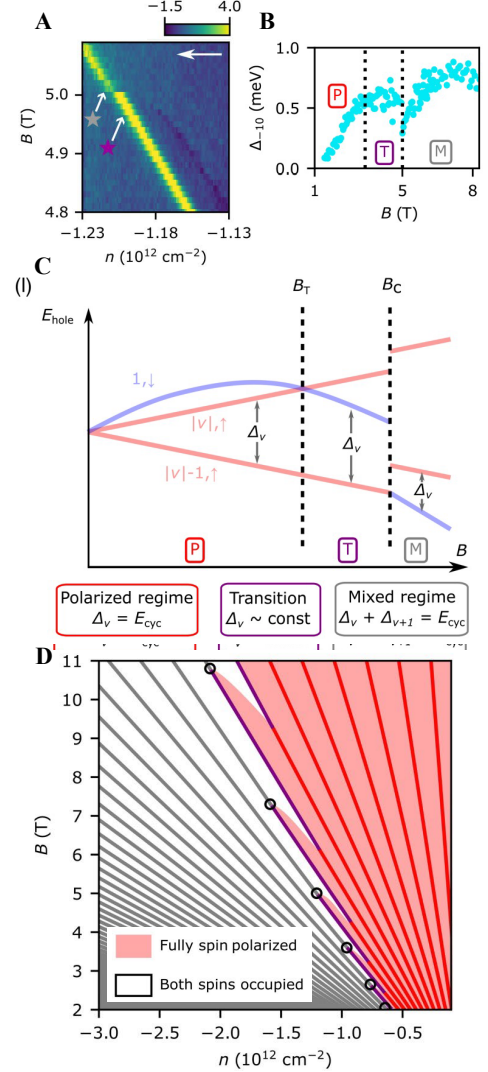


Figure 2. **A**, Inverse compressibility of monolayer WSe₂ showing a phase transition between fully spin polarized (purple star) and mixed spin polarization (grey star). **B**, Anomalous behavior of the LL gap as a function of magnetic field exhibiting three distinct scaling regimes. **C**, Corresponding calculated energetics of LLs near the Fermi level in each regime. **D**, Full phase magnetic diagram of ground and excited states deduced from the measurements.

similar transitions and proposed a theoretical model based on density-dependent exchange enhancement to explain them. Our measurements revealed that the prior model breaks down in the vicinity of the phase transitions. Unlike any other known material, the LL gaps in WSe₂ are approximately constant over a broad (up to several Tesla) range of magnetic fields immediately preceding the transitions (“T”, Fig. 2B). Through theoretical calculations (Fig. 2C), we showed that this is due to the critical influence of LL filling on the exchange interactions. Namely, the near-constant gaps arise due to a spin-polarized ground state with spin-flip excitations. The relatively weak field dependence occurs due to competing effects from interactions and single-particle behavior that approximately cancel. Our measurements thus allow us to deduce the spin character of both the ground states *and* the lowest-energy excitations over the entire phase diagram. We further resolve a sawtooth boundary between full and partial spin-polarization (Fig. 2D), and thus re-entrant magnetism as a function of density and magnetic field.

3. Magnetic Hofstadter cascade in twisted bilayer WSe₂

Twisted moiré materials are also an excellent testbed to investigate Hofstadter’s butterfly physics, where a fractal energy spectrum emerges due to interference between the electronic (moiré) modulation and the magnetic length scale. Combining aspects of both the above studies, we directly probed magnetic transitions within the Hofstadter butterfly regime in tWSe₂. In addition to providing spin-resolved information about the Hofstadter spectrum, our measurements disentangle the role of material and moiré effects on the nature of the correlated ground states.

We observed a series of negative compressibility features as a function of carrier density and magnetic field (Fig. 3A, diagonal dark blue lines). Using a Maxwell relation, we were able to translate the measured compressibility to obtain the magnetization and its dependence on carrier density (Fig. 3B), which showed that these features were in fact magnetic transitions. We then showed the cascade of transitions arises from changes in the occupation spin-minority Hofstadter subbands as they are sequentially populated (Fig. 3C). Thus, we achieved a spin-resolved probe of the spin-

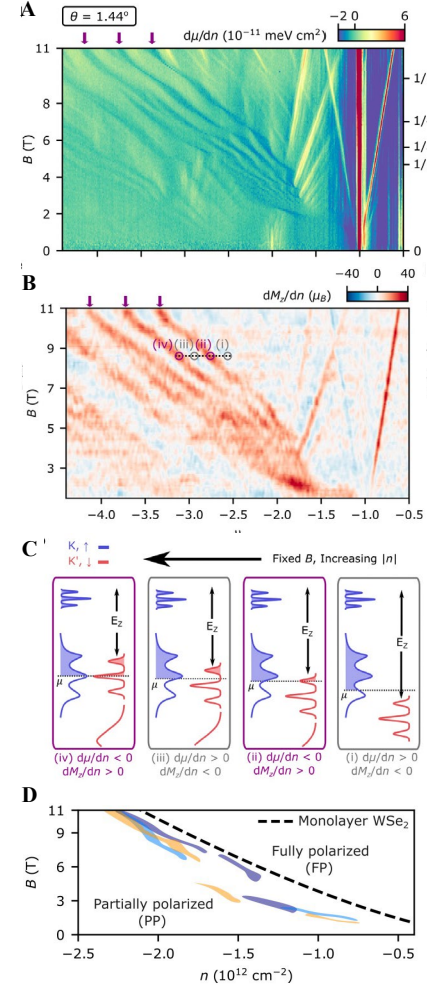


Figure 3. **A**, Series of transitions indicated by negative electronic compressibility (dark blue, see purple arrows) in twisted bilayer WSe₂. **B**, Corresponding change in magnetization obtained from a Maxwell relation, showing these are spin transitions. **C**, Schematic showing how the cascade of transitions arises from sequential filling of spin minority Hofstadter subbands. **D**, The onset of minority spin population only depends weakly on twist angle (colors).

minority Hofstadter spectrum in tWSe₂. This is especially important in TMD systems, where there is a unique energetic hierarchy between states of differing spin, and the Hofstadter spectra themselves are different for each spin due to inversion symmetry breaking. Not only is this the first characterization of the Hofstadter spectrum and its subband connectivity in a TMD system, but we were able to obtain spin-selective information even though states from both spins were overlapping, i.e. the system was compressible/metallic, which is not possible using conventional spectroscopy.

We also obtained additional insight about the magnetic transitions from spatially resolved measurements in locations with different twist angles. Surprisingly, the onset of transitions occurs along a near-universal curve that depends primarily on carrier density and is independent of twist angle (Fig. 3D). The magnetic transitions in both monolayer and bilayer WSe₂ also lie along a similar curve. This indicates that while the magnetic transitions have pronounced effects on many-body states driven by the moiré superlattice, the positions of the transitions themselves are primarily dictated by the underlying material properties, which has important implications for on-demand design of desired quantum electronic phases.

4. Additional work in progress: twisted multilayer WSe₂ and new scanning probe development

We have several other ongoing projects. We measured thicker portions of the twisted WSe₂ flake with different alignments at the moiré interface. These include 1+4 layers of AA- and AB-stacking, which realize different symmetries and exhibit different electronic characteristics. One has larger gaps; the other has a sawtooth in compressibility reminiscent of magic-angle graphene. We are working with theorists to understand this phenomenology. We have also made progress toward a hybrid SET/Hall bar nanoscale scanned probe to correlate magnetic and electronic signatures. We established a fabrication procedure to obtain high-quality SETs and are currently in the process of developing the fabrication procedure for the adjacent Hall probes.

Future Plans

Our future efforts will be focused on the following key goals. First, we seek to develop capabilities to tune displacement field over a broader range while maintaining the high spatial resolution and sensitivity of the scanning SET. Preliminary efforts indicate this should be possible by incorporating an additional graphene or TMD monolayer that can serve as both sensor and top gate. This will open new opportunities to study the displacement field dependence of topological and correlated states in moiré heterostructures (both TMD- and graphene-based) as well as other quantum materials. New opportunities include study and imaging of topological phase transitions as well as changes to the underlying band structure in the vicinity of superconducting phases.

We will also continue to develop and apply new scanning probe approaches to provide additional and complementary insights. This includes hybrid magnetic (Hall probe) and electronic (SET) sensors to study coupled magnetoelectric phenomena at the nanoscale. We further seek to establish new scanning tunneling microscope based techniques to conduct thermodynamic

measurements which extend the spatial resolution below the moiré limit. If successful, this will open new avenues for imaging quantum states down to the atomic scale.

Publications

1. B. A. Foutty, C. R. Kometter, T. Devakul, A. P. Reddy, K. Watanabe, T. Taniguchi, L. Fu, B. E. Feldman. *Mapping twist-tuned multiband topology in bilayer WSe_2* . Science **384**, 343-347 (2024).
2. B. A. Foutty, V. Calvera, Z. Han, C. R. Kometter, S. Liu, K. Watanabe, T. Taniguchi, J. C. Hone, S. A. Kivelson, B. E. Feldman. *Anomalous Landau level gaps near magnetic transitions in monolayer WSe_2* . Phys. Rev. X **14**, 031018 (2024).
3. B. A. Foutty, A. P. Reddy, C. R. Kometter, K. Watanabe, T. Taniguchi, T. Devakul, B. E. Feldman. *Magnetic Hofstadter cascade in a twisted semiconductor homobilayer*. arXiv: 2412.20334 (2024). [Currently under review]

Imaging Ultrafast Polar-Vortex Dynamics with Ultrafast Electron Microscopy

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Keywords: ferroelectric/dielectric superlattice, pulsed electron beam, femtosecond photoexcitation, pump-and-probe

Research Scope

Our recent work is delineated along two distinct but interrelated thrusts: **(1)** the quantification and optimization of low repetition rate (f_{rep}), laser-based (femtosecond, fs) ultrafast transmission electron microscopy (UEM), and **(2)** the direct imaging of ultrafast structural dynamics of emergent ordered lattice distortions in ferroelectric/dielectric superlattices. The connection between these two thrusts is that the viability of advances made in thrust **(1)** are determined by applying the new methods, techniques, and instrument advances on the materials that are the subject of thrust **(2)**. One main aim of the work is to quantitatively establish the resolution limits and imaging capabilities of laser-driven fs UEM. We are establishing these limits and capabilities by employing experimental approaches guided by statistical outcomes. Key specific goals to thrust **(1)** include **(i)** establishing the lowest-possible f_{rep} at which the highest-possible spatial resolution can be achieved *with in-situ fs specimen photoexcitation*, **(ii)** quantifying the key limiting factors to achieving **(i)** (e.g., measuring the electron-packet density at which resolvable features first become unresolved), and **(iii)** determining the limits of photocurrent stability on a range of experimentally-valid timescales. Further, we are supporting the experimental efforts of thrust **(1)** with General Particle Tracer simulations and calculated field maps of the precise architecture of the electron-gun region in the FEI Tecnai Femto UEM. A second main aim of the work is to use what we learn in thrust **(1)** to enable the direct imaging of ultrafast photoexcited polar-vortex dynamics in superlattices of PbTiO₃/SrTiO₃ (PTO/STO). Key specific goals to thrust **(2)** include **(i)** quantifying the spatiotemporal response of polar-vortex structures to *in-situ* fs photoexcitation, **(ii)** correlating local structural/morphological dynamics to excitation laser fluence, and **(iii)** directly imaging polar-vortex domain-wall dynamics.

Recent Progress

(a) *Stability and viability of alternative photoemission geometries*

When using pulsed beams in a transmission electron microscope (TEM), whether for conducting pump-probe measurements¹ or for mitigating specimen damage,² a compromise is made between electron-packet density, f_{rep} , and measurement duration. Average pulsed-beam photoelectron current in laser-driven UEMs ($\overline{I_{pe}}$) can be written in terms of laser parameters, $\overline{I_{pe}} = \left[\left(\frac{E_{lp}}{h\nu} \cdot \eta(h\nu, T) \right) \cdot CE \right] e \cdot f_{rep}$. Here, E_{lp} is the pulse energy of the fs laser, $h\nu$ is the photon

energy, η is the quantum efficiency of the photoelectron source, CE is the collection efficiency, and e is the fundamental charge. The $\left(\frac{E_p}{h\nu} \cdot \eta\right)$ term determines the number of electrons per packet. For a certain $\overline{I_{pe}}$ and a certain acquisition time, f_{rep} and electron number are inversely related. This has serious implications for how broadly applicable UEM can be for the study of materials phenomena.³

Notably, limitations based solely on the relationship above can be redefined if extremely stable photoelectron sources are employed in extremely stable lab environments. In this context, stable sources are important owing to the stroboscopic nature of UEM data acquisition – inherently low beam currents can be effectively compensated for by

increasing acquisition time provided stability is prioritized. Historically, both thermionic-based and field-emission-based UEMs suffer from the same issue: a decaying average beam current with time, similar to conventional operation. Here, using an off-axis photoemission configuration, we demonstrated that relatively stable and usable photoelectron beams can be generated from the Ni Wehnelt aperture surface (Fig. 1). In particular, for the UV probe-laser settings used, we demonstrated a pulsed electron-beam ($f_{rep} = 200$ kHz) consisting of 460 ± 5 electrons/packet (14.7 ± 0.1 pA) for 70 minutes, with deviation from stability amounting to 0.02 electrons/packet (0.5 fA/min.). Further, the observed stability is immediate and reproducible over several laser-on/laser-off cycles. We also experimentally quantified the impact of prior source heating on the stability, as well as the shift in time-zero position due to the differing physical position and field effects.

(b) Energy filtering via off-axis photoemission

We supported the off-axis photoemission-geometry work with General Particle Tracer simulations of electron trajectories in the precise gun-region architecture of the FEI Tecnai Femto 200 kV thermionic-based UEM. The first set of simulations are intended to establish foundational behaviors by determining statistical distributions of key parameters from 50,000 single, non-interacting electrons. There are several notable findings that emerged. First, electrons generated from the off-axis configuration reached the target (a virtual screen located approximately at the X-ray aperture) ~ 25 ps earlier than those from conventional on-axis emission. This is in good agreement with the experiments noted above and with measurements in other laser-based UEM

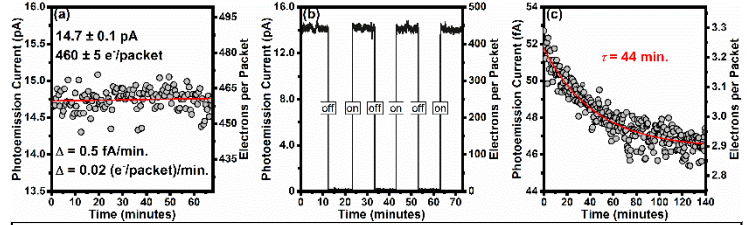


Figure 1. Photocurrent stability from the Ni Wehnelt aperture surface. (a) Typical stability behavior. (b) Cycling laser-on/laser-off settings. (c) Typical decays due to aperture cooling following heating the LaB₆ to thermionic emission.

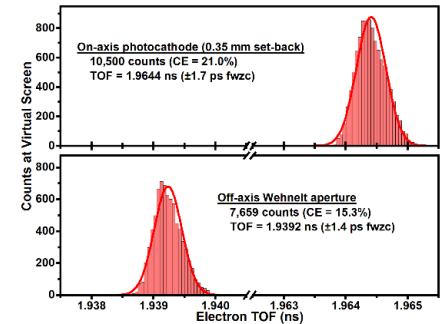


Figure 2. Temporal distributions of on-axis and off-axis photoemission geometries.

instruments.⁴ Second, and more importantly, while the *CE* was lower for off-axis emission, as expected, the temporal distribution (full-width at zero counts) was narrower by ~ 300 fs (Fig. 2). This is due to electrons initially emitted at higher transverse angles being excluded from entering the anode, thus effectively filtering those electrons and producing a narrower energy distribution. This suggests a simple yet compelling method for improving UEM spatial resolution that merits further exploration.

(c) *Low f_{rep} imaging of polar vortex dynamics*

With the off-axis photoemission geometries described above, and with the enhanced photoemission stabilities, we demonstrated the ability to resolve the 5-nm and 10-nm periodicities of polar vortices in PTO/STO superlattices⁵ with an f_{rep} as low as 10 kHz. Further, and most importantly, we demonstrated that the structures remained resolved during photoexcitation with pump-laser fluences of ~ 1 mJ/cm² (max fluence tested thus far) (Fig. 3). This is an important milestone in laser-based UEM development and application, as it opens the way to true fs imaging of nanoscale structural dynamics. Indeed, we now have results showing that we can directly image polar-vortex domain melting dynamics with 1-ps time resolution and single-nanometer spatial resolution. New findings stemming from this capability include discovery of preferential domain melting, subtle fluence dependencies, and domain-boundary movement and velocities.

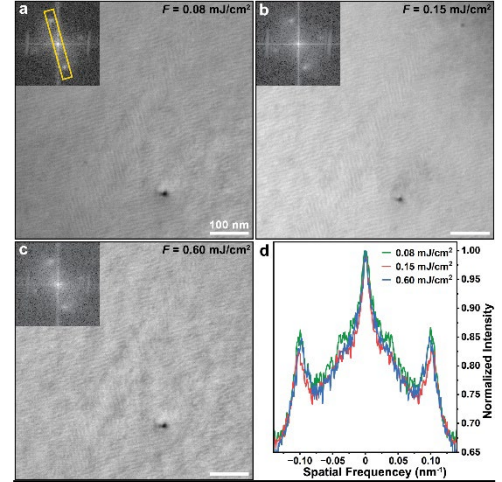


Figure 3. BF UEM imaging of polar vortices under fs photoexcitation. Fluences and FFTs are shown as insets. Panel (d) compiles line profiles for each fluence using the ROI shown in (a).

Future Plans

We intend to aggressively build off of the breakthrough in laser-based UEM spatiotemporal resolution capabilities with *in situ* specimen fs photoexcitation summarized above as follows:

- (1) While the advances above represent new milestones in laser-based UEM development, we are not yet convinced that we have reached the limits of what can be done with this type of UEM. To be clear, the limits we are referring to are with respect to spatiotemporal limits *with fs photoexcitation and f_{rep} values at or below 10 kHz*. Importantly, major improvements could be realized with a new, highly-sensitive detector – currently, we have made the noted breakthroughs with a scintillator-based detector (Gatan OneView).
- (2) In collaboration with theorists, we intend to development a quantum model of the new findings enabled by our UEM measurements. This model will be based on solutions to the Schroedinger equation for the emergence and dynamics of the polar vortex structures in

ferroelectric/dielectric superlattices. Accordingly, UEM data will be gathered on a larger number of structures with variations in unit-cell and layer stacks, and theory will seek to include atomic interfacial arrangements and re-orientations during fs photoexcitation.

- (3) We will refine and optimize the methods described above with the goal of demonstrating high-resolution, laser-based UEM imaging: $5 \text{ \AA} + 1 \text{ ps}$ with $f_{\text{rep}} < 100 \text{ kHz}$. Our test system will be polar vortices, particularly the domain-boundary interfacial regions.

References

1. D. J. Flannigan and A. H. Zewail, *4D Electron Microscopy: Principles and Applications*, Acc. Chem. Res. **45**, 1828 (2012).
2. E. J. VandenBussche and D. J. Flannigan, *Reducing Radiation Damage in Soft Matter with Femtosecond-Timed Single-Electron Packets*, Nano Lett. **19**, 6687 (2019).
3. D. J. Flannigan, W. A. Curtis, E. J. VandenBussche, and Y. Zhang, *Low Repetition-Rate, High-Resolution Femtosecond Transmission Electron Microscopy*, J. Chem. Phys. **157**, 180903 (2022).
4. K. Bückner, M. Picher, O. Crégut, T. LaGrange, B. W. Reed, S. T. Park, D. J. Masiel, and F. Banhart, *Electron Beam Dynamics in an Ultrafast Transmission Electron Microscope*, Ultramicroscopy **171**, 8 (2016).
5. A. K. Yadav, *et al.*, *Observation of Polar Vortices in Oxide Superlattices*, Nature **530**, 198 (2016).

Publications

1. J. Chen, S. A. Shadman, and D. J. Flannigan, *Pulsed-Beam Imaging with Photoexcitation of Polar Vortices Using a Laser-Driven Ultrafast Electron Microscope*, (submitted)
2. T. LaGrange, P. Cattaneo, B. Barwick, D. J. Flannigan, J. Weissenrieder, and F. Carbone, *Laser-Driven Ultrafast Transmission Electron Microscopy*, Nat. Rev. Methods Primers (in press)
3. S. A. Willis, J. Chen, S. A. Shadman, and D. J. Flannigan, *Stability and Viability of Off-Axis Photoemission Geometries in 4D Ultrafast Electron Microscopy*, Microsc. Microanal. **31**, 1199 (2025).
4. D. J. Flannigan and Y. Zhang, *Revealing Defect-Seeded and Interfacial Generation Mechanisms of Photoinduced Coherent Phonons with 4D Ultrafast Electron Microscopy*, Microsc. Microanal. **31**, 1165 (2025).
5. S. A. Willis and D. J. Flannigan, *Influence of Photoemission Geometry on Timing and Efficiency in 4D Ultrafast Electron Microscopy*, ChemPhysChem **26**, e202401032 (2025).
6. J. Chen, S. A. Willis, and D. J. Flannigan, *Delineation of the Impact on Temporal Behaviors of Off-Axis Photoemission in an Ultrafast Electron Microscope*, Rev. Sci. Instrum. **95**, 093705 (2024).
7. S. A. Willis, W. A. Curtis, and D. J. Flannigan, *Wehnelt Photoemission in an Ultrafast Electron Microscope: Stability and Usability*, J. Appl. Phys. **136**, 024901 (2024).

Spatiotemporal Imaging of Magnetization Dynamics of van der Waals ferromagnets

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Keywords: Nitrogen-vacancy center, scanning probe microscopy, van der Waals ferromagnet

Research Scope

This research project investigates magnetic properties and magnetization dynamics in van der Waals magnetic materials at the single flake level, avoiding heterogeneities associated with large crystals. To this end we use scanning a scanning nitrogen-vacancy center magnetic microscope that can probe the sample with nanometer spatial resolution and microtesla magnetic sensitivity. Our approach integrates atomic force microscopy (AFM) with a diamond probe containing a single NV center, enabling high-resolution imaging of stray magnetic fields. Scanning NV magnetometry supports multiple measurement modalities, making it a powerful and flexible platform for probing both static and dynamic magnetic phenomena in low-dimensional materials. From a material perspective, we focus on van der Waals magnetic materials with a Curie temperature (T_c) near and above room temperature, with Fe_5GeTe_2 (F5GT) being a first candidate system because of its high Curie temperature, T_c , and because it is a model system in which the iron positions in the lattice drive a structure-function relationship.¹

We report on three principle aims. First, we seek to understand the material properties of F5GT at the single flake level as the material evolves through its T_c . We focus on understanding the onset of ferromagnetism and how the local environment of a single flake, including the morphology of how it sits on the substrate, influences its magnetic behavior. Second, to support the first aim, we extend the capabilities of our NV center microscope to variable temperature operation around room temperature by implementing a thermoelectric (TEC) sample stage capable of stabilizing the sample temperature by $\sim \pm 20^\circ\text{C}$ with respect to ambient conditions. Third, we are interested in the material-limited dynamical properties of F5GT at the single flake level, where the properties are not limited by defects and inhomogeneity in the crystal.

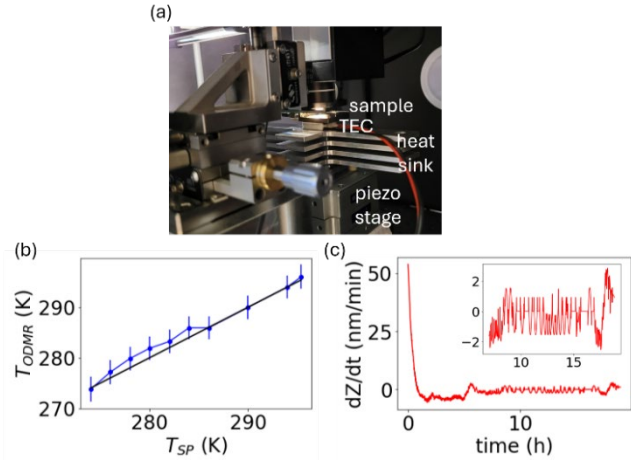


Figure 1. (a) Thermoelectric cooler (TEC) stage incorporated into the scanning NV setup. (b) Sample holder temperature setpoint (T_{SP}) compared with temperature characterized by the optically detected magnetic resonance (ODMR) spectra of the NV center (T_{ODMR}). The solid line indicates where T_{SP} is equal to T_{ODMR} . (c) An example of the change in sample stage height (Z) over time.

Recent Progress

We start by discussing our second aim – developing a variable-temperature scanning NV center microscope to enable temperature-dependent studies of magnetic properties and magnetization dynamics with resolution at the nanometer scale. Later we discuss the measurements made using this set-up.

We have recently integrated a TEC unit with the sample stage, a Lakeshore temperature controller, resistance temperature detectors (RTDs), and a custom-designed heat sink (Fig. 1(a)). The TEC-controlled sample mount is stacked on the XYX piezo scanning stage. Critical issues we considered include sample stability at the nanometer scale, weight of the system on the piezoscanners, and the temperature range that the piezoscanners can tolerate. We also implemented continuous purging with dry nitrogen to prevent condensation and carry away heat. To cool the sample, the TEC element must get hot on its opposite surface, which is then managed using a stage with heat sink fins that radiate the heat away from the stages. We also used ceramic spacers to thermally isolate the piezo stage – keeping it within 5 °C of ambient temperature.

Temperature feedback control is supported by an RTD mounted on the side of the sample holder, which informs the controller's voltage output to the TEC. A second RTD on the heat sink monitors its temperature, which significantly influences the sample stage height through thermal expansion. To validate the accuracy of the sample holder temperature measurement, we compare its readings with temperatures inferred from the optically detected magnetic resonance (ODMR) spectra of single NV centers in a diamond sample mounted in place of the usual magnetic sample. The NV center's zero-field splitting D shifts linearly with temperature, thus it can serve as a sample-embedded thermometer that we can use to calibrate the RTD reading against the true sample temperature. Using a known temperature coefficient of $dD/dT = -74.2 \text{ kHz/K}$,² we extract the NV-based temperature (T_{ODMR}) and found close agreement with the RTD setpoint (T_{SP}), confirming the RTD's reliability for temperature calibration (Fig. 1(b)).

We also characterize the thermal and mechanical stability of the setup. Although the heat sink is optimized to dissipate heat, its temperature depends on the TEC drive set-point. Its temperature strongly affects the sample stage height, and if the temperature is changing then sample stage height will drift quickly. We observe a correlation between heat sink temperature and sample height that we monitor, also using the diamond contain NV centers based on the NV center focus position. We find that a 1 K rise in temperature corresponds to a $\sim 1.5 \mu\text{m}$ increase in height. Given our typical probe-sample distance of $\sim 30 - 100 \text{ nm}$, we monitor the RTD temperature over hours and only start scanning when the temperature is stabilized to a drift rate equivalent to 5 nm/min (Fig. 1(c)).

We use this variable-temperature scanning NV setup to pursue our aim of studying the magnetic properties of a single FGT lake through its T_c . The flake is $\sim 20 \text{ nm}$ thick and capped with an 18 nm hBN layer, then transferred onto a patterned loop antenna for NV-based magnetic imaging (Fig.

2(a)). We acquire static magnetic field images at 295 K, 290 K, 285 K, and 280 K over a region indicated in Fig. 2(a) (Figs. 2(b)–(e)). At room 295 K, a localized magnetic signal appears near a height variation, likely caused by a ~ 10 nm-thick particle embedded beneath the flake (Fig. 2(b)). As the temperature decreases, the magnetic contrast becomes more pronounced, with domain features nucleating from the initially magnetic region. By 280 K, the stray field contrast reaches approximately 8 G, suggesting the stabilization of ferromagnetic order (Fig. 2(e)).

Interestingly, the onset of magnetic contrast coincides spatially with the location of the height bump. Atomic force microscopy reveals a smooth, diffuse profile around this feature, indicating that the underlying particle may induce local strain in the flake, which in turn influences the material T_c . This observation raises the possibility that strain—introduced by substrate inhomogeneities—plays a role in stabilizing ferromagnetism in the as-exfoliated F5GT flake.

We now discuss our third aim of understanding the dynamical properties of F5GT at the single flake level. A recent ferromagnetic resonance (FMR) study³ has asserted that bulk F5GT crystal exhibit effective damping comparable to permalloy (NiFe) with a Gilbert damping coefficient of $\alpha = 0.01$, suggesting its potential for room-temperature spintronic applications. The bulk measurements in that work showed inhomogeneous linewidth broadening far larger than the contribution from viscous (Gilbert) damping. To better assess the material damping, we target single-flake level FMR detection using exfoliated F5GT flakes, which are expected to be more structurally pristine.

We transfer a 25 nm F5GT flake capped with a 10 nm hBN flake onto a 4 GHz lumped-element superconducting resonator, which exhibits a loaded Q-factor of $\sim 10^4$ at 0.44 K (Fig. 3(a)). We observe a decrease in the “intrinsic” Q-factor (Q_i) at a static magnetic field of 0.046 T. This reflects that as the F5GT flake comes into resonance, it is drawing energy out of the superconducting

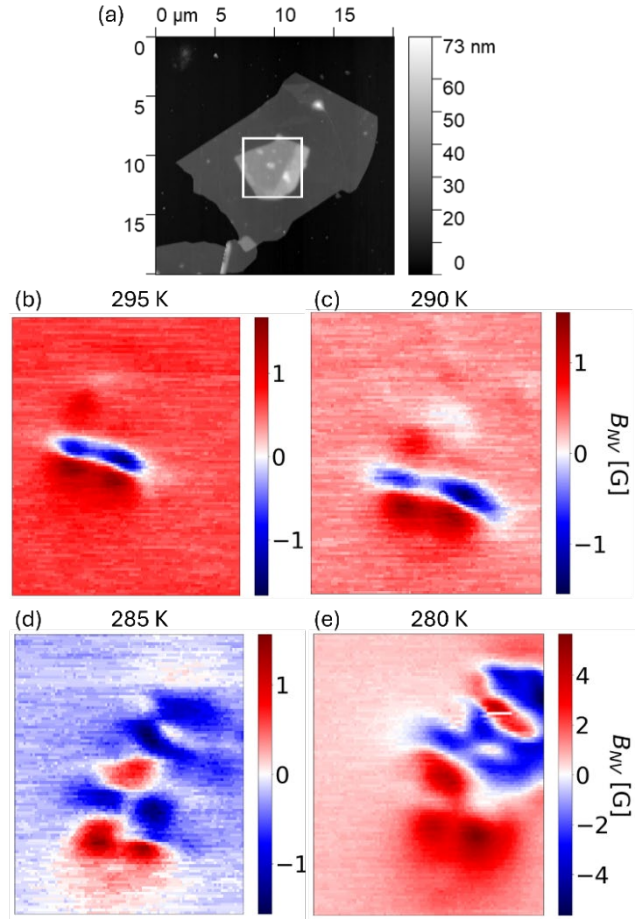


Figure 2. (a) Atomic Force Microscopy (AFM) image of a F5GT (20 nm)/hBN (18 nm) flake. (b-e) Static magnetic field imaging of F5GT flake at (b) 295 K, (c) 290 K, (d) 285 K, and (e) 280 K. The scan areas ($5 \mu\text{m} \times 5 \mu\text{m}$) are approximately what is indicated as a squared region in (a).

resonator, which results in an apparent decrease in Q_i (Fig. 3(b)). This measurement confirms the coupling between the flake and the resonator and demonstrates successful single-flake FMR detection.

We estimate an upper bound to the Gilbert damping parameter (α^*) by analyzing the FMR linewidth under the assumption of negligible inhomogeneous broadening. The extracted α^* values are slightly lower but comparable to than those reported for bulk F5GT at 10 K ($\alpha \approx 0.007$) [3], indicating reduced damping in the exfoliated sample. Interestingly, we observe that α decreases with temperature in the range of 0.4 – 1.2 K (Fig. 3(c)).

Future Plans

We plan to continue in two areas. First, we will build on our variable-temperature scanning NV measurements to further explore the onset and evolution of ferromagnetism in exfoliated F5GT flakes. Key goals include imaging flakes transferred onto corrugated nanostructures to investigate strain-induced magnetic ordering, measuring static magnetic field at higher temperatures to identify the temperature threshold at which magnetic features vanish, and probing magnetic fluctuations through relaxometry and Ramsey coherence techniques. Second, we will continue our effort in the single-flake FMR detection by designing quarter-wavelength superconducting resonators with optimized Q-factors, targeting values exceeding 10^6 . A key advantage of this approach is that we will use the many overtone resonances, each as a separate frequency probe, which will allow us to distinguish viscous Gilbert damping from inhomogeneous linewidth broadening.

References

1. A. F. May, D. Ovchinnikov, Q. Zheng, R. Hermann, S. Calder, B. Huang, Z. Fei, Y. Liu, X. Xu, and M. A. McGuire, *Ferromagnetism Near Room Temperature in the Cleavable van der Waals Crystal Fe_5GeTe_2* , ACS Nano **13**, 4436 (2019)
2. V. M. Acosta, E. Bauch, M. P. Ledbetter, A. Waxman, L.-S. Bouchard, and D. Budker, *Temperature Dependence of the Nitrogen-Vacancy Magnetic Resonance in Diamond*, Phys. Rev. Lett. **104**, 070801 (2010)
3. L. Alahmed, B. Nepal, J. Macy, W. Zheng, B. Casas, A. Sapkota, N. Jones, A. R. Mazza, M. Brahlek, W. Jin, M. Mahjouri-Samani, S. S.-L. Zhang, C. Mewes, L. Balicas, T. Mewes, and P. Li, *Magnetism and spin dynamics in room-temperature van der Waals magnet Fe_5GeTe_2* , 2D Mater. **8**, 045030 (2021)

Publications

No new publications in this period.

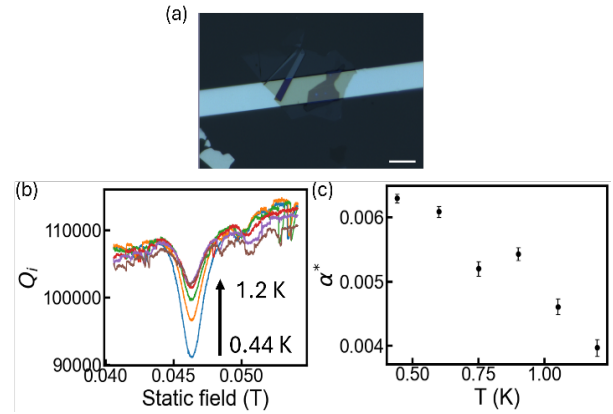


Figure 3. (a) F5GT flake transferred onto the patterned inductor line of the 4 GHz superconducting resonator. A larger, close-to-transparent flake is the hBN flake capping the F5GT flake. The scale bar represents 10 μm . (b) FMR line at various temperatures. (c) Estimated upper limit in Gilbert damping α^* at various temperatures

Sub-diffraction Imaging of Carrier Dynamics in Perovskite Semiconductors: Passivation, Ion Motion, and Applying Convolutional Neural Networks

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Keywords: halide perovskites, time-resolved electrostatic force microscopy, neural networks,

Research Scope

Probing charge carrier motion in condensed-phase systems below the diffraction limit is a key challenge facing researchers seeking to elucidate the structure/property relationships of new materials for energy harvesting, energy storage, high-performance electronics, and emerging quantum electronics. In this period, we are developing new microscopy capabilities that merge hardware, software, and simulation to demonstrate and interpret fast time-resolved scanning probe methods for operando probing of perovskite semiconductors. We achieved a long-standing goal of connecting dynamics measured via sub-diffraction mechanical imaging with spatially averaged dynamics measured via optical time-resolved photoluminescence.

Recent Progress

We employed time-resolved electrostatic force microscopy (trEFM) to spatially investigate photocarrier dynamics in halide perovskite semiconductors by monitoring how surface potentials equilibrate under illumination. By examining surfaces treated with distinct passivation agents, we demonstrated that trEFM captures dynamics closely tied to surface recombination velocities (SRV) and carrier lifetimes, showing good agreement with complementary time-resolved photoluminescence (trPL) measurements. Our observations highlight nanoscale spatial variability in recombination dynamics resulting from surface passivation treatments, as well as heterogeneity in surface potential equilibration times linked to perovskite film morphology.

By combining wavelength- and intensity-dependent trEFM data with drift-diffusion simulations, we explored the different effects of contributions from electronic carrier recombination and ionic movement to the measured surface potential dynamics. This work demonstrates the capability of mechanical-based detection to probe electronic recombination dynamics below the optical diffraction limit, emphasizing the potential for improving passivation uniformity at the nanoscale. Additionally, we advanced the use of convolutional neural networks to streamline the analysis of trEFM imaging data.

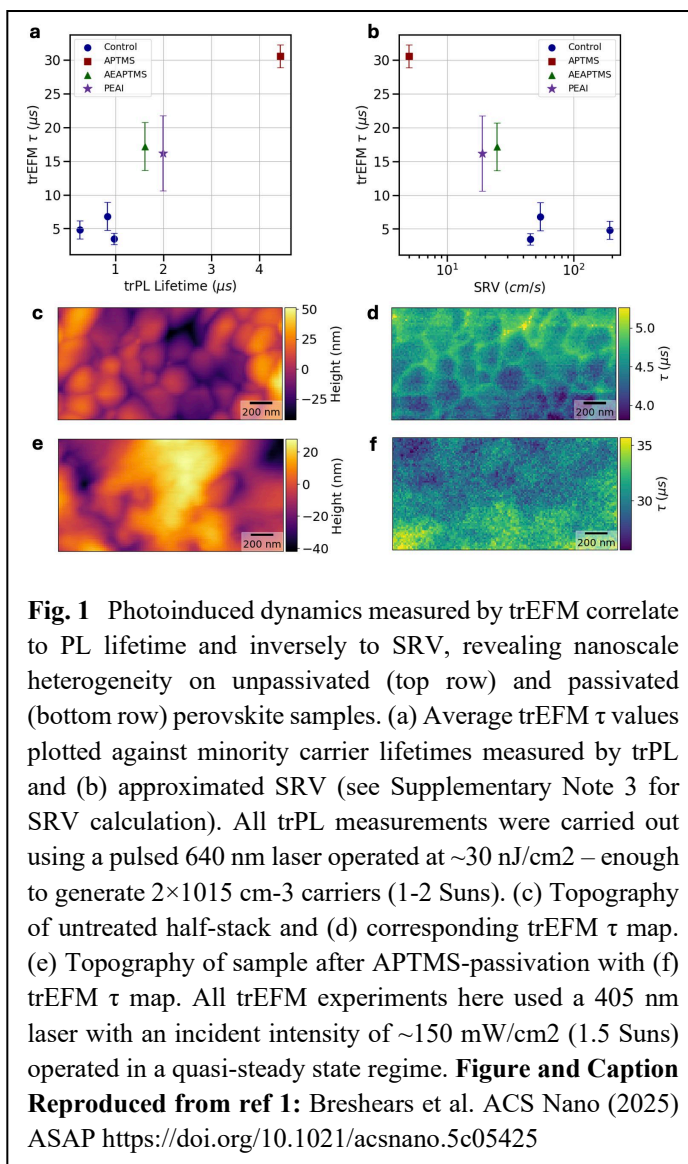
We illuminated halide perovskite films deposited on indium tin oxide (ITO) substrates through the ITO layer. Utilizing a laser with approximately a 2 ns rise time, we recorded the transient changes in cantilever dynamics of the scanning probe to capture the semiconductor's short-term electronic response following illumination. Upon photoexcitation, the transient population of carriers evolves toward a new equilibrium state, manifesting as time-dependent variations in surface potential, capacitance, and dissipative characteristics of the film. These transient phenomena temporarily

perturb the cantilever from its steady-state oscillation, encoding critical details of the short-term electronic environment that we reconstructed using empirical calibration methods and machine-learning-assisted analyses.

We further investigated how trEFM-derived surface equilibration times correlated with electronic carrier dynamics by evaluating the impact of three known surface passivators:

(3-aminopropyl)trimethoxysilane (APTMS), [3-(2-aminoethylamino)propyl] trimethoxysilane (AEAPTMS), and phenethylammonium iodide (PEAI). These tests were conducted on semiconductor films formed with the architecture glass/ITO/phosphonic acid modifier/Cs_{0.22}FA_{0.78}Pb(I_{0.85}Br_{0.15})₃.

Importantly, we found that trEFM equilibration times, while proportional to the trPL results, were consistently larger in magnitude than the minority carrier lifetimes derived from trPL. We also extracted SRVs, revealing a robust inverse relationship between trEFM time constants and local SRVs. Our trEFM images showed notable contrast between perovskite grains and their boundaries, an observation altered unexpectedly by passivation. Notably, grain boundaries exhibited slower equilibration dynamics prior to passivation but appeared indistinct after surface treatments.



Through systematic studies incorporating power-, wavelength-, and surface chemistry-dependent trEFM and trPL measurements, alongside drift-diffusion simulations, we clarified that trEFM primarily probes local surface potential equilibration influenced by electronic recombination and ion motion. Our results establish that passivation treatments prolong equilibration by substantially suppressing SRV, and importantly, trEFM detects local variability in SRV post-passivation, emphasizing the necessity of spatially resolved optimization. Further, we attribute the slower

dynamics observed at grain boundaries in untreated samples to heightened defect densities promoting increased ion mobility contributions.

These findings underscore trEFM's capability to explore how nanoscale structural features of perovskite films impact local electronic dynamics, highlighting its utility for assessing passivation efficacy below the optical diffraction limit. This approach promises to guide optimization of perovskite semiconductors and their passivation strategies at nanometer scales critical to advanced device performance.

Future Plans

We have two significant goals for further developing this technique in the near future. First, we are developing a cross-sectional sample holder for measuring dynamics changes in cross-sectioned device stacks to understand ion motion and electrochemistry in operating perovskite semiconductors under voltage bias and light stress. Second, we plan to advance our signal demodulation and denoising work and apply these methods and algorithms to studying quantum emitters in a vacuum microscope once it is delivered.

References

1. M. D. Breshears, J. Pothoof, R. Giridharagopal, D. S. Ginger. “*Subdiffraction imaging of carrier dynamics in Halide perovskite semiconductors: Effects of passivation, morphology, and ion motion.*” ACS Nano. ASAP. DOI: 10.1021/acsnano.5c05425 (2025).

Publications from 2023 to 2025 on DOE-BES Award DE-SC0013957:

1. M. D. Breshears, J. Pothoof, R. Giridharagopal, D. S. Ginger. “*Subdiffraction imaging of carrier dynamics in Halide perovskite semiconductors: Effects of passivation, morphology, and ion motion.*” ACS Nano. ASAP. DOI: 10.1021/acsnano.5c05425 (2025).
2. M. D. Breshears, R. Giridharagopal, D. S. Ginger. “*Multioutput convolutional neural network for improved parameter extraction in time-resolved electrostatic force microscopy data.*” J. Chem. Inf. Model. **65**, 5352–5359 (2025).
3. C. Pederson, R. Giridharagopal, F. Zhao, S. T. Dunham, Y. Raitses, D. S. Ginger, K.-M. C. Fu. “*Optical tuning of the diamond Fermi level measured by correlated scanning probe microscopy and quantum defect spectroscopy.*” Phys. Rev. Mater. **8**, 036201 (2024).
4. R. J. E. Westbrook, M. Taddei, R. Giridharagopal, M. Jiang, S. M. Gallagher, K. N. Guye, A. I. Warga, S. A. Haque, D. S. Ginger. “*Local Background Hole Density Drives Nonradiative Recombination in Tin Halide Perovskites.*” ACS Energy Lett. **9**, 732–739 (2024).
5. J. Wang, L. Zeng, D. Zhang, A. Maxwell, H. Chen, K. Datta, A. Caiazzo, W. H. M. Remmerswaal, N. R. M. Schipper, Z. Chen, K. Ho, A. Dasgupta, G. Kusch, R. Ollearo, L. Bellini, S. Hu, Z. Wang, C. Li, S. Teale, L. Grater, B. Chen, M. Wienk, R. Oliver, H. Snaith, R. A. J. Janssen, E. Sargent. “*Halide homogenization for low energy loss in 2-eV-bandgap perovskites and increased efficiency in all-perovskite triple-junction solar cells.*” Nat. Energy **9**, 70–80 (2023).
6. F. Akrami, F. Jiang, R. Giridharagopal, D. S. Ginger. “*Kinetic Suppression of Photoinduced Halide Migration in Wide Bandgap Perovskites via Surface Passivation.*” J. Phys. Chem. Lett. **14**, 9310–9315 (2023).
7. J. Pothoof, R. J. E. Westbrook, R. Giridharagopal, M. D. Breshears, D. S. Ginger. “*Surface Passivation Suppresses Local Ion Motion in Halide Perovskites.*” J. Phys. Chem. Lett. **14**, 6092–6098 (2023).
8. C. A. R. Perini, A.-F. Castro-Mendez, T. Kodalle, M. Ravello, J. Hidalgo, M. Gomez-Dominguez, R. Li, M. Taddei, R. Giridharagopal, J. Pothoof, C. M. Sutter-Fella, D. S. Ginger, J.-P. Correa-Baena. “*Vapor-*

- Deposited $n = 2$ Ruddlesden–Popper Interface Layers Aid Charge Carrier Extraction in Perovskite Solar Cells.* ACS Energy Lett. **8**, 1408–1415 (2023).
9. H. Contreras, A. O’Brien, M. Taddei, Y. Shi, F. Jiang, R. J. E. Westbrook, Y. Zhang, R. Giridharagopal, P. A. Lee, S. Barlow, S. R. Marder, N. R. Armstrong, D. S. Ginger. “*Deposition-dependent coverage and performance of phosphonic acid interface modifiers in Halide perovskite optoelectronics.*” arXiv [physics.app-ph] (2025). <http://arxiv.org/abs/2506.19205>.

Development of atomic resolution spin dynamics imaging scanning tunneling microscopy (SDI-STM)

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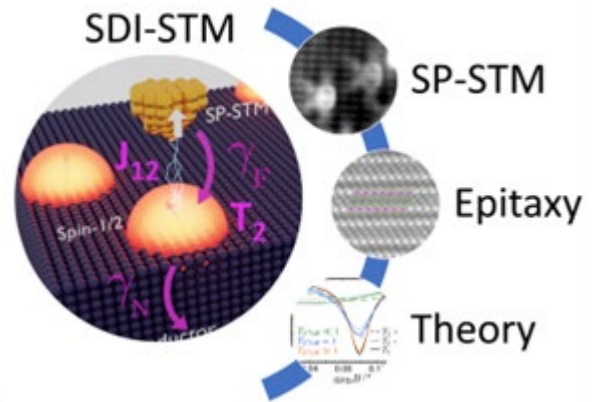
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Keywords: 2D magnets, spin polarized STM, spin transport theory, magnetic semiconductors, magnetic topological insulators

Program Scope

In this program we will develop a new technique, *spin dynamics imaging scanning tunneling microscopy* (SDI-STM), as conceptually illustrated in the figure. Prior work by the team has developed a theoretical foundation for this new technique, modeling charge and spin transport through single spin defects in a variety of tunnel junction configurations with both magnetic and non-magnetic contacts (1–4). These theoretical studies emphasize the importance of exchange coupling between defects and nuclear spins, spin- and charge-dependent tunneling rates to/from the defects, and the influence of microwave excitation. At the device level for example, it has been demonstrated that the tunneling current is resonantly enhanced by the ESR response of electrically active point defects in the junction. We find that *spin blockade dynamics* produce similar features near zero magnetic field. This **dc magnetoresistance** (dcMR) can be measured to extract quantitative information on e.g., spin lifetimes of single defects. We will demonstrate that spin-polarized STM (SP-STM) detection in this regime can provide atomic-scale information on how the local environment influences spin dynamics. To validate the theoretical predictions and extract quantitative information, a central requirement is systematic tuning of tunneling rates to and from the defects. Experimentally, our approach is to combine materials synthesis (e.g. charge and magnetic doping) and STM atomic manipulation of the local electrostatic landscape to systematically tune these rates and extract spin dynamics information.



Our program objectives are to:

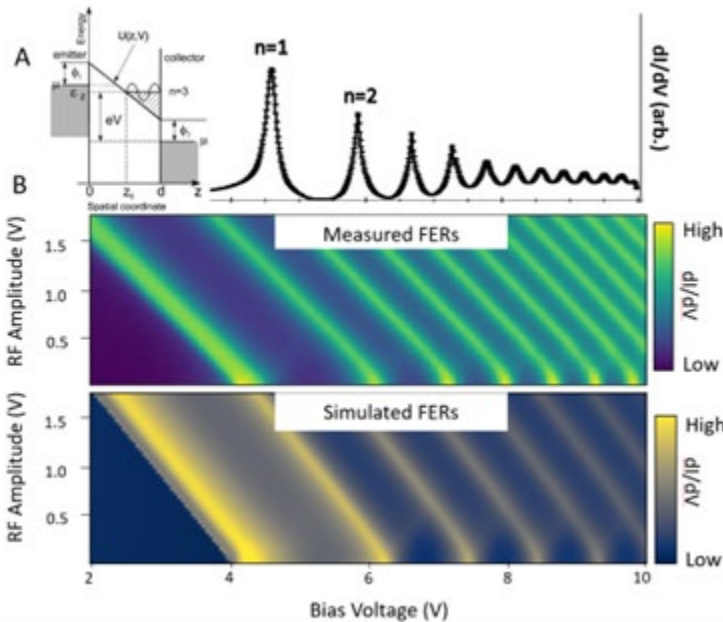
(i) **Validate dcMR mechanism through SP-STM studies in van der Waals TIs:** Here we will build on preliminary data on Fe adatoms on Bi₂Te₃ topological insulator (TI) surfaces, where we found differential contrast in SP-STM dI/dV maps that we attribute to variations in spin lifetime with local environment. We have recently developed the capability for atomistic density functional theory calculations of this system, to complement our atomistic tight-binding calculations and spin coherent transport theory. By modeling tunneling rates to/from the adatom, and comparing with systematic STM studies with varying bias voltage, tip height, applied magnetic field and local environment, we will confirm the SDI-STM imaging mechanism and develop protocols for extracting quantitative estimates of relevant dynamical parameters such as T₂.

(ii) **Compare SDI-STM single spin measurements with optical spin lifetime measurements in 2D DMS:** Here we will first develop and refine the growth of transition metal-doped MoSe₂ and WSe₂,

prototype 2D dilute magnetic semiconductors (2D DMS). Single crystal thin films down to the monolayer limit will be grown by molecular beam epitaxy, with varying electronic and magnetic doping. Structural characterization by conventional STM will be used as feedback to the growth effort to refine the materials. These materials offer the possibility for quantitatively comparing SDI-STM dynamical information with ensemble spin lifetimes from ultrafast magneto-optical Kerr effect measurements.

Recent Progress

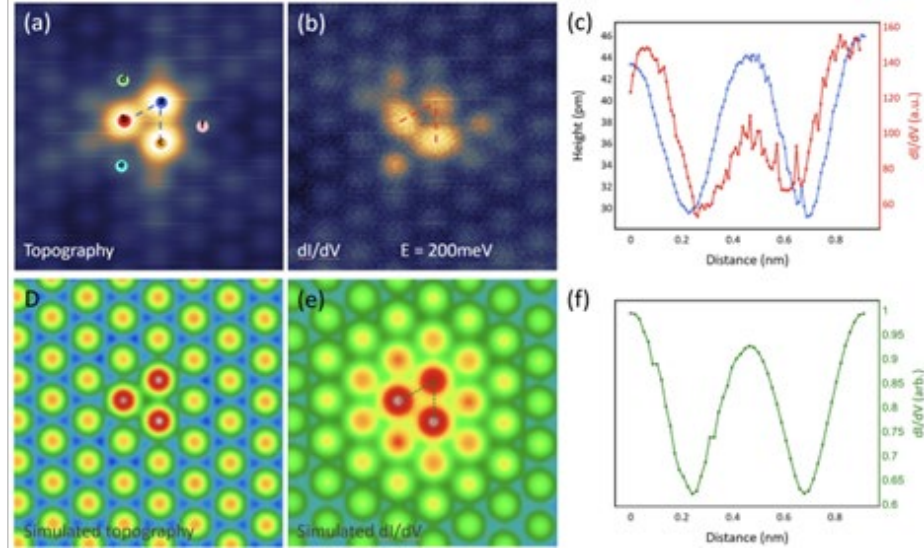
Microwave-tunable resonant tunneling in the field emission regime: During the prior award period, we discovered a new microwave-induced shift of resonant states in STM spectroscopy (5). When the applied bias becomes larger than the tip/sample work functions, a triangular well forms, leading to a series of quasi-bound electronic states above the sample surface. These states manifest as sharp increases in the Fowler-Nordheim field emission current at specific biases corresponding to the resonance conditions. While FERs have been extensively studied in the context of STM, the influence of time-varying bias on these resonances has remained unexplored. As shown in the figure, with increasing RF amplitude (at 1GHz), the FER states first predominately broaden, before systematically shifting toward lower voltage. This effect can be understood as a rectification effect in resonant



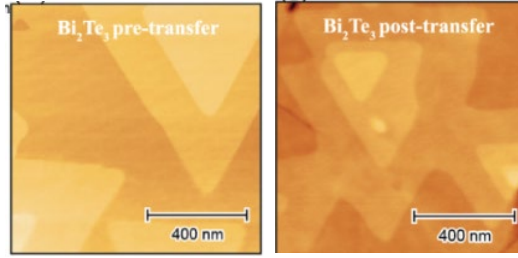
tunneling, transitioning between regimes set by the relative RF amplitude to the resonant state linewidth. We extended the theoretical framework for resonant tunneling into FERs by Gundlach to include a time-varying bias, and our simulations are in semi-quantitative agreement with the experiments. This methodology can be extended to other resonant tunneling contexts in STM, providing insights into the tunneling dynamics, and also enables a practical method for characterizing the instrumental transmission at RF and higher frequencies.

Reduced symmetry of Fe adatoms on a TI surface:

To validate the integration of first-principles theoretical calculations and STM measurements needed for SDI-STM, we have performed systematic STM measurements and density functional theory calculations of Fe adatoms on Bi_2Te_3 (6, 7). Fe adatoms on this surface adsorb at two three-fold symmetric hollow sites, differentiated by the underlying (Bi,Te) atoms. The figure below shows an STM topographic image and spectroscopic dI/dV map of an Fe adatom in the fcc hollow site. The topographic image shows the expected three-fold symmetry, with bright spots corresponding to neighboring Te atoms, highlighted by their interactions with the Fe adatom in the center. Surprisingly, a reduced symmetry is evident in the dI/dV map, with one lobe much lower in contrast than the other two. Our DFT calculations suggest this is due to a lowering of system energy upon a slight displacement of the Fe adatom from the hollow site. DFT-simulated topographic and local density of state maps reproduce the lowered symmetry, and are in qualitative agreement with the experimental STM data.



UHV transfer of MBE-grown vdW films: To facilitate materials integration and complementary SDI-STM and optics measurements, we have developed a polymer-assisted dry transfer method and successfully performed full-film transfer of various MBE-grown 2D vdW materials including



transition metal dichalcogenides, topological insulators and 2D magnets (8). For example, we have transferred air-sensitive 2D magnets, characterized their magnetic properties, and compared them with as-grown materials. The results show that the transfer technique does not degrade the magnetic properties, with the Curie temperature and hysteresis loops exhibiting similar behaviors after the transfer.

Future plans: Our overarching plan is to validate the principle for SDI-STM in measurements of magnetic adatoms on Bi_2Te_3 , and then quantitatively compare dynamical information between single-spin and ensembles in 2D DMS. MBE growth will be used to tune the charge/spin doping of these materials, and the new dry transfer technique will facilitate materials integration for STM and optical measurements. Combined with a foundation of atomistic theory, we will extend the capability for using STM to quantify how the local environment influences spin dynamics at the single spin level. We have recently taken some steps in this direction by validating tight-binding simulations for acceptor states in silicon (9) and extending the formalism pioneered by us to superconducting bound states around a defect at a surface (Shiba states)(10), and in preparation for STM measurements on 2D materials with competing charge density wave and superconducting phases we have provided an ab initio simulation of NbSe_2 (11).

References

1. S. R. McMillan, N. J. Harmon, M. E. Flatte, Image of Dynamic Local Exchange Interactions in the dc Magnetoresistance of Spin-Polarized Current through a Dopant. *Phys. Rev. Lett.* **125**, 257203 (2020).
2. N. J. Harmon, M. E. Flatte, Theory of oblique-field magnetoresistance from spin centers in three-terminal spintronic devices. *Phys. Rev. B* **103**, 035310 (2021).

3. S. R. McMillan, M. E. Flatté, Theory of spin-polarized current flow through a localized spin triplet state. *arXiv:2112.14805 [cond-mat]* (2021).
4. N. J. Harmon, M. E. Flatté, Theory of spin-coherent electrical transport through a defect spin state in a metal/insulator/ferromagnet tunnel junction undergoing ferromagnetic resonance. *Physical Review B* **98**, 035412 (2018).
5. W. Koll, K. Maleki Sanukesh, M. E. Flatté, J. A. Gupta, Microwave-tunable tunneling into STM field emission resonances (in preparation).
6. D. Nguyen, H. Paudyal, J. Sink, M. E. Flatté, J. A. Gupta, Reduced symmetry of Fe adatoms on Bi₂Te₃ (in preparation).
7. D. Nguyen, J. A. Gupta, Scanning Tunneling Microscope Tip-Induced Formation of Bi Bilayers on Bi₂Te₃. *arXiv* arXiv:2507.16081 [Preprint] (2025). <https://doi.org/10.48550/arXiv.2507.16081>.
8. Z. Li, W. Zhou, M. Swann, V. Vorona, H. Scott, R. K. Kawakami, Full-film dry transfer of MBE-grown van der Waals materials. *2D Materials* **12**, 035003 (2025).
9. M. Siegl, J. Zanon, J. Sink, A. R. da Cruz, H. Hedgeland, N. J. Curson, M. E. Flatté, S. R. Schofield, Imaging the Acceptor Wave Function Anisotropy in Silicon. *arXiv* arXiv:2505.13041 [Preprint] (2025). <https://doi.org/10.48550/arXiv.2505.13041>.
10. J. Sink, H. Paudyal, D. Jyoti, A. J. Heinrich, D.-J. Choi, N. Lorente, M. E. Flatté, Microscopic Scattering Approach to In-Gap States: Cr Adatoms on Superconducting β -Bi₂Pd. *arXiv* arXiv:2507.08740 [Preprint] (2025). <https://doi.org/10.48550/arXiv.2507.08740>.
11. H. Paudyal, M. E. Flatté, Suppression of charge-density wave and superconductivity in a lithiated NbSe₂ monolayer. *arXiv* arXiv:2507.11856 [Preprint] (2025). <https://doi.org/10.48550/arXiv.2507.11856>.

Award publications since 2023

1. Nguyen, D. & Gupta, J. A. Scanning Tunneling Microscope Tip-Induced Formation of Bi Bilayers on Bi₂Te₃. Preprint at <https://doi.org/10.48550/arXiv.2507.16081> (2025).
2. Paudyal, H. & Flatté, M. E. Suppression of charge-density wave and superconductivity in a lithiated NbSe₂ monolayer. Preprint at <https://doi.org/10.48550/arXiv.2507.11856> (2025).
3. Sink, J. *et al.* Microscopic Scattering Approach to In-Gap States: Cr Adatoms on Superconducting β -Bi₂Pd. Preprint at <https://doi.org/10.48550/arXiv.2507.08740> (2025).
4. Siegl, M. *et al.* Imaging the Acceptor Wave Function Anisotropy in Silicon. Preprint at <https://doi.org/10.48550/arXiv.2505.13041> (2025).
5. Siegl, M. *et al.* Imaging the Acceptor Wave Function Anisotropy in Silicon. *arXiv.org* <https://arxiv.org/abs/2505.13041v1> (2025).
6. Li, Z. *et al.* Full-film dry transfer of MBE-grown van der Waals materials. *2D Mater.* **12**, 035003 (2025).
7. Limbu, Y. *et al.* Functionalized Cr₂SC MXenes: Novel Magnetic Semiconductors. Preprint at <https://doi.org/10.48550/arXiv.2503.15695> (2025).
8. Guo, J. *et al.* Moiré-Tunable Localization of Simultaneous Type I and Type II Band Alignment in a MoSe₂/WS₂ Heterobilayer. Preprint at <https://doi.org/10.48550/arXiv.2502.14138> (2025).
9. Li, Z. *et al.* Full-film dry transfer of MBE-grown van der Waals materials. *2D Materials* **12**, 035003 (2025).
10. Goff, B. M. & Gupta, J. A. MacroQueue: Automating Measurements in High-Dimensional Parameter Spaces. Preprint at <https://doi.org/10.48550/arXiv.2406.15412> (2024).
11. Chen, X. *et al.* Antiferromagnetic order in the layered magnetic topological insulator MnBi₂Se₄ probed by resonant soft x-ray scattering. *Phys. Rev. B* **109**, 184418 (2024).
12. Goff, B. M. *et al.* Scanning tunneling microscopy study of epitaxial Fe₃GeTe₂ monolayers on Bi₂Te₃. *2D Mater.* **11**, 025012 (2024).
13. Cheng, S. *et al.* Atomic layer molecular beam epitaxy of kagome magnet RMn₆Sn₆ (R = Er, Tb) thin films. *APL Mater.* **12**, 041129 (2024).
14. Zhang, Y. *et al.* Quantum octets in high mobility pentagonal two-dimensional PdSe₂. *Nat. Commun.* **15**, 761 (2024).
15. Paudyal, H., Flatté, M. E. & Paudyal, D. Implications of the electron-phonon coupling in CuPb₉(PO₄)₆O for superconductivity: An *ab initio* study. *Phys. Rev. Mater.* **8**, L011801 (2024).
16. Goff, B. M. Scanning Tunneling Microscopy Characterization of Two-Dimensional Magnetic, Topological Heterostructures. (The Ohio State University, United States -- Ohio, 2024).
17. Bishop, A. J. Synthesis and Characterization of 2D Chalcogenide Materials Towards Applications. (The Ohio State University, 2024).
18. Cheng, S. *et al.* Room-temperature magnetic skyrmions in Pt/Co/Cu multilayers. *Phys. Rev. B* **108**, 174433 (2023).
19. Zhou, W. *et al.* Tuning the Curie temperature of a two-dimensional magnet/topological insulator heterostructure to above room temperature by epitaxial growth. *Phys. Rev. Mater.* **7**, 104004 (2023).
20. Repicky, J. J., Goff, B., Cheng, S., Kawakami, R. K. & Gupta, J. A. Observation of skyrmion bubbles in multilayer [Pt/Co/Cu]_n using spin-polarized STM. *J. Magn. Magn. Mater.* **580**, 170913 (2023).
21. Cheng, S. *et al.* Epitaxial Kagome Thin Films as a Platform for Topological Flat Bands. *Nano Lett.* **23**, 7107–7113 (2023).

Visualizing the atomic-scale dynamics of charge-ordered phases in quantum materials

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Keywords: scanning tunneling microscopy, quantum materials, charge density wave, sliding

Research Scope

Understanding how electric charge moves through quantum materials is of critical importance to the fundamental science of solids and to unlocking the full potential of these materials for next-generation energy and quantum information technologies. Notably, a conspicuous number of quantum materials host a charge density wave (CDW), a collective charge-ordered state that breaks the symmetry of the host crystal. When the CDW has a periodicity that is incommensurate with the crystal lattice, an electric field of sufficient strength can de-pin it from local defects causing the entire collective CDW to slide through the material¹, resulting in technologically desirable properties such as non-linear current-voltage behavior and memory effects. Although bulk probes have shed much light on the micrometer-scale dynamic properties of CDWs², nearly half a century after sliding behavior was first detected, direct atomic-scale investigations of sliding and defect pinning is still lacking.

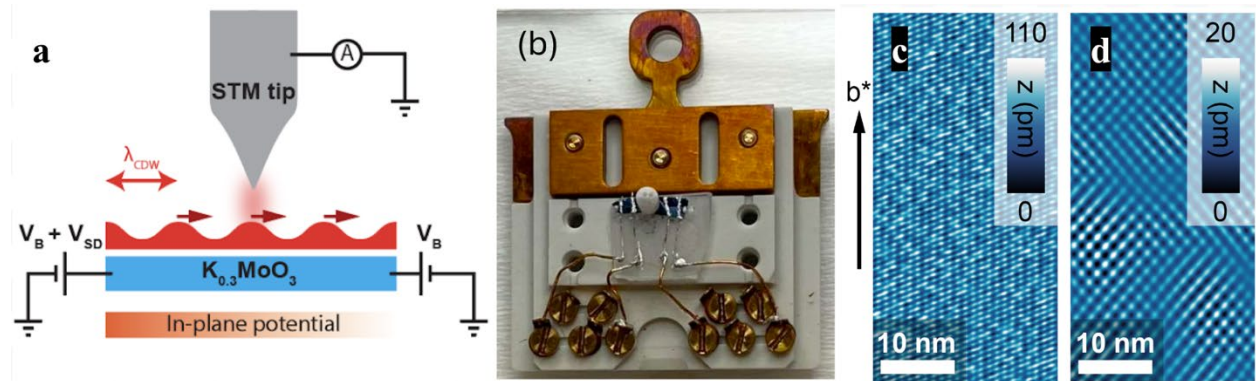


Fig. 1. **a**, Schematic diagram of our current tuned STM/STS setup. An additional source-drain voltage, V_{SD} , drives an in-plane current and tunes the local Fermi level under the tip. **b**, Photo of our sample holder with 4-probe contacts to a K_{0.3}MoO₃ crystal (with cleavage post). **c**, STM image of K_{0.3}MoO₃ with chain direction along the vertical. **d**, Fourier-filtered image of (c) to selectively highlight the CDW.

This project aims to reveal a new microscopic view of how current flows in CDW materials through the development of current tuned scanning tunneling microscopy/spectroscopy (CT-STM/STS), which combines atomically-resolved surface STM/STS measurements with simultaneous multi-probe bulk electron transport (Fig. 1). The primary goals of this project are to: (i) develop CT-STM/STS to probe electric field-coupling and sliding in well-known quasi one-dimensional CDW systems; (ii) demonstrate control and tunability of CDW sliding using surface patterning and strain; and (iii) discover novel surface sliding in two dimensional CDW systems that have never displayed bulk sliding behavior. Our results will provide fundamental insights into

the nature of collective current flow in charge-ordered correlated materials while also developing CT-STM/STS as a powerful scanned probe method for visualizing atomic-scale dynamics in a host of other quantum materials.

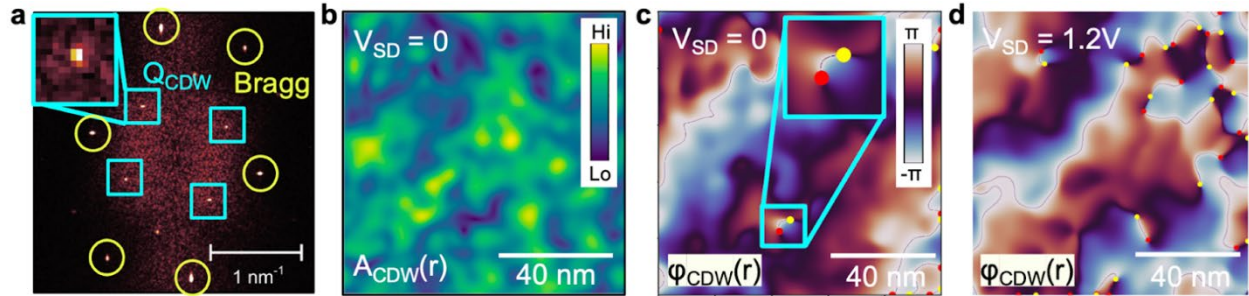


Fig. 2. **a**, High-resolution FT-STM of $K_{0.3}MoO_3$ at $T < T_{CDW}$ and $V_{SD} = 0$ with atomic Bragg and CDW peaks marked. Inset zoom: Sharp, highly coherent CDW peak. **b**, CDW amplitude map extracted from the FFT in (a) at $V_{SD} = 0$ and displaying spatial inhomogeneity. **c**, CDW phase map extracted from the FFT in (a) showing a single pair of $\pm 2\pi$ vortices. **d**, At large $V_{SD} = 1.2V$ (along vertical chain direction), in the bulk sliding regime, the number of vortex pairs increases dramatically.

Future Plans

To achieve the goals of this new project, we will first develop CT-STM/STS and benchmark its capabilities to visualize electric field control of CDW dynamics by focusing on quasi-1D CDW systems that are well-known to display bulk sliding, such as “blue bronze” $K_{0.3}MoO_3$ and transition metal trichalcogenides, TaS_3 and $NbSe_3$. To disentangle the effects of finite source-drain voltage, V_{SD} , on the STM tunneling bias, V_B , we will perform CT-STS measurements and carefully track the Fermi energy as a function of V_{SD} . Early proof-of-principle CT-STM measurements on $K_{0.3}MoO_3$ (Fig. 1c,d) have shown that the surface is atomically clean and flat which allows for high-resolution imaging in real and reciprocal space (Fig. 2a). Geometric phase analysis on these high-resolution CT-STM images allows us to visualize the local CDW amplitude (Fig. 2b) and phase (Fig. 2c), including the creation of phase dislocations in the bulk sliding regime (Fig. 2d). Next experiments will investigate the nature of these phase vortices near the electrical contacts where open questions remain on how gapped, collective CDW charge current converts to/from gapless single-particle charge³ and how sliding responds to artificial structures of deposited K atoms assembled atom-by-atom using the STM tip.

References

1. G. Grüner, *The dynamics of charge-density waves*. Rev. Mod. Phys **60**, 1129–1181 (1988).
2. T. L. Adelman, M. C. de Lind van Wijngaarden, S. V. Zaitsev-Zotov, D. DiCarlo, R. E. Thorne, *Spatially resolved studies of charge-density-wave dynamics and phase slip in $NbSe_3$* . Phys. Rev. B **53**, 1833–1849 (1996).
3. N. P. Ong, G. Verma, K. Maki, *Vortex-Array Model for Charge-Density-Wave Conduction Noise*. Phys. Rev. Lett. **52**, 663–666 (1984).

Non-Contact Near-Field Radiative Thermal Imaging to Understand the Energy Transport across a PN Junction

PIs: Qing Hao (University of Arizona), Liping Wang (Arizona State University)

Keywords: Near-field radiation, scanning thermal microscopy, PN junction, Monte Carlo simulation

Research Scope

This project aims to use near-field non-contact radiative Scanning Thermal Microscopy (SThM) to obtain nanoscale temperature distributions across an operating PN junction, with varied electric fields and doping levels. The obtained nanoscale temperature distribution will provide unprecedented insights into non-equilibrium electron and phonon transport across the junction, which is a fundamental problem in electrical engineering. PN junctions are critical components in many electronic devices, and understanding their behavior is essential for improving their performance. In these junctions, current flow is controlled by the diffusion of minority carriers (i.e., holes in the n-type region and electrons in the p-type region) and their recombination with majority carriers. By studying the nanoscale temperature distribution across the junction, researchers can gain a better understanding of the electron and phonon behavior at a general interface, such as stacked 2D materials, superlattices, and grain boundaries.

The state-of-the-art SThM technique, used for nanoscale thermal imaging of a device, is typically based on a temperature-sensing Atomic Force Microscope (AFM) tip (with fabricated thermocouple or electrical-resistance thermometer) in close proximity to a sample surface (**Fig. 4a**).¹ High spatial resolutions (~10–50 nm) for the thermal imaging of various structures were demonstrated. The contact mode (i.e., continuous tip-sample contact) or tapping mode (i.e., intermittent tip-sample contact) of an AFM is often used. The thermal imaging of an operating device may suffer from various issues: 1) electrical disturbance or possible device damage in the contact mode; 2) the temperature difference between the tip and the scanned surface, which results from the heat leakage Q through the AFM cantilever (**Fig. 1b**); 3) heat conduction through air and a water meniscus formed between the tip and the sample; 4) limited knowledge of near-field radiation in the tip-sample heat transfer and ballistic phonon transport from the ultra-small tip-sample contact region into the sample (**Fig. 1c** as results from PI Hao's phonon Monte Carlo simulation).

Considering problems for existing SThM studies, ***non-contact thermal measurements*** with a minimized impact on the device performance are preferred. Along this line, far-field temperature imaging techniques have spatial resolutions that are fundamentally limited by the radiation wavelength (e.g., sub- μm for Raman spectroscopy, several micrometers for infrared microscopy, and micrometers for thermoreflectance), known as the diffraction limit. In this aspect, ***near-field thermometry*** has been explored to beat the diffraction limit and obtain a high spatial resolution for thermal imaging. In prior studies, near-field SThM using a thermocouple-fabricated AFM tip

under a high vacuum has been demonstrated.² However, the heat loss through the AFM tip and the radiative thermal resistance (R_{Rad}) between the tip and the sample surface still lead to a temperature difference between the tip and sample. In addition, the fabricated Au-Cr thermocouple on the AFM tip has a relatively low $S=16.28 \mu\text{V/K}$, which limits the sensitivity of temperature reading.

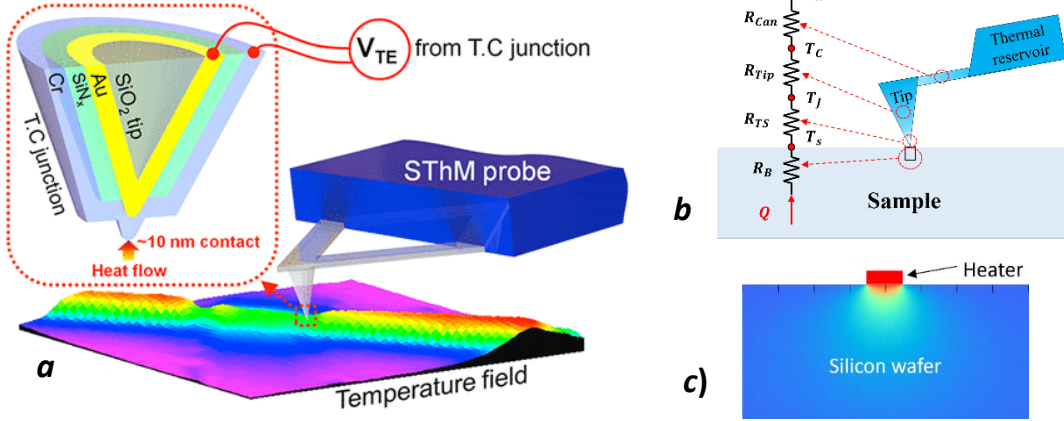


Fig. 1. *a)* Schematic of the AFM-based thermal microscopy.¹ *b)* Thermal circuit for the SThM setup. *c)* Simulated temperature profile for a metal-line heater on Si, with a ballistic thermal resistance R_B introduced at the contact spot.

In this project, we propose a near-field non-contact SThM technique to directly measure the nanoscale temperature distribution across an operating PN junction, with minimized disturbance on the device operation (**Fig. 2**). A metal tip on a suspended nanowire device will be used to receive the near-field radiation out of the scanned surface. The temperature rise of the metal tip is converted into measurable Seebeck voltage signals with a thermocouple formed between a suspended high-Seebeck-coefficient semiconducting nanowire (*e.g.*, doped Si film) and a metal nanowire. Our proposed technique offers dramatically improved accuracy and sensitivity for temperature readings, in comparison with existing SThM studies using thermocouples made of low-Seebeck-coefficient metals like Au and Cr. The suspended nanowire device has a much higher thermal resistance than that of typical AFM tips. Being used in the non-contact mode, the nanowire device as a temperature sensor has minimized influence on the sample temperature distribution. Our measurements will be carried out in a high vacuum to eliminate complexities due to air conduction and condensed water at the tip-sample interface. The measurement results will be compared with coupled electron and phonon Monte Carlo simulations to gain new

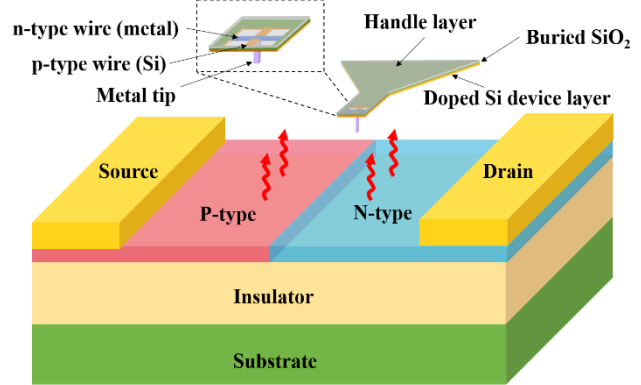


Fig. 2. The proposed non-contact near-field temperature scanning of an operating lateral PN junction. Near-field radiation from the sample surface is used to heat up the absorber (*e.g.*, platinum or gold nanotip) and the temperature rise at the nanowire thermocouple junction is converted into a Seebeck voltage signal to be measured.

insights into the fundamental problem of electron-phonon interactions across a PN junction.

Recent Progress

PI Hao has carried out electro-thermal simulations on a single PN junction. The phonon Monte Carlo simulations are used to describe the phonon transport, where frequency-dependent phonon mean free paths and phonon transmissivity across the PN junction can be exactly specified. The transport and scattering of individual phonons are tracked in phonon Monte Carlo simulations, as an alternative way to solve the phonon Boltzmann Transport Equation (BTE). To account for electron-phonon interactions, the phonon Monte Carlo simulations were seamlessly integrated with electron simulations of the device utilizing Charon—a sophisticated software package developed by Sandia National Laboratories specifically for device simulations.

At the University of Arizona, Hao's lab has successfully fabricated the proposed thermocouple junction for temperature imaging (**Fig. 2**). The thermocouple junction is fabricated using electron beam lithography (EBL) to deposit a gold coating onto one beam and the adjacent electrodes. EBL is subsequently employed again to define the dimensions of both beams, enabling full suspension. Photolithography is used to define soldering pads for wire bonding, which are connected to the smaller electrodes previously patterned by EBL. In the current design, the beam coated with gold - mechanically reinforced by the additional metal layer exhibits a Seebeck coefficient similar to that of gold. In contrast, the uncoated silicon beam maintains the high Seebeck coefficient characteristic of lightly doped semiconductors. Currently, systematic thermal measurements are carried out, using the gold-coated beam as the heater and thermometer in the electrical measurements. The thermal time constant can be extracted from such thermal measurements. For radiation response studies, a laser light source is activated, and the Seebeck voltage at the thermocouple junction is monitored using an oscilloscope to determine the device's thermal response time (see similar studies on a Ni/Au thin film junction³).

For the proposed thermal imaging, a nanopillar will be deposited at the center of the thermocouple junction. One approach involves using focused ion beam (FIB)-assisted platinum deposition to fabricate micrometer-length pillars (**Fig. 3**). Alternatively, electron beam evaporation will be explored. The nanopillar tip will be subsequently sharpened using FIB milling to achieve a reduced radius.

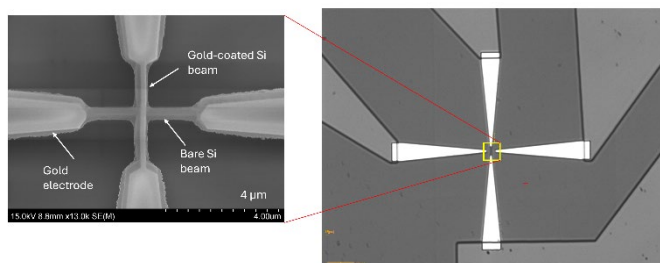


Fig. 2. A suspended thermocouple junction fabricated by Hao's lab.

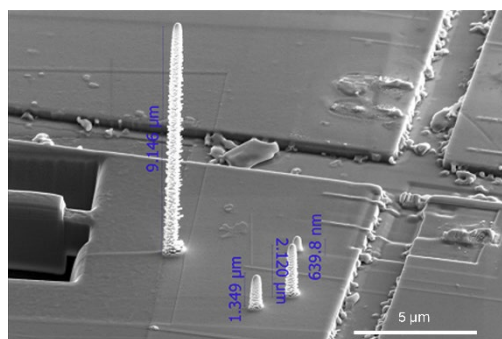


Fig. 3. Pt pillars fabricated by FIB metal deposition, with heights of 639.8 nm to 9.1 μm.

At Arizona State University, Co-PI Wang has developed three high vacuum scanning probe microscopy systems. One system is home-built with a laser-deflection based AFM head and a 3D piezo stage (1-nm resolution and 100- μm scanning range) in an 18-inch vacuum chamber. This setup uses a bi-material cantilever to carry a 100- μm silica sphere for studying near-field radiative heat transfer between the silica sphere and underneath planar samples with vacuum distance down to 30 nm (see previous studies^{4,5}). Different materials such as glass, metal films, silicon, and SiC meta-surfaces are being measured to study near-field radiative heat transfer. A second system is developed based on a modular AFM kit, which is custom integrated with a 12-inch vacuum chamber. It uses laser-deflection cantilevers along with position-sensitive detector (PSD) for contact surface scanning, while tuning fork cantilevers along with a phase-lock loop (PLL) controller are currently being introduced into the system for non-contact scanning. Additional channels for electrical signals besides topography are available during scanning. It is planned to use this system for conducting initial scanning with the novel SThM probes fabricated by PI Hao to demonstrate the feasibility. A third system is a commercial RHK Beetle STM/AFM, which has been upgraded with a wobble stick to facilitate the operation and handling of the scanning head in the vacuum chamber, and a new six-contact head to enable simultaneous readouts of electrical signals for SThM during scanning. The system calibration tests are underway, while it is planned in Year 3 to use this highly stable commercial AFM system for the surface temperature scanning with the novel probe fabricated by PI Hao to demonstrate high sensitivity.

Future Plans

In Year 3 of the project, our team will carry out thermal imaging for the proposed PN junction. In comparison, we have purchased an infrared (IR) microscope with 5 μm spatial resolution. The rough temperature distribution near a PN junction or nanofabricated heating elements can be measured. The nanoscale temperature distribution will be measured with our proposed thermal imaging technique. In calibration, a thin-film metallic heating line will be used to justify the accuracy and spatial resolution of the developed thermal imaging technique.

References

1. K. Kim, W. Jeong, W. Lee, & P. Reddy, *Ultra-High Vacuum Scanning Thermal Microscopy for Nanometer Resolution Quantitative Thermometry*, ACS Nano **6**, 4248-4257 (2012).
2. L. Cui, W. Jeong, V. Fernández-Hurtado, J. Feist, F. J. García-Vidal, J. C. Cuevas, E. Meyhofer, & P. Reddy, *Study of radiative heat transfer in Ångström- and nanometre-sized gaps*, Nature communications **8**, 14479 (2017).
3. D. Chu, D. T. Bilir, R. F. W. Pease, & K. E. Goodson, *Thin film nano thermocouple sensors for applications in laser and electron beam irradiation* in TRANSDUCERS'03. 12th International Conference on Solid-State Sensors, Actuators and Microsystems. Digest of Technical Papers (Cat. No. 03TH8664) **2**, 1112-1115 (2003).
4. A. Narayanaswamy, S. Shen & G. Chen, *Near-field radiative heat transfer between a sphere and a substrate*, Physical Review B **78**, 115303 (2008).
5. S. Shen, A. Narayanaswamy & G. Chen, *Surface Phonon Polaritons Mediated Energy Transfer between Nanoscale Gaps*, Nano Letters **9**, 2909-2913 (2009).

Publications

1. C. Horne, L. P. Wang, and Q. Hao, *Nanowire Thermocouple Junctions for Ultra-fast Radiative Heat Detection* (under preparation).
2. C. Horne, L. P. Wang, and Q. Hao, *Nanoscale scanning thermal microscopy using improved thermocouple probes* (under patent application).

Cryogenic Electron Microscopy for Topological Spin Textures in Two-Dimensional van der Waals Magnetic Materials

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Keywords: cryogenic transmission electron microscopy, 2D materials, topological spin textures, magnetic skyrmion

Research Scope

Two-dimensional (2D) van der Waals (vdW) magnetic materials have attracted considerable attention due to their unique intrinsic magnetism and the related topological spin textures at the 2D atomic limit [1, 2]. The overarching goal of this project is to create, identify, understand, and manipulate the topological spin textures in 2D vdW magnetic materials and elucidate the underlying spin-orbit and spin-lattice interactions using cryogenic transmission electron microscopy (cryo-TEM) and spectroscopy approaches. As a model 2D magnet, Fe_3GeTe_2 (FGT) [3] is a material of interest that can exhibit topologically protected skyrmion spin textures by controlling the temperature and applied magnetic field. The scope of the current research over last two years includes: 1) developing specialized tools and protocols that enable reliable characterization for beam- and ambient-sensitive materials; 2) observing and measuring topological spin textures of FGT; 3) exploring scalable synthesis of FGT with wide composition tunability and spin transport properties. Our findings can enhance the mechanistic understanding of fundamental interplays between spin and the other competing orbit and lattice orders that may lead to the enhanced control of 2D magnetic ordering and correlated spin-charge transport.

Recent Progress

In the past two years, our team has investigated the 2D magnetic FGT thin crystals, obtaining research accomplishments summarized as follows.

1. Top-down and bottom-up approaches to create 2D magnetic FGT single-crystal layers

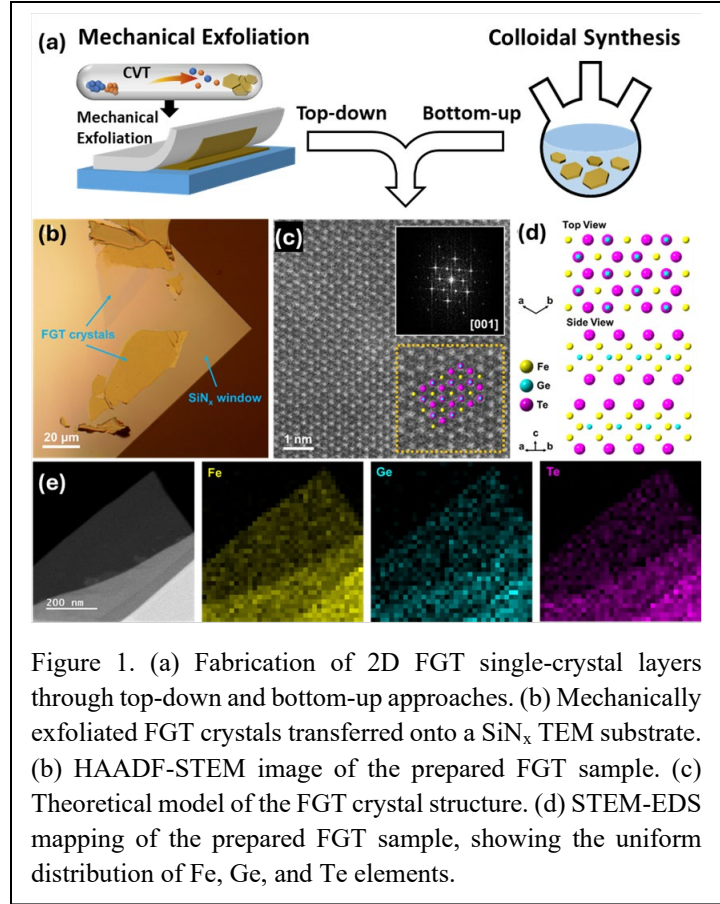
We envision leveraging both top-down and bottom-up approaches to fabricate 2D FGT layered single crystals and have made such attempts using mechanical exfoliation and colloidal chemistry, respectively, as shown in Figure 1a. On one hand, we have synthesized 2D layered FGT single crystals (in millimeter sizes) via chemical vapor transport (CVT) approach, which were prepared into thin samples containing few-layer thickness by mechanical exfoliation, followed by dry transfer onto silicon nitride (SiN_x) membrane TEM substrate. The whole process was performed within an Ar-filled glovebox to prevent surface degradation caused by oxidation or other side reactions, manifesting a reliable protocol for sample preparation. The FGT with several atomically thin steps was prepared and transferred onto a SiN_x membrane substrate using the dry

transfer method (Figure 1b). The atomic structure revealed by the HAADF-STEM image (Figure 1c) confirms the high crystallinity of the prepared FGT. This observation is consistent with the theoretical 2D layered crystal structure (Figure 1d). Furthermore, STEM-EDS mapping (Figure 1e) demonstrates a uniform distribution of Fe, Ge, and Te atoms throughout the entire sample. Despite the feasibility and reliability of mechanical exfoliation to produce few layer and monolayer FGT crystals, it is not a scalable method for application in industry and mass production and lacks the tunability of composition. Colloidal synthesis is an alternative approach to produce ultrathin single-crystal FGT flakes via the bottom-up approach. Inspired by the success of colloidal synthesis of $\text{Cr}_2\text{Ge}_2\text{Te}_6$ [4], we attempted to design and prepare FGT

via a similar hot injection method. Specifically, we implemented two synthetic strategies with multiple reaction paths. The first strategy was a one pot synthesis where all the precursors were loaded in a three-neck flask in an amide assisted growth. In spite of its promise to offer a simple experimental path to generate FGT ternary compounds, the existence of impurity phases requires future experimental optimizations. The second strategy of synthesis focused on seed growth by initially forming a binary compound and later injecting the third element solution at elevated temperatures to form FGT. Due to difference in reactivity and reaction temperatures of precursors, we carried out a series of experimental paths to initially form FeTe, and GeTe seeds. We have been under continued investigation to achieve FGT crystals and the ongoing work is to refine the synthetic parameters and precursor ratios to tune the stoichiometry and phase purity.

2. Precise measurement of the thickness of 2D layered FGT single crystals

As the number of 2D layers in atomically thin vdW crystals plays a vital role in their exotic physical properties, the ability to measure the layer thickness accurately and reliably at the monolayer prevision is highly desired. To avoid unnecessary sample transfer between different tools and minimize exposure to the air, our goal is to develop a robust approach to measure the atomic layer thickness solely based on TEM techniques. We use atomic force microscopy (AFM) to measure the layer thickness using identical samples and calibrate it with TEM measurements



based on STEM contrast and electron energy-loss spectroscopy (EELS) plasmon excitation, as shown in Figure 2. The obtained STEM and AFM contrast in the intensity maps are in good agreement with each other. The Z-contrast intensity profile from HAADF-STEM imaging exhibits a linear dependence with the FGT flake's thickness profile, which is quantitatively aligned with the AFM height measurement. Furthermore, the EELS-based thickness measurement using the log-ratio technique to determine the sample thickness relative to its electron scattering mean free path (referred to as t/λ) also exhibits excellent consistency with STEM intensity and AFM thickness profiles. In addition, we also performed converged beam electron diffraction (CBED) and electron holography (EH) to provide quantitative assessment of layer thickness, and the results further confirm the consistency in thickness determination with precision at the single atomic layer level. This cross-check of thickness measurement lays a technical foundation to investigate layer-dependent spin textures and spin transport behaviors by solely using TEM-based techniques, which is essential and critical for meaningful scientific interpretation.

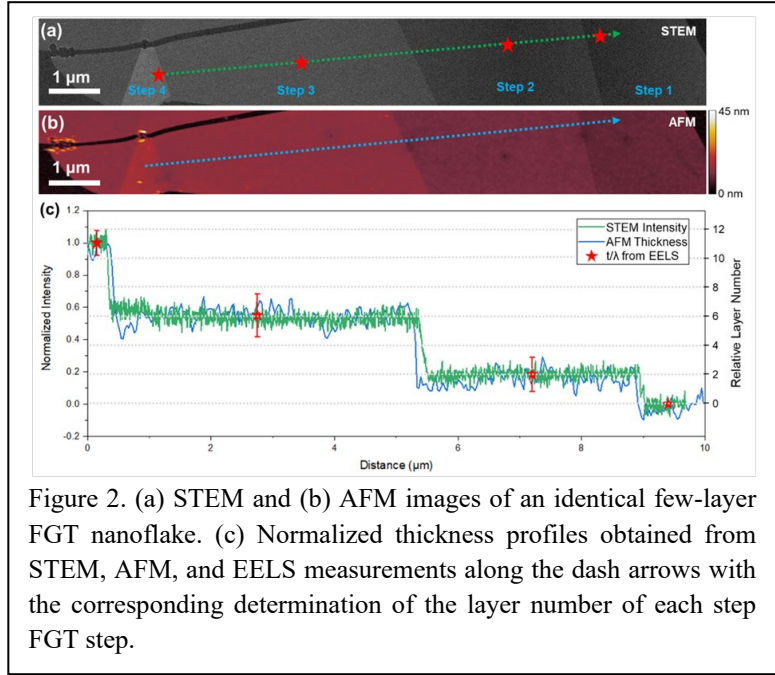


Figure 2. (a) STEM and (b) AFM images of an identical few-layer FGT nanoflake. (c) Normalized thickness profiles obtained from STEM, AFM, and EELS measurements along the dash arrows with the corresponding determination of the layer number of each step FGT step.

3. Observation of topological spin textures in 2D layered FGT

Using mechanically exfoliated FGT flakes, we performed Lorentz TEM (LTEM) at cryogenic conditions to observe the temperature-dependent evolution of magnetic spin textures. We found the evolution of magnetic spin textures as temperature decrease. Upon cooling the sample below the Curie temperature, stripe domains gradually emerged, manifesting a ferromagnetic phase transition, and further evolved into topologically distinct skyrmion textures at lower temperatures, as shown in Figure 3a. This implies that the perpendicular magnetic anisotropy (PMA) in FGT increases as the temperature decreases, leading to the magnetic phase transition as a function of temperature. Furthermore, we also verified that the magnetic phase transitions were reversible in repeated cooling and heating experiments. Then, we determined the detailed topological characteristics of magnetic spin textures in FGT. Through a series of sample tilting experiments, we confirmed that the quasiparticle-like magnetic contrast was attributed to the Néel-type skyrmion. Intriguingly, we discovered two distinct skyrmion-like patterns under zero magnetic field, denoted as Type I and Type II in Figure 3b. We performed theoretical simulations

based on quantitative phase tomography to reconstruct the in-plane magnetic configurations, revealing the two distinct Néel skyrmionic spin textures. To validate this, we also constructed representative skyrmionic models and simulated the corresponding LTEM images using the open-source PyLorentz code (Figure 3 c, d). The simulated contrast shows good agreement with our experimental observations of FGT. The formation and transformation of these spin textures are of fundamental interest due to the underlying nontrivial topological charge. This subject is worth further investigation in-depth, since such topological charge evolutions have been theoretically predicted but rarely observed in experiments.

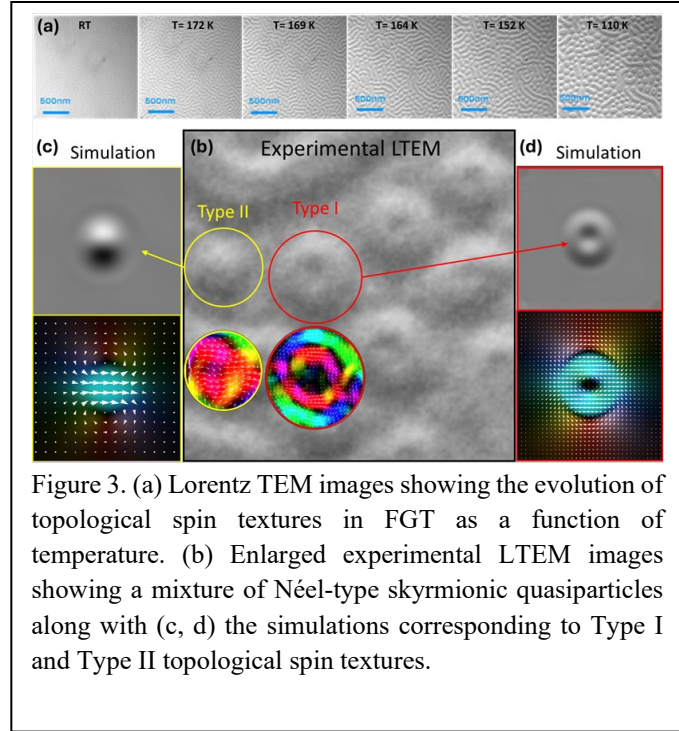


Figure 3. (a) Lorentz TEM images showing the evolution of topological spin textures in FGT as a function of temperature. (b) Enlarged experimental LTEM images showing a mixture of Néel-type skyrmionic quasiparticles along with (c, d) the simulations corresponding to Type I and Type II topological spin textures.

Future Plans

We will continue focusing on the 2D FGT magnetic system and conduct systematic experiments to (1) explore skyrmion topological spin textures in 2D FGT in full temperature-field space and map out the related phase diagram with respect to T-B variables; (2) study the topological spin textures for FGT samples with varied numbers of layers and identify the thickness-dependent skyrmion formation and its impact on spin topological charges; and (3) tune the stoichiometric FGT compositions via colloidal synthesis to find out how it impacts the formation and transition between different skyrmion topological textures.

References

1. C. Gong, L. Li, Z. Li, H. Ji, A. Stern, Y. Xia, T. Cao, W. Bao, C. Wang, Y. Wang, Z. Q. Qiu, R. J. Cava, S. G. Louie, J. Xia, X. Zhang, Discovery of intrinsic ferromagnetism in two-dimensional van der Waals crystals. *Nature* **546**, 265–269 (2017).
2. B. Huang, G. Clark, E. Navarro-Moratalla, D. R. Klein, R. Cheng, K. L. Seyler, D. Zhong, E. Schmidgall, M. A. McGuire, D. H. Cobden, W. Yao, D. Xiao, P. Jarillo-Herrero, X. Xu, Layer-dependent ferromagnetism in a van der Waals crystal down to the monolayer limit. *Nature* **546**, 270–273 (2017).
3. Y. Deng, Y. Yu, Y. Song, J. Zhang, N. Z. Wang, Z. Sun, Y. Yi, Y. Z. Wu, S. Wu, J. Zhu, J. Wang, X. H. Chen, Y. Zhang, Gate-tunable room-temperature ferromagnetism in two-dimensional Fe_3GeTe_2 . *Nature* **563**, 94–99 (2018).
4. D. Parobek, C. R. DeLaney, J. Watt, S. A. Ivanov, Synthetic Understanding for Magnetic CrGeTe_3 Nanoplatelets. *Chem. Mater.* **35**, 521–528 (2023).

Publications

1. C. Li, H. Zheng, K. He, Quantitative Determination of 2D Layer Thickness of Atomically Thin Fe_3GeTe_2 in STEM, *Microscopy and Microanalysis* **30**, 1182 (2024).
2. K. He, Cryogenic electron microscopy for emerging materials research: From quantum materials to energy applications, *MRS Communications* **12**, 471 (2022).
3. M. He, C. Li, T. R. Moosavy, R. A. Welser, J. Liu, L. A. Jauregui, K. He, Direct observation of skyrmionic topological spin textures and their transformations in 2D layered Fe_3GeTe_2 single crystals. in preparation.

The Identification, Characterization, and Control of Two-Level Quantum Systems

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Keywords: Two-Level Quantum Systems, Quantum Stochastic Rectification, Electromagnetic-Matter Interactions, Coherence and Entanglement, Space-Time Scanning Tunneling Microscopy

Research Scope

Two-level quantum systems serve as fundamental building blocks in quantum information science and technology. In addition to their role as natural qubit candidates, their quantum properties can be harnessed for sensing the surrounding environment. Molecules that exhibit two levels are especially advantageous due to their atomic-scale dimensions, inherent quantum characteristics, and chemical versatility. The identification and characterization of two-level molecules with control in their positions on a solid surface would broaden the platform for advancing quantum information science. These molecules adsorbed on, trapped within the nanocavity of the scanning tunneling microscopy (STM) tunnel junction, or embedded in atomic defects of the crystalline solid surface are quantum systems with localized two-level properties. Low temperature STM integrated with acoustic to terahertz and visible electromagnetic waves provides spectroscopic images and measures driven quantum dynamics of two-level systems with spatial and temporal resolutions. The transitions and time evolution of the two levels can be controlled to be random quantum stochastic or deterministically coherent. By modulating the quantum noise with a sinusoidal periodic drive of varied frequency as in the Floquet theory or with ultrashort pulsed lasers to incur Ramsey oscillations, measurement can be made of the relaxation time in the two-level transition dynamics. Besides adsorbing molecules on the surface or captured within the STM tunnel junction, individual defects can be created to trap molecules to form an ensemble of two-level systems. Quantum stochastic rectification associated with nonlinear I-V arising from inelastic electron tunneling provides a general method to extract signals from the quantum noises associated with the two-level transitions and superposition. This project develops new methodologies in space and time based on the electromagnetic wave-STM and seeks to prepare, probe and understand two-level systems functioning as qubits and quantum sensors.

Recent Progress

Electromagnetic waves spanning from sub-Hz to visible light having CW and as low as 10 fs pulse duration were integrated with low temperature STM to enable light-matter interactions and precision measurements to advance quantum information science. We demonstrated specifically atomic-scale rectification spectromicroscopy over this broad range of wavelengths of CW and pulsed electromagnetic waves. Our setup enabled time domain measurements of the coherent superposition of two levels in single hydrogen and pyrrolidine

molecule trapped in the nanocavity of the STM tunnel junction to demonstrate the quantum superposition microscope.

A single hydrogen molecule was confined in the STM nanocavity formed by the tip and the copper nitride (Cu_2N) sample surface. The heteroatomic surface composed of the regular lattice of Cu and N atoms led to the heterogeneity in the charge distribution. The hydrogen molecules exhibited two different configurations in the STM junction to form a molecular two-level system (TLS). From the THz pump-probe time domain measurements, the temporal oscillations and decoherence in the superposition of the two-level hydrogen system showed

spatial variations at the sub-Ångström scale due to Stark shift from the surface electric field, as shown in Fig. 1.

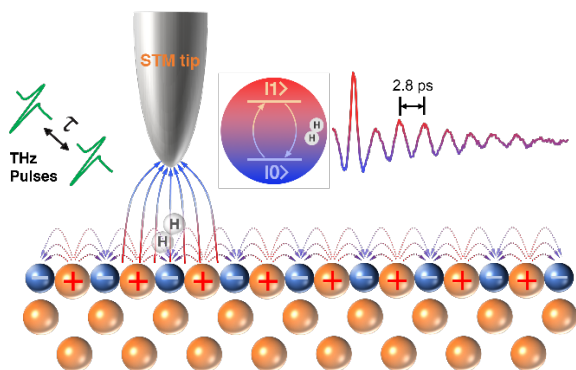
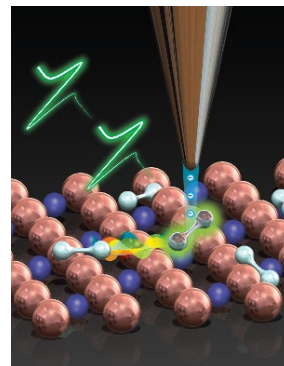


Fig. 1: Atomic scale electric field detected by quantum superposition microscope: Excited by ultrashort Terahertz pulses, Ramsey oscillations from the coherent superposition of two levels for hydrogen molecule trapped in the junction of the STM sense the electric field from the Stark effect.

In publication #1, entitled “Electrical Manipulation of Quantum Coherence in a Two-Level Molecular System”, we demonstrated voltage control of the ultrafast quantum coherence in a single molecular qubit of hydrogen molecule. The ultrafast quantum coherence in the superposition of the two-level hydrogen system was manipulated by a combination of the surface electrostatic field and the DC electric field from the applied sample bias. A quantum state transition was observed due to the avoided crossing of the energy levels by tuning the sample bias. In addition, the coherence manipulation over different positions of the Cu_2N surface further quantified the surface electrostatic field. Manipulation of quantum coherence is central in quantum information processing. The present effort fulfilled the goals of manipulating qubit coherence at the femtosecond scale and with the convenience of an electric field from a DC voltage.

In publication #2, two spectral signatures were measured that revealed interactions among multiple H_2 molecules. First, the avoided level crossing featured by energy gaps ranging from 20 to 80 GHz were detected, arising from level repulsion between two H_2 molecules. Second, the tip sensed the signal of H_2 outside the tunnel junction through the projective measurement on the H_2 inside the junction, owing to the entangled states created through their

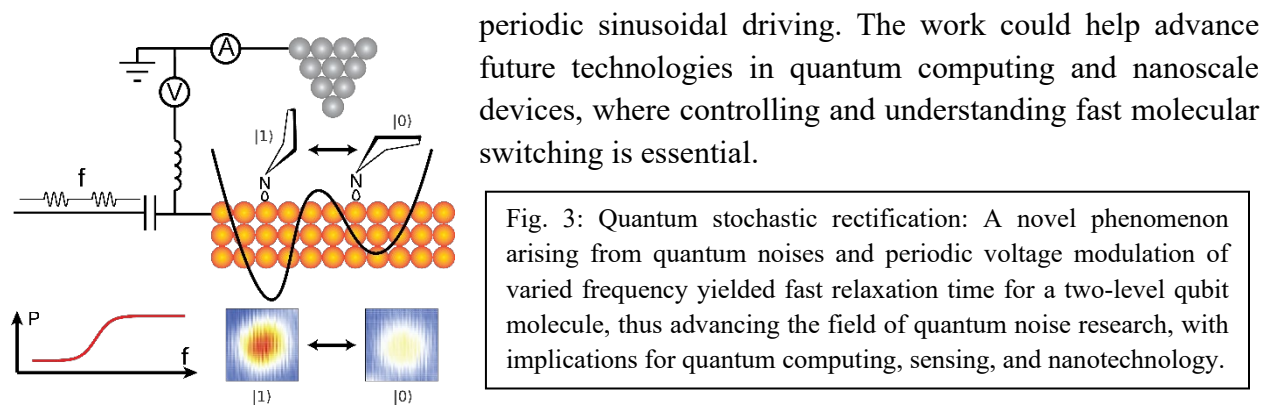
Fig. 2: Interacting and entanglement of hydrogen molecules detected by the quantum superposition microscope: Excited by ultrashort terahertz pulses, the coherent superposition of two levels can be utilized to extract the strength of interactions and entanglement with nearby hydrogen molecules on a copper nitride surface.



interactions. A dipolar-type interaction was integrated into the tunneling two-level system (TLS) model of H_2 , enabling an accurate reproduction of the observed behaviors. Our results obtained by the quantum superposition microscope revealed the intricate quantum mechanical interplay among H_2 molecules and additionally provide a two-dimensional platform to investigate unresolved questions of amorphous materials.

In publication #3, we demonstrated that THz pulses behaved like photons and could be absorbed by single hydrogen molecules, while simultaneously maintaining their field nature. THz-photon absorption created a superposition of the two levels in a single hydrogen molecule when the energy difference of the two levels lied within the bandwidth of the sub-cycle THz sub-picosecond pulses. The associated hydrogen dynamics led to a coherent oscillation in the DC tunneling current obtained from pump-probe measurements. Such oscillation was derived from two mechanisms, and each was related to the wave-particle nature of THz pulses. A comprehensive theory was derived to account for the single-molecule coherence that was found to be highly sensitive to the electric field at the sample's surface.

In publication #4, a new way was demonstrated to measure how fast a single molecule changes between two conformational states, or a qubit's two states, on a solid surface. Tiny alternating voltages was applied to a single pyrrolidine molecule on a copper surface, as in the Floquet theory, and the resulting direct current was recorded. This process, known as quantum stochastic rectification, converted quantum noises into a measurable signal. The key finding was that the molecule's current response and its state population changed significantly depending on the frequency of the applied signal. By analyzing this response, the molecule's rapid relaxation time was extracted. Unlike traditional methods, this approach did not require fast electronics or short pulses, making it easier to implement and measure single-molecule's two states modified by a



In addition to the published results, we have completed studies that showed temperature dependence of the transition rate between two conformations of single pyrrolidine molecules, revealing thermally activated and tunneling mechanisms. These measurements demonstrated massive tunneling involving motions of the entire skeletal structure and direct visualization of tunneling induced two-level transitions. In a separate study, we measured resonantly enhanced

two-level transitions via vibrational overtone absorption in single pyrrolidine molecules, demonstrating further the ability of light to control two-level systems at the atomic scale. To further probe magnetic states as qubits, we demonstrated that spin exchange interactions between two magnetic molecules exhibited spatial variations from ferromagnetic to antiferromagnetic couplings, i.e. singlet and triplet states. Papers summarizing these results are in the final review stages before submission for publication. Furthermore, initial results have been obtained on the spectroscopy and imaging of charge and spin density waves on the antiferromagnetic Cr(001) surface, and a single surface defect (missing Cr atom) could trap a hydrogen molecule exhibiting two-level transitions.

Future Plans

Systems with two levels in a double well are considered one of the qubit candidates. As qubits form the basis for quantum information science and technology, plans for research continue to further identify, characterize, and control molecule-based qubits. Efforts continue to develop new methodology for probing two-level systems and as sensors of quantum materials with atomic scale spatial resolution and sub-picosecond temporal resolution based on electromagnetic wave-STM. In addition, the scientific understanding and technological applications of two-level systems require the ability to assemble them in quantity and well-defined positions. Recent results on single defects trapping two-level hydrogen demonstrated a new media for housing qubits. Further studies are needed to investigate single defects as two-level systems and the feasibility of creating defect arrays to implement an ensemble of qubits and study mutual interactions and entanglements among the qubits. Our continuing efforts to develop new methodologies lead us to extend the work in publication #4 to GHz and THz frequencies to probe faster dynamics of two-level systems and explore the connection between quantum stochasticity and coherence.

References

1. M. C. Gutzwiller, *Quantum Chaos*, Scientific American, January, 78 (1992).
2. T. Oka and S. Kitamura, *Floquet Engineering of Quantum Materials*, Ann. Rev. Cond. Matt. Phys. **10**, 387 (2019).

Publications

1. L. Wang, D. Bai, Y. Xia, and W. Ho, *Electrical Manipulation of Quantum Coherence in a Two-Level Molecular System*, Phys. Rev. Lett. **130**, 096201 (2023).
2. Y. Xia, L. Wang, D. Bai, and W. Ho, *Avoided Level Crossing and Entangled States of Interacting Hydrogen Molecules Detected by the Quantum Superposition Microscope*, ACS Nano **17**, 23144 (2023).
3. Y. Xia, L. Wang, and W. Ho, *Mechanisms Underlying a Quantum Superposition Microscope Based on THz-Driven Coherent Oscillations in a Two-Level Molecular Sensor*, Phys. Rev. Lett. **132**, 076903 (2024).
4. J. Yao, S. Chen, W. Shi, and W. Ho, *Quantum Stochastic Rectification in a Single Molecule*, Phys. Rev. Lett. **135**, 026201 (2025).

Control, Order, and Melting of 2D Charge Density Waves from 20K to 700K

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Keywords: charge density waves; 2D melting; liquid-helium TEM; in-situ TEM; quantum materials

Research Scope

Dramatic electronic changes occur when atoms are pushed just a few picometers in a charge density wave crystal. Charge density waves mediate metal-insulator transitions, compete with superconductivity, and are promising candidates for ultrafast, efficient non-volatile memory switching. Unfortunately, these coherent quantum states occur at low temperature. Room temperature access to coherent charge density waves would provide beyond-CMOS switching and information processing that is a paradigm shift toward energy efficient computing, low-voltage logic, and high-temperature devices. In order to both control and understand these quantum electronic phase changes, this work engineers nanostructured 2D devices for in-situ TEM observation and control of the coarsening mechanics of these novel phase transitions in charge density waves—from picometer displacements to micro-domains.

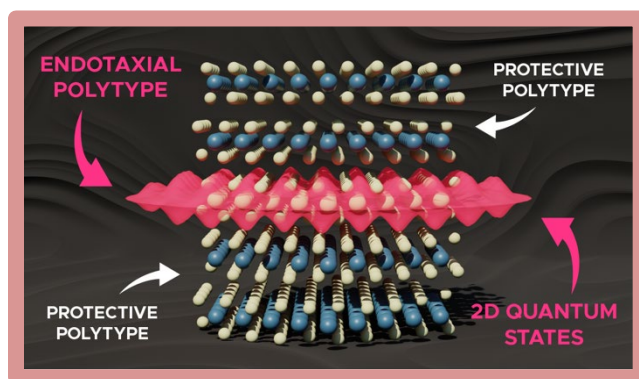


Figure 1: A 3D render of an endotaxial crystal that hosts a 2D quantum state. Here, one of the atomic layers in TaS₂ has a charge crystal wave drawn within it.

Using innovative low temperature high-resolution scanning / transmission electron microscopy (S/TEM)—from 20K to 700K—combined with electronic control we unveil the microscopic nature of charge ordered phases and the mechanics of CDW transformation. We show the critical temperature for spatially-coherent CDW in 1T-TaS₂ can be raised to well above room temperature (~150 K above the expected transition) by synthesizing clean interleaved 2D polytypic heterostructures. In-situ S/TEM with electrical and temperature measurement on nanostructured devices then provide a dynamic atomic and microscopic understanding of the path dependent metal-to-insulator transition that accompanies a change in commensuration of charge density waves (CDW) with the underlying lattice. These techniques reveal how elasticity and topological breaks in the structure of quantum order parameters govern these phase transitions [1,2].

Recent Progress

Three new fields of research have emerged from recent progress of this work:

1. This project reports a new quantum phase of matter synthesized by the PI, where low-temperature commensurate charge density waves are stabilized at room temperature through out-of-plane charge twinning in 2D layers of TaS₂[3]. Rather than the typical approach of exfoliating and peeling off individual atomic layers to make a 2D material, the 2D material was grown inside of another matrix. At higher temperatures, novel ordered incommensurate states emerge, suggesting **fragile quantum states can be enhanced**. The implications are significant—showing quantum phases have malleable critical temperatures in 2D materials by suppressing charge disorder. Moreover, this commensurate charge density wave enables metal-insulator transitions that become switchable.

2. Here we introduce a side-entry specimen holder capable of liquid helium cooling while achieving atomic resolution[4]. This ultra-cold cryogenic TEM specimen holder demonstrates millikelvin temperature stability maintained for hours near liquid helium temperatures in a modern aberration-corrected TEM. A base temperature of 23K is maintained over 4 hours. Moreover, the thermal stability is better than 2 mK, a significant improvement over existing instruments. Thermal stability is directly associated with the reduction of specimen drift. We report mean drift speed of 0.37 Å/s; this is comparable to side-entry liquid nitrogen holders (0.75 Å/s), and approaches the stability of room-temperature holders (0.18 Å/s). By maintaining stable cryogenic temperatures with liquid helium for extended durations, scientists can conduct intricate experiments without grappling with unpredictable temperature fluctuations or recurrent dewar refills. Ultra-low temperature Cryo TEM is providing access to high-resolution imaging of quantum phases. This work is defining new low-temperature characterization techniques using the ultra-cold TEM technology developed at the University of Michigan (Hovden Lab) in collaboration with Harvard (El Baggari Lab). Preliminary observation of CDWs below 32K have demonstrated sub-Angstrom imaging and shown distinct CDW structure in NbSe₂.

3. This work has **achieved 3D chemical imaging of nanomaterials at unprecedented resolutions (~1 nm)**[5]. Traditionally, researchers must choose either 2D chemical imaging or 3D structure imaging. However, by inventing a multi-modal measurement approach, inelastic and elastic signals are combined to allow chemical imaging in 3D. Here, high-resolution

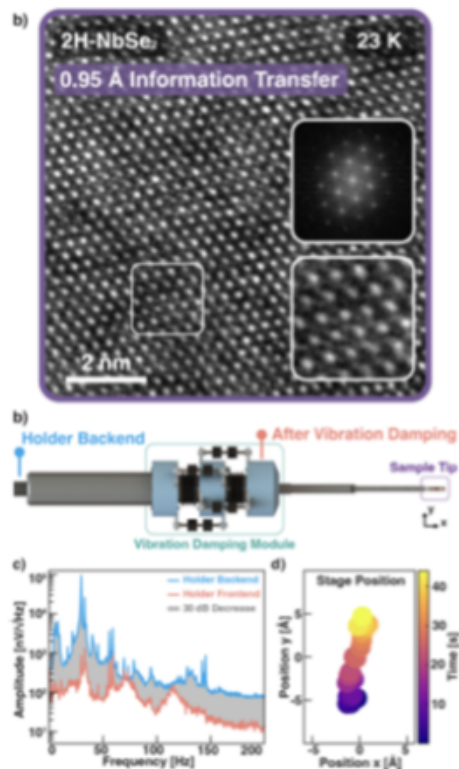


Figure 2: Imaging stability of side-entry liquid helium cryo-TEM a) Atomic resolution BF-TEM image of 2H-NbSe₂ with 0.95 Å information transfer demonstrated at 23 K. b) Vibration isolation is critical for achieving sub-Angstrom information transfer TEM imaging. A vibration damping module isolates incoming mechanical instabilities at holder backend from the sample tip. c) Spectral analysis of vibration measurements on the holder shows ~30 dB reduction in holder vibration. d) Drift stability of 0.37 ° A/s is achieved through millikelvin temperature stability. Both vibrational stability and drift stability are critical for achieving sub-Angstrom information transfer.

3D chemical imaging is achieved near or below one-nanometer resolution in an Au-Fe₃O₄ metamaterial within an organic ligand matrix, Co₃O₄-Mn₃O₄ core-shell nanocrystals, and ZnS-Cu_{0.64}S_{0.36} nanomaterial using fused multi-modal electron tomography. Multi-modal data fusion enables high-resolution chemical tomography often with 99% less dose by linking information encoded within both elastic (HAADF) and inelastic (EDX/EELS) signals. We thus demonstrate that sub-nanometer 3D resolution of chemistry is measurable for a broad class of geometrically and compositionally complex materials.

Future Plans

1. The top priority of future work will be to study the broader class of charge density wave materials that emerge at ultra-cold temperatures previously not accessible by modern TEM. Leveraging the liquid helium stage by h-Bar Instruments (installed at U. Michigan) the team will cool to low and intermediate temperatures in order to map CDW formation at and across critical phase transitions.

2. Using newly stabilized 2D charge density waves (CDWs) we will reveal novel quantum melting processes in low-dimensional materials and establish a unified, quantitative picture for continuous (hexatic/nematic) melting of the electronic states. Using in-situ selected-area electron diffraction on 2D 1T-TaS₂, we track three concurrent signatures of CDW melting—(i) azimuthal broadening of superlattice peaks, (ii) contraction of the CDW wavevector q , and (iii) decay of integrated superlattice intensity—and show that they arise from elastic distortions and the proliferation of topological defects in the CDW. A Landau framework that incorporates nonlinear coupling between wavefront distortions and longitudinal strain, combined with a grand-canonical simulation of a ‘charge crystal,’ explains wavelength expansion (q -contraction) within a rigid host lattice volume and the attenuation of CDW amplitude near defect cores. We will further compile evidence from the literature indicating that these melting features are broadly present across incommensurate CDW systems.

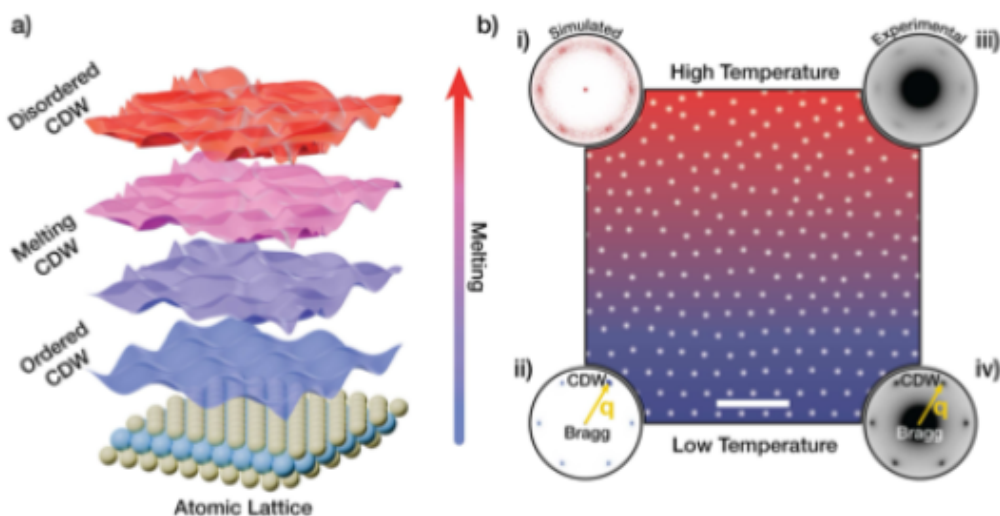


Figure 3: Melting of two-dimensional charge density wave. a) Illustration of progressively melted 2D CDW. The CDW becomes less spatially coherent, melting independently of the underlying atomic lattice. b) Melting of CDW modeled with a lattice of CDW peaks (white dots). Scale bar is 5 nm. At higher temperatures CDW fluctuations

become large, disordered. Comparison of experimental 2D 1T-TaS₂ CDW diffraction (i, iii) with simulated CDW diffraction (ii, iv) at low and high temperatures. Molecular dynamic simulation of CDW melting qualitatively matches experimental electron diffraction.

3. We seek to directly observe the reshaping and depinning of electronic structure CDW phases under electrical bias across temperatures (20 to 700K) at the atomic to micro scale and correlate the measured behavior to quantum molecular dynamics models to ultimately reveal the kinetics of quantum order parameters. We will utilize the CDW devices designed for in-situ electronic characterization and structural observation using scanning / transmission electron microscopy. We will conduct atomic resolution measurements of electronic restructuring of charge density waves in order to understand the coarsening mechanisms, hysteresis, and path-dependent electronic states in a 2D material. Here, we aim to understand the atomic restructuring of CDW phases and characterize it across T_c using ultra-cold scanning transmission electron microscopy.

References

- [1] El Baggari, I., Savitzky, B. H., Admasu, A. S., Kim, J., Cheong, S. W., **Hovden, R.**, & Kourkoutis, L. F. Nature and evolution of incommensurate charge order in manganites visualized with cryogenic scanning transmission electron microscopy. *Proceedings of the National Academy of Sciences*, 115(7), 1445-1450 (2018)
- [2] Cheng, Y., Zong, A., Wu, L., Meng, Q., Xia, W., Qi, F., Zhu, P., Zou, X., Jiang, T., Guo, Y. and van Wezel, J., 2024. Ultrafast formation of topological defects in a two-dimensional charge density wave. *Nature Physics*, 20(1), pp.54-60.
- [3] S. H. Sung, N. Agarwal, I. El Baggari, P. Kezer, Y.M. Goh, N. Schnitzer, J. M. Shen, T. Chiang, Y. Liu, W. Lu, Y. Sun, L. F. Kourkoutis, J. T. Heron, K. Sun, **R. Hovden***, *Endotaxial stabilization of 2D charge density waves with long-range order* **Nature Communications** **15**, 1403 (2024)
- [4] E. Rennich, S.H. Sung, N. Agarwal, M. Gates, R. Kerns, **R. Hovden***, I. El Baggari, *Ultra-Cold Cryogenic TEM with Liquid Helium and High Stability* **Proc. National Academy of Sciences**, *accepted* (2025)
- [5] J. Schwartz, Z. Wendy Di, Y. Jiang, J. Manassa, J. Pietryga, Y. Qian, M. G. Cho, J. L. Rowell, H. Zheng, R. Robinson, J. Gu, A. Kirilin, S. Rozeveld, P. Ercius, J. A. Fessler, T. Xu, M. Scott, **R. Hovden*** *Imaging 3D chemistry at 1nm resolution with fused multi-modal electron tomography* **Nature Communications** **15**, 3555 (2024)

Publications

- E. Rennich, S.H. Sung, N. Agarwal, M. Gates, R. Kerns, **R. Hovden***, I. El Baggari, *Ultra-Cold Cryogenic TEM with Liquid Helium and High Stability* **Proc. National Academy of Sciences**, *accepted* (2025)
- S. Li, Z. Sun, N. J. McLaughlin, A. Sharmin, N. Agarwal, M. Huang, S. H. Sung, H. Lu, S. Yan, H. Lei, **R. Hovden**, H. Wang, H. Chen, L. Zhao, C. R. Du, *Observation of stacking engineered magnetic phase transitions within moiré supercells of twisted van der Waals magnets* **Nature Communications** **15**, 5712 (2024)

- J. Schwartz, Z. Wendy Di, Y. Jiang, J. Manassa, J. Pietryga, Y. Qian, M. G. Cho, J. L. Rowell, H. Zheng, R. Robinson, J. Gu, A. Kirilin, S. Rozeveld, P. Ercius, J. A. Fessler, T. Xu, M. Scott, **R. Hovden***, *Imaging 3D chemistry at 1nm resolution with fused multi-modal electron tomography*
Nature Communications **15**, 3555 (2024)
- C. Mook-ki, S.H. Sung, **R. Hovden**, E. B. Tadmor, *Elastic plate basis for the deformation and electron diffraction of twisted bilayer graphene on a substrate*
Phys. Rev. B **110** (2024)
- S. H. Sung, N. Agarwal, I. El Baggari, P. Kezer, Y.M. Goh, N. Schnitzer, J. M. Shen, T. Chiang, Y. Liu, W. Lu, Y. Sun, L. F. Kourkoutis, J. T. Heron, K. Sun, **R. Hovden***, *Endotaxial stabilization of 2D charge density waves with long-range order*
Nature Communications **15**, 1403 (2024)
- M. Huang, Z. Sun, G. Yan, H. Xie, N. Agarwal, G. Ye, S. H. Sung, H. Lu, J. Zhou, S. Yan, S. Tian, H. Lei, **R. Hovden**, R. He, H. Wang, L. Zhao, C. R. Du, *Revealing intrinsic domains and fluctuations of moiré magnetism by a wide-field quantum microscope*
Nature Communications **14**, 5259 (2023)
- W. Millsaps, J. Schwartz, Z. W. Di, Y. Jiang, **R. Hovden***, *Autonomous Electron Tomography Reconstruction with Machine Learning*
Microsc. & Microanalys. **29** 1650-1657 (2023)

Deciphering Electrochemical Transformation Pathways on the Nanometer Scale: Advancing Fundamental Discovery for Material Innovation

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Energy storage is one of the most rapidly developing sectors of the economy, underpinning applications from electrical vehicles and mobile electronics to grid storage. This global transition necessitates the development of broad range of battery chemistries optimized to individual sectors based on cost, safety, energy/power densities, and other parameters. However, the materials development and optimization cycle from the laboratory scale to the viable technology is extremely slow due to the long testing cycles required to establish the performance and stability of the fabricated battery. In other words, establishing the potential of each new material combination (cathode, electrolyte, and anode) requires months-long testing at each step from laboratory to manufacturing.

The overall rate of introducing new energy technologies can be significantly accelerated if the fundamental knowledge on relevant materials properties such as diffusion and Vegard strain coefficients, electrochemical reactivity and overpotentials for primary and stray reactions, and phase transformation pathways can be made available faster than classical coin-cell based strategies, both for materials screening and predictive modelling. The North Star goal of the proposed work is to explore the fundamental mechanisms of electrochemical polarization and second phase nucleation at the tip-surface junction via the combination of the strain-based electromechanical scanning probe microscopy and time- and voltage domain spectroscopies, extend these studies to probe spatial inhomogeneity of these behaviors and decode structural and electrochemical transformation pathways.

We hypothesize that local studies of electrochemical functionalities on short time- and small length scales can be both an approach for **quantitative exploration** of fundamental electrochemical mechanisms on the nanoscale, and a **predictive method** for long-term battery behaviors. For the former, local studies will allow rapid characterization of electrochemical parameters of interest including diffusivity, mobility, overpotentials for the primary (intercalation) and deleterious (plating, decomposition) reactions, and corresponding overpotential-dependent kinetic laws. These parameters can be directly used as a part of the numerical models in commercial battery design packages such as PyBAMM, MPET, and LIONSIMBA. The unique aspect of local studies is that these will yield not only ensemble averages, but also distribution of these characteristics and their correlation with the microstructural elements, allowing for the identification and potentially mitigation of the unwanted phenomena and connecting these to parameters observable during fabrication. Indeed, all battery materials are highly inhomogeneous with the disorder spanning the atomistic length scales of the point defects and antiphase boundaries to dislocations to grain boundaries. The observed variability of the local electrochemical behaviors is the proxy signal for the prediction of the long-term prediction of battery stability and degradation. Jointly, these approaches will accelerate by orders of magnitude the discovery and optimization of new energy storage and conversion technologies and the lab to fab transition.

The enabling technique for the proposed work is ML-controlled quantitative scanning probe microscopy, allowing to explore the behavior of cathode materials and cathode-electrolyte pairs over a broad range of bias and time conditions via simultaneous current and strain detection and allowing for ML-driven dynamic experiment planning. In this approach, the electrochemical driving forces are induced directly by the SPM tip; the same tip acts as mobile electrode to collect current and strain signal, offering the advantage of spatial resolution. These dynamic electrochemical strain measurements by ESM open the window for probing the reversible (electrochemical polarization) and irreversible (second phase nucleation, dislocation nucleation, cracking) electrochemical phenomena at the fundamental length- and time scales of electrochemical processes in solids. To ascertain this, we note that the characteristic probe size in SPM is $L \sim 10$ nm. For materials with the typical diffusion coefficients $D \sim 10^{-11} - 10^{-10}$ cm²/s, the corresponding relaxation times L^2/D are 0.01 – 0.1 s, well within the frequency range accessible by ESM. The recent

(2023) introduction of interferometric SPMs now allows quantitative continuous detection of frequency-dependent responses across broad (0.1 Hz – 1 MHz) frequency ranges and spectroscopies in the (partially overlapping) 10 mHz – 100 Hz ranges. Previously, the detection was limited only to discrete cantilever resonances. Jointly, these developments suggest that ESM can offer insights into nanoscale mechanisms of electrochemical phenomena in solids complementing the macroscopic impedance spectroscopy measurements.

We plan to build upon the automated SPM methods developed in the PI group at UTK as illustrated in **Figure 1** to explore statistically relevant aspects of electrochemical behaviors for reversible and irreversible electrochemical processes, including spatial inhomogeneity of reactivity, nucleation potentials, and diffusion coefficients. The missing elements required to realize this vision is **interpretability**, i.e. the theoretical framework that allows connecting ESM signals to the fundamental materials properties such as concentration-dependent diffusion constants and Vegard strain tensors, **experiment design** allowing for probing and discovering relevant microstructural elements for partially reversible and irreversible transformations, and **connection** to chemical transformations pathways that can be further benchmarked against macroscopic studies.

The **overarching goal** of the proposed work is to explore the fundamental mechanisms of electrochemical polarization and second phase nucleation at the tip-surface junction via the combination of the scanning probe microscopy and time- and voltage domain spectroscopies, extend these studies to probe spatial inhomogeneity of these behaviors and decode structural and electrochemical transformation pathways from the ESM data. In this, we hypothesize that:

1. The quantitative probing of electromechanical response and spectroscopic exploration of its evolution with the dc bias offsets and as a function of frequency and amplitude of slow spectroscopic sweeps can be harnessed as a quantitative tool for probing the ionic density of states and concentration-dependent diffusion coefficients in ionically conductive solids and mixed electronic-ionic conductors. This data in combination with the crystallographic orientation data from EBSD data for polycrystalline materials can be used to extract the diffusion and Vegard strain tensor components for realistic materials.
2. ESM spectroscopies can be extended to probing the nucleation processes in solids and in combination with the ML-enabled SPM experiments can be used to establish the statistically significant aspects of microstructure-dependent materials behaviors
3. ESM mechanisms can be directly linked to the actual chemical transformation pathways including ion incorporation and phase transformations and aim demonstrate the proof of concept for control of these processes via surface modification. If successful, we will create a pathway for rapid identification of the solid-state reaction pathways from their fingerprints in fast SPM spectroscopies.

Overall, now we are ideally positioned to launch a new era of exploration of nanoscale electrochemical mechanisms operational in the energy storage and conversion devices and provide fast proxy signals that can be used to accelerate discovery of the fundamental physical mechanisms and optimization of new battery chemistries and lab to the fab transition. This direction is well aligned with the DOE BES and national priorities and is strongly rooted in development of SPM methods and theory for probing electrochemical phenomena on the nanometer scales.

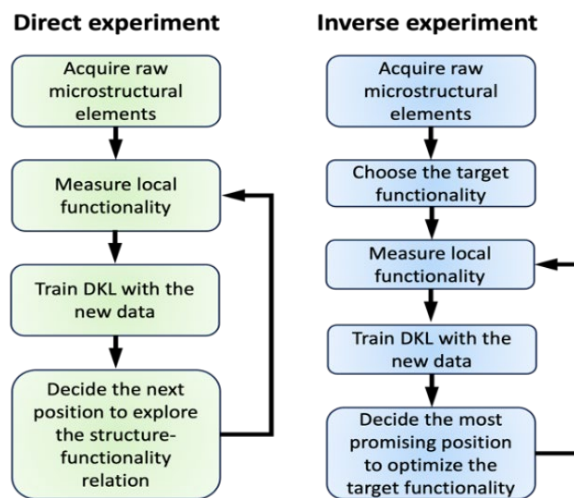


Figure 1: Direct and inverse workflows of the SPM AE. In direct AE, functionality of a priori known microstructural elements is explored. In the inverse experiment, AE seeks microstructural elements that maximize certain responses using deep kernel learning (DKL), e.g. hysteresis or nucleation bias.

Probing Correlated Phenomena in Graphene Constrictions

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Keywords: nano constriction, Quantum point contact, electrode-free AFM-based local anodic oxidation (LAO) nanolithography, moiré matter, Fractional quantum Hall

Research Scope

Understanding quantum electronic properties of confined charge carriers in graphene-based nano structures has recently attracted increasing attention mainly due to their potential applications for the development of innovative quantum devices. This project focuses on performing innovative research to enable engineering clean and tunable graphene-based nano constrictions and probing correlated phases in these systems. In the last couple of years, we successfully fabricated various types of constrictions with various widths by combining clean van der Waals (vdW) heterostructures and atomic force microscopy (AFM) based nanolithography. We have also characterized these constrictions employing low temperature transport measurement at zero magnetic field. The current research focuses on studying these nano constrictions in an applied magnetic field to achieve quantum point contact (QPC) operation in integer and fractional quantum Hall regimes. Overall, the research questions to be answered are: **how the correlation effects are manifested in narrow constrictions and what potential do they hold for developing novel types of qubits? What are the charge and statistics of emergent quasiparticles of Fractional quantum Hall (FQH) states?** This research will lead to further advancement of the field of condensed matter physics with potential implications in future quantum technologies.

Recent Progress

1. Transport characterization of wider graphene constrictions with QPC operation:

Previously, we performed fabrication and quantum transport measurements of bilayer graphene nano constriction devices utilizing the recently developed *electrode-free* AFM-based LAO nanolithography [1]. We showed the electronic properties in these constrictions are tunable by changing the width of the constriction. In wider constrictions, we observed bulk transport characteristics. However, as the constriction's width is reduced below 70 nm, a transport gap appears. Single quantum dot (QD) formation was observed within the narrowest constriction (Fig. 1).

In the current phase, our research is focused on detailed transport characterization of wider constrictions which generally showed the behavior expected for bulk graphene. For this we have made multiple devices with widths larger or comparable to 100 nm. A closer inspection of these

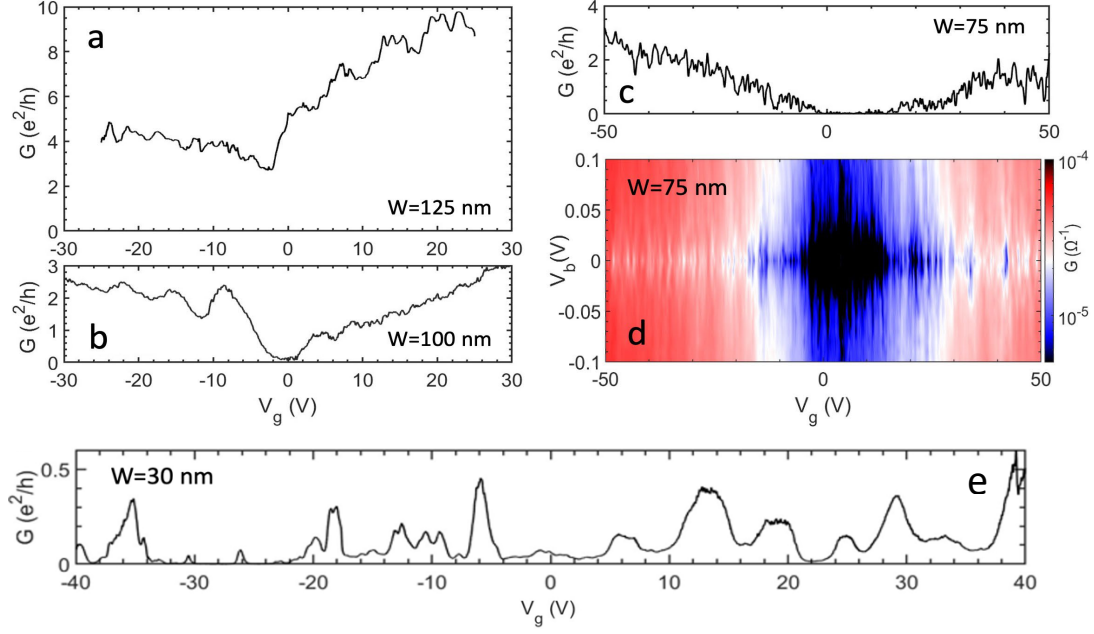


FIG. 1: Transport measurements of bilayer graphene nano constrictions with varying width. Conductance versus V_g measured for (a) device P1 with $W=125 \pm 5$ nm (b) device P2 with $W=100 \pm 5$ nm, (c) device P3 with a width of $W=75 \pm 5$ nm measured at $T = 1.6$ K. (d) The differential conductance ($G=dI/dV_b$) as a function of the bias voltage, V_b , and back gate voltage V_g measured at $T = 1.6$ K for device P3. A gapped region specified by a dark blue area is observed in the V_g - V_b plane where both band edges lie outside the bias window. (e) Conductance vs back gate voltage, V_g , for device P4 with $W=30 \pm 5$ nm measured at $T=1.6$ K showing coulomb peaks [1].

constrictions has revealed quantum size effects expected in a QPC. For QPC operation, the mean free path should be comparable to the constriction's width. However, when the edge roughness is comparable to the width, single or multi QD formation is expected depending on the channel's dimensions. Therefore, OPC operation is only observable for wider constrictions.

Figure 3. displays transport measurements of a representative wider constriction. At zero magnetic field, we observe reproducible kinks in the conductance which show a spacing of $\sim e^2/h$, a strong indication of quantized conductance through the constriction. This is distinct from previous studies on constrictions patterned by e-beam lithography with a channel width larger than ~ 200 nm for which the quantized kinks were observed with a spacing of $\sim 4 e^2/h$.

To characterize the conductance quantization in more detail, we performed magnetic field

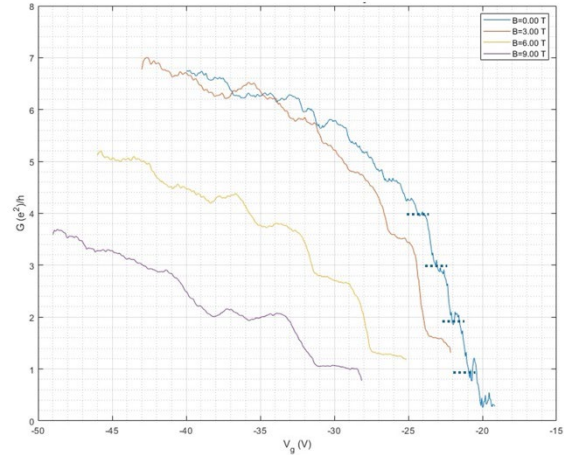


FIG. 2: Transport characterization of a graphene QPC. Conductance measured for the graphene constriction at various magnetic fields. At zero field, conductance shows kinks with quantization close to integer multiples of e^2/h . By increasing magnetic field, some of these kinks evolve into plateaus signifying QH states.

dependence and the transition to QH regime. As shown in Fig. 2, we observe a transition from zero field quantized kinks to Landau levels by increasing magnetic field.

Moreover, at the highest magnetic field we have observed signatures of interaction effects in these constrictions in the form of a quantized plateau around $0.7 e^2/h$ suggestive of 0.7 anomaly. We are currently measuring more devices (to confirm our results) and are performing simulations to understand the observed transition from zero field quantization to QPC operation in QH regime [2].

2. QPC operation in the FQH regime

This project is focused on transport studies of quasiparticle tunneling of FQH states in weak tunneling regime by utilizing clean/tunable QPCs. Here we use the alternate method of creating nano constrictions using split gate devices where the QPC is defined by the top and bottom gates. We started this phase last year and already have a few devices which we characterized in IQH regime and confirmed QPC operation in this regime. We have also succeeded on making higher quality devices where strong FQH states appear at low magnetic fields (Fig. 3). The current goal (ongoing experiments) is to understand QPC operation and inter edge tunneling in FQH regime.

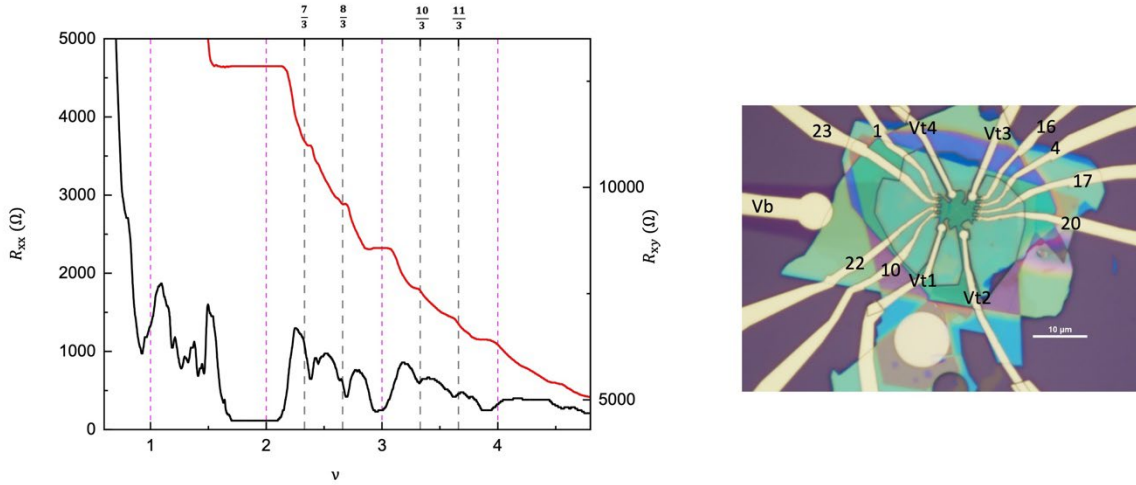


FIG. 3: QPC in FQH regime. Longitudinal and Hall resistivity vs bottom back gate measured in a graphene QPC shown on the right. FQH states are observable in fields as low as 7 T. The top split gates are floating in this measurement. The next step is to form a constriction by applying a voltage to both top and bottom gates and study charge flow in FQH regime through the constriction.

3. **Characterization of moiré graphene QPCs.** Experiments in this project have been originally focused on realizing superconducting QPCs in graphene-based moiré systems. This project was started by making twisted graphene devices at the magic angle. While characterizing these type of devices, we have developed thermopower measurements for further characterization. During the process, we have found out that thermal transport can be a more sensitive probe of moiré materials. Figure 4 displays a comparison between resistivity and thermopower signal measured for a twisted trilayer graphene. Strikingly, we observe more features in thermal signal compared to conventional resistivity. Our results show that thermopower as a measure of entropy can be a more sensitive probe of moiré materials compared to resistivity measurements. We are currently collecting more data on various devices to confirm these findings.

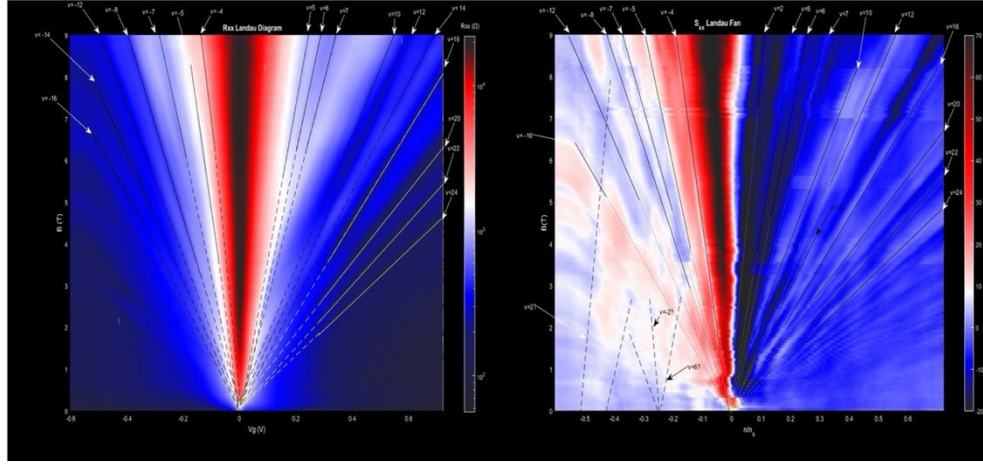


FIG. 4: Thermopower vs resistivity. Comparison between resistivity (left) and thermopower(right) measured for a twisted trilayer graphene.

Future Plans

Overall, we have succeeded in both fabrication and low temperature characterization of graphene based nano constrictions so far. The next phases will focus on more detailed studies of these structures in interacting regime to address the important fundamental questions of this proposal.

- 1- **Studies of FQH states in graphene based QPCs:** Once we establish OPC operation in FQH regime, we focus on tunneling experiments to probe the properties of emergent quasiparticles as they pass through these structures.
- 2- **Characterization of moiré graphene QPCs:** After fully characterizing moiré samples, the next steps will be: 1) to acquire a deeper insight on thermopower properties of moiré materials, 2) to fabricate complicated devices with top and bottom gates where superconducting QPCs can be created and characterized.

Publications

1. R. Rienstra, N. Sultana, En-Min Shih, Evan Stocker, K. Watanabe, T. Taniguchi, Curt A. Richter, Joseph Strosio, Nikolai Zhitenev and F. Ghahari, “Electron transport in bilayer graphene nano constrictions patterned using atomic force microscope nanolithography”, *Phys. Rev. B* **11**, 115145 (2025).
2. R. Rienstra, N. Sultana, K. Watanabe, T. Taniguchi, Joseph Strosio and F. Ghahari, “Conductance quantization in mechanically defined graphene nano”, *in preparation*
3. R. Rienstra and F. Ghahari, “electrode-free AFM-based local anodic oxidation nanolithography of graphene nanostructures”, *in preparation*

Towards Real-Space Characterization of Photo-Excited Quantum Materials

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Keywords: STEM, EELS, 4D-STEM

Research Scope:

The overall goals of this program are to combine state-of-the-art atomic-resolution, scanning transmission electron microscopy (STEM) and electron spectroscopies with in-situ photo-excitation of nano-scale hetero-structures to determine the atomic-scale mechanisms governing charge-carrier separation and lifetimes in photo-active nanoscale materials. This program addresses fundamental questions in photoactive quantum structures and hetero-interfaces about the structure/property relationships for efficient carrier separation, increased carrier lifetimes and the effects of defects at the hetero-interfaces on non-radiative recombination. In fact, there is a *knowledge gap* between the information that can be obtained from optical experimental measurements and the ex-situ structural characterization that is achievable to date.

The knowledge generated by this program will impact basic energy science research in areas including quantum materials, hydrogen production, and materials characterization beyond equilibrium, by demonstrating how atomic-resolution microscopy and spectroscopy can be combined with in-situ photo-excitation to study phenomena at the atomic scale that were previously limited to optical or surface-probe approaches. This program will utilize the atomic-resolution instrumentation at UIC, including the new TimePix3 detector and IDES Luminary Micro laser systems, as well as the new JEOL Z200MF-MONO STEM, the first monochromated, magnetic-field-free, double aberration-corrected STEM instrument.

Recent Progress:

During the first year of this program, we collaborated with the groups at the University of Chicago and the University of Delaware to establish the 4D-STEM capabilities using the available STEM instrumentation at UIC. In parallel, we have also been working on installing the *Quantum Detector* Cheetah Timepix3 detector, as well as the IDES Luminary Micro Laser system at UIC.

The *CheeTah TP3* is a hybrid pixel electron detector with 512 x 512 pixels, that allows for dwell times as low as 1.5625 ns. Under sparse conditions, event-based detection makes a huge difference in the data handling efficiency of the detector. For example, the size of a *TimePix3*-based 4D-STEM dataset discussed in Verbeeck *et al.* [1] is only 6.6 GB, compared to a 33-GB dataset that would be generated by a frame-based detector operating in 1-bit mode. The most significant advantage of the *TimePix3* detector is its throughput of data, which is determined solely by the

electron intensity on the detector. If no electrons arrive, no data is sent out. The maximum hit rate of the *CheeTah T3 Quad* is 120×10^6 counts per second or 457 counts per pixel per second. With the installation of the *Timepix3* detector completed, we are now working with *Amsterdam Scientific Instruments* on developing the necessary data acquisition and analysis tools to utilize the event-driven data stream for efficient data visualization, data analysis, especially during 4D-STEM acquisition, electron ptychography, and virtual detector imaging under ultra-low-dose conditions.

In collaboration with the Comes group at the University of Delaware, we combined 4D-STEM, electron energy-loss spectroscopy, density-functional theory calculation, and molecular-beam epitaxy to examine the role of strain on the structural stability in oxide thin films. We studied thin film samples of SrHfO_3 (SHO) grown on TbScO_3 (TSO, pseudocubic lattice parameter, $a = 3.954 \text{ \AA}$), and GdScO_3 (GSO, $a = 3.963 \text{ \AA}$) using atomic-resolution high-angle annular dark-field imaging, 4D-STEM and electron energy-loss spectroscopy combined with first-principles density functional theory calculations. Total energy calculations using DFT were carried out over a wide range of compressive and tensile strain to determine the thermodynamic stability of various phases of SHO. The electronic structure of the film and its dependence on the compressive strain was measured using EELS and compared with the electronic density of states calculations. The presence of polar distortions was investigated using atomic resolution and 4D-STEM.

Figure 1 shows a summary of the STEM annual dark-field (ADF) and 4D-STEM imaging analysis, which was used to determine that while the epitaxial film quality was sufficient to establish

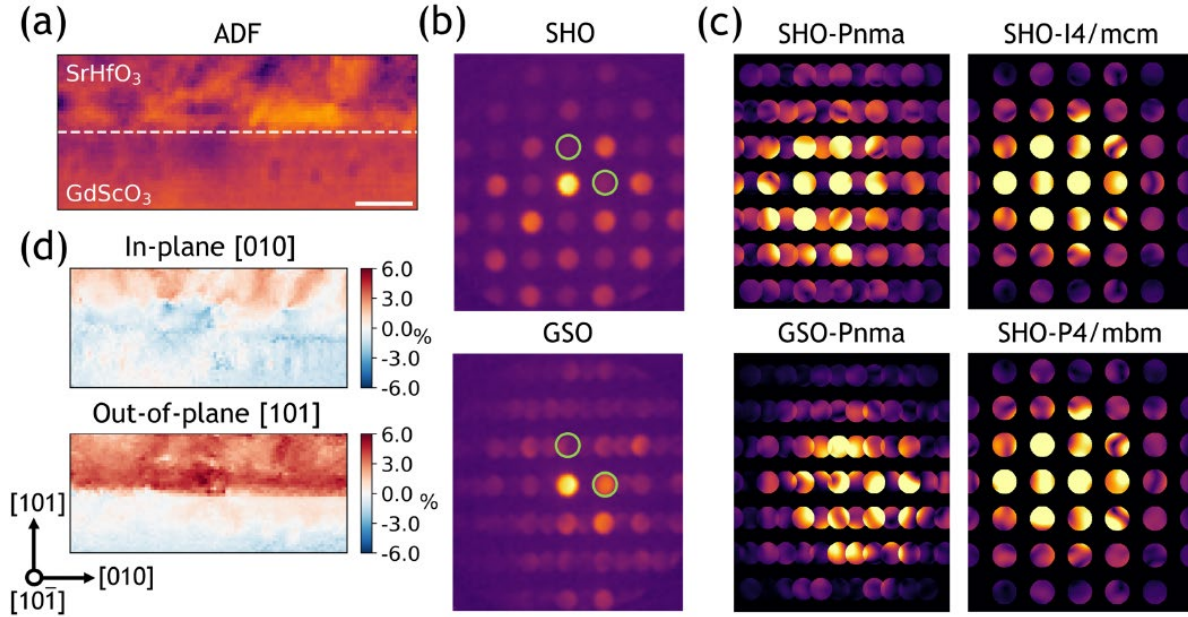


Figure 1: ADF image simultaneously acquired during 4D-STEM data collection for (a) SHO-GSO samples. The dashed white lines mark the SHO-GSO interface. CBED patterns for (b) SHO-GSO integrated over the area of the film and substrate. Simulated CBED patterns for (c) SHO-GSO. The crystallographic orientations corresponding to the experimental and simulated data are provided in (d) for SHO-GSO samples. Strain maps for (d) SHO-GSO samples, where strain is calculated with respect to the substrate. Bragg disks used for strain mapping are marked as green circles in (b) for SHO-GSO. The CBED patterns have been rotated post acquisition to match the real-space substrate orientation. Scale bar in (a) corresponds to 10 nm.

epitaxial strain, the expected polar polymorphs of SHO were not stabilized under either compressive or tensile strain. In fact, we reported the first synthesis of SHO with -3% biaxial in-plane strain, as confirmed by 4D-STEM measurements. While previous DFT studies predicted that SHO films would exhibit the polar P4mm phase when synthesized under compressive strain, our measurements indicated the samples are centrosymmetric and ruling out the presence of the P4mm phase. The absence of polar distortions is in agreement with previous computational studies and synthesis experiments. However, this contradicts a previous study that found SHO-STO films exhibited the P4mm phase, despite having less experimentally-determined compressive strain than the films synthesized in this work.

In a second collaborative project with the Alivisatos group at the University of Chicago, we studied colloidal metal phosphide nanocrystals. Colloidal synthesis of semiconductor nanocrystals yields tunable carrier densities, which can be modulated through the concentration of intrinsic defects, composition, and/or activation during synthesis, making them desirable for the aforementioned applications. As a result, systematic colloidal synthesis can achieve precise control of the photophysical properties in such semiconductor nanocrystals, including localized surface plasmon resonances (LSPRs) in the NIR or mid-IR regions. Unlike copper chalcogenides, which undergo phase transformations with dynamic redox tuning accompanied by the formation of disordered vacancies, Cu_{3-x}P exists as a stable sub-stoichiometric phase with ordered intrinsic vacancies. The possibilities for distinct surface chemistries and the above-mentioned phase stability of Cu_{3-x}P

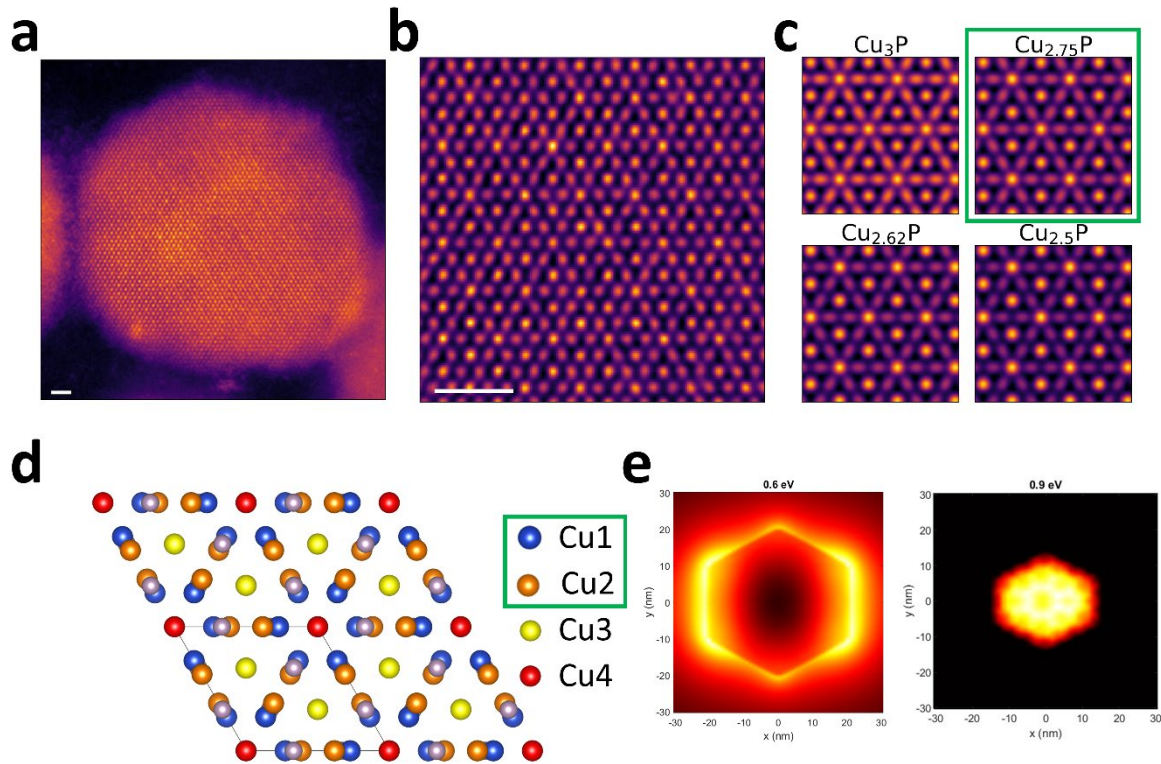


Figure 2: (a) STEM-HAADF image showing a typical Cu_{3-x}P nanoplatelet oriented along (001). (b) Atomic-resolution HAADF image showing the region highlighted as a red box in (a). (c) Simulated HAADF image along Cu_{3-x}P (001) for various vacancy concentrations. (d) Atomic model of fully stoichiometric Cu_3P along (001). Scale bars correspond to 1 nm for (a) and (b). (e) Simulated energy loss intensity maps for two predominant plasmonic modes for a nanoplatelet of size 25 nm.

could potentially lead to a unique system for colloidal semiconductor nanoplasmonics with a tailored plasmonic response (see Figure 2). Furthermore, the optoelectronic properties of these nanocrystals can be tuned by controlling their composition, size, and shape via colloidal semiconductor nanocrystal synthesis.

As shown in Figure 2, we have used atomic-resolution transmission electron microscopy (TEM) and image simulations to reveal the presence of ordered vacancies, such as in Cu_{3-x}P . Furthermore, first-principles density functional theory (DFT) calculations and boundary element method-based simulations are used to understand the role of morphology and composition on LSPRs. Through this comprehensive analysis of reaction mechanisms and products, we expect that the utilization of defined prenucleation metal-aminophosphine-alkylamine complexes as precursors for metal phosphide nanocrystal synthesis could pave the way toward synthesizing high-quality phosphide nanocrystals. Additionally, this precise synthesis control has the potential to yield plasmonic nanocrystals with a tailored plasmonic and optoelectronic response.

Future Plans:

During the next year, we will focus on establishing the in-situ illumination approaches and demonstrate that the effects on the sample stability will be minimal when the intensity of the laser illumination is controlled. The initial studies will focus on the system studied during Year 1 of this program and reported herein. In addition, we will test his hypothesis that the photo-excited charge carriers separate the length of the system, with the electrons accumulating in the Pt tips and the holes accumulating in the CdSe seeds, which is driven by the band-off sets at the hetero-interfaces and optimized in 60 nm long CdS rods with 2.3 diameter CdSe dots.

References

- [1] Jannis, D., C. Hofer, C. Gao, X. Xie, A. B     , T.J. Pennycook, and J. Verbeeck, *Event driven 4D STEM acquisition with a Timepix3 detector: Microsecond dwell time and faster scans for high precision and low dose applications*. Ultramicroscopy, 2022. **233**: p. 113423.

Publications

- [1] Gemperline, P.T., A.S. Thind, C. Tang, G.E. Sterbinsky, B. Kiefer, W. Jin, R.F. Klie, and R.B. Comes, "Strain Effects in SrHfO_3 Films Grown by Hybrid Molecular Beam Epitaxy," *ACS Applied Electronic Materials*, **7**, 983, (2025)
- [2] Dong Young Chung, Jinglong Guo, Jinyeop Kim, Nannan Shan, Jimun Yoo, Pedro Farinazzo Bergamo Dias Martins, Jongsu Noh, Munjung Jung, Peter Zapol, Bongjin Simon Mun, Robert Klie, Pietro Papa Lopes, Nenad M. Markovic, "Deciphering catalyst-support interaction for highly active and durable oxygen evolution catalysis," *Journal of the American Chemical Society*, **147(19)**, 16340-16349 (2025)

Visualizing light-induced non-equilibrium states in correlated insulators with ultrafast electron diffraction and nonlinear optics

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Keywords: Ultrafast electron diffraction, nonlinear optics, hidden states, charge density waves, antiferromagnetism

Research Scope

This project aims to uncover new optical phenomena, phase-transition pathways, and emergent states of matter that arise when correlated materials are driven far from equilibrium by intense femtosecond light pulses [1]. To directly visualize these transient states, we have developed two complementary probes: ultrafast electron diffraction, which tracks structural dynamics with atomic resolution, and time-resolved second harmonic generation, which is uniquely sensitive to changes in electronic symmetry.

By photo-exciting materials with complex energy landscapes, we can manipulate macroscopic properties and access quantum states inaccessible under thermal equilibrium. Our approach uses ultrafast light in two distinct regimes: (i) Optical quench – exploiting the femtosecond duration of the pulses to impulsively modify a microscopic parameter in the Hamiltonian, triggering novel non-equilibrium dynamics and (ii) Floquet engineering – using the time-periodic electric field of the light to stabilize symmetry-broken electronic states while leaving other degrees of freedom largely unaffected. The ability to control and characterize such non-equilibrium states will provide new strategies for designing ultrafast optoelectronic functionalities and advancing the fundamental understanding and eventual technological application of quantum materials for energy-related technologies.

Recent Progress

Progress has been achieved in three main directions

1. Development of a variable-temperature, RF-compressed ultrafast electron diffraction apparatus

We have fully commissioned a state-of-the-art lab-based ultrafast electron diffraction apparatus [2]. The instrument is now fully operational with variable pump wavelength capability, low and high temperature access, RF compressed electron pulses with 150 fs (RMS) temporal resolution and high signal-to-noise ratio in order to measure diffuse scattering signals. High temporal resolution (<300fs) in such instruments is typically difficult to achieve due to the space charge inherent to short electron pulses. To realize high temporal resolution, we have implemented a vector feedback protocol to stabilize phase and amplitude drifts in the RF cavity. Our instrument now functions with minimal drift over scan periods of over 48 hours, which enables high quality data acquisition of non-equilibrium crystal structures.

2. Observation of a non-equilibrium charge density wave liquid in 1T-TaS₂

Charge density waves (CDWs) have long been speculated to melt into a spatially textured electronic liquid [3]. Though they have not been previously detected, liquid CDWs may nonetheless be fundamental to the phase diagrams of many correlated electron systems, including high temperature superconductors and quantum Hall states. In 1T-TaS₂, one of the most promising materials capable of hosting a liquid CDW, a structural phase transition (from 1T to 2H) impedes its observation. By irradiating the material with a femtosecond light pulse, we circumvent the structural phase transition to reveal how topological defect dynamics govern the otherwise invisible CDW correlations. Upon photo-excitation, the CDW diffraction peaks broaden azimuthally and the system undergoes a solid-hexatic-liquid transition through the unbinding first of dislocations and then of disclinations. The liquid CDW phase is evidenced by a ring of diffuse scattering around the primary Bragg peaks. Our work provides the first compelling

evidence of an elusive liquid charge density wave state, which is hidden in 1T-TaS₂ under equilibrium conditions by an intervening phase transition. This work paves the way to the discovery of equilibrium liquid charge density waves and to a deeper understanding of how topological defects govern the physics of phase transitions in CDW systems.

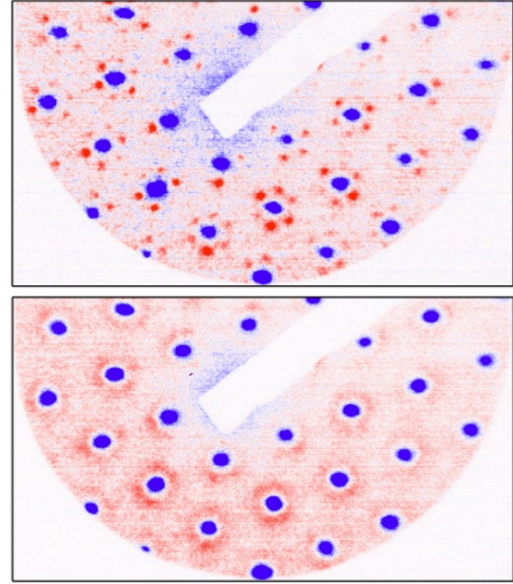


Figure 1. Ultrafast electron diffraction images demonstrating the discovery of a liquid CDW phase. Intensity difference images showing the changes in the diffraction pattern following a full suppression of the CDW after photo-excitation. At 360K (top) a solid CDW phase recovers, while at 520K (bottom) only a liquid phase is observed.

3. Breaking purely electronic symmetries of materials using light in Cr₂O₃

In a solid, the electronic subsystem can exhibit incipient order with lower point group symmetry than the crystal lattice [4]. Ultrafast external fields that couple exclusively to electronic order parameters have rarely been investigated, however, despite their potential importance to inducing exotic effects. When inversion symmetry is broken by the antiferromagnetic order in Cr₂O₃, transmitting a linearly polarized light pulse through the crystal gives rise to an in-plane rotational symmetry breaking via optical rectification. Using interferometric time-resolved second harmonic generation, we showed that the ultrafast timescale of the symmetry reduction is indicative of purely electronic response; the underlying spin and crystal structures remain unaffected. The symmetry-broken state exhibits a dipole moment, and its polar axis can be controlled with the incident light. Our results establish a coherent nonlinear optical protocol by which to break electronic symmetries and produce unconventional electronic effects in solids.

Future Plans

Dislocations and disclinations in liquid CDW states via UED

While conventional CDWs are well understood as periodic modulations of electronic density, we recently showed that strongly-coupled, two-dimensional materials, like 1T-TaS₂, may exhibit a liquid CDW in which phase coherence is disrupted by a dense network of topological defects. We will investigate the dynamics of topological defects – dislocations and disclinations – in the liquid-like CDW phase in 1T-TaSe₂ and chemically substituted 1T-Ti_xTa_{1-x}S₂. These systems serve as model platforms for exploring fluctuation CDW states that exhibit local order but lack global phase coherence due to the proliferation of defects. Using ultrafast electron diffraction, we will quantify the temporal evolution and correlation of the defect networks, and assess how disorder introduced by Ti substitution influences the stability and connectivity of these liquid like textures. This work will address fundamental questions about the prevalence and universality of CDW liquids in strongly coupled systems and establish defect dynamics as a central mechanism for controlling phase evolution.

Circular shift current and linear injection current in Cr₂O₃ and PT-symmetric insulators

Though we did not realize it at the time, subsequent theoretical work (in preparation), has shown that the effect we observed in Cr₂O₃ is due to the development of linear injection current, a novel phenomenon that is allowed in *PT*-symmetric (*P*: parity, *T*: time-reversal) systems. Such a linear injection current, which is forbidden in systems possessing time-reversal symmetry but broken inversion symmetry, arises due to the quantum geometry of the eigenstates through the quantum metric dipole. A second corresponding effect, which has not yet been observed, is a circular shift current. Such a response is only allowed in *PT*-symmetric systems and arises due to the presence of an induced Berry phase [5]. Using interferometric methods in our second harmonic generation setup provides a high sensitivity method to search for the predicted nonlinear optical effect. Such an observation would pave the way to a new family of photocurrent generating solids that may be relevant to energy applications in solar technology.

References

1. D.N Basov, R.D. Averitt, and D. Hsieh, *Towards properties on demand in quantum materials*, Nature Materials **16**, 1077 (2017).
2. T.M. Sutter, J.S.H. Lee, A.V. Kulkarni, P. Musumeci, and A.Kogar, *Vector-based feedback of continuous wave radio-frequency compression cavity for ultrafast electron diffraction*, Structural Dynamics **11**, 024303 (2024).
3. H. Dai and C.M. Lieber, *Solid-hexatic-liquid phases in two-dimensional charge-density waves*, Physical Review Letters **69**, 1576 (1992).
4. E. Fradkin, S.A. Kivelson, M.J. Lawler, J.P. Eisenstein, and A.P. Mackenzie, *Nematic Fermi fluids in condensed matter physics*, Annual Reviews of Condensed Matter Physics **1**, 153 (2010).

5. Q. Ma, R.K. Kumar, S.-Y. Xu, F.H.L. Koppens, and J.C.W. Song, *Photocurrent as a multiphysics diagnostic of quantum materials*, Nature Reviews Physics **5**, 170 (2023).

Publications

1. T.M. Sutter, J.S.H. Lee, A.V. Kulkarni, P. Musumeci, and A.Kogar, *Vector-based feedback of continuous wave radio-frequency compression cavity for ultrafast electron diffraction*, Structural Dynamics **11**, 024303 (2024).
2. X. Zhang, T. Carbin, K. Du, B. Li, K. Wang, C. Li, T. Qian, N. Ni, S.-W. Cheong, and A. Kogar, *Directionally asymmetric nonlinear optics in planar chiral MnTiO₃*, arXiv:2410.18086 (2025)
3. X. Zhang, T. Carbin, A.B. Culver, K. Du, K. Wang, S.-W. Cheong, R. Roy, and A. Kogar, *Light-induced electronic polarization in antiferromagnetic Cr₂O₃*, Nature Materials **23**, 790 (2024).
4. T. Carbin, X. Zhang, A.B. Culver, H. Zhao, A. Zong, R. Acharya, C.J. Abbamonte, R. Roy, G. Cao, and A. Kogar, *Evidence for bootstrap percolation dynamics in a photoinduced phase transition*, Physical Review Letters **130**, 186902 (2023).
5. X. Guo, A. Kogar, J. Henke, F. Flicker, F. de Juan, S.X.-L. Sun, I. Khayr, Y. Peng, S. Lee, M.J. Krogstad, S. Rosenkranz, R. Osborn, J.P.C. Ruff, D.B. Lioi, G. Karapetrov, D.J. Campbell, J.P. Paglione, J. van Wezel, T.C. Chiang, and P. Abbamonte, *In-plane anisotropy of charge density wave fluctuations in 1T-TiSe₂*, arXiv:2501.09968 (2025) (accepted for publication in Physical Review Letters).
6. T.M. Sutter, C. Lindenau, S. Sharma, A. Flueraşu, L. Wiegart, G. Karapetrov, A. Kogar, and X.M. Chen, *Metastable short-range charge order in superconducting CuxTiSe2*, arXiv:2504.033176 (2025)
7. Y. Cheng, A. Zong, L. Wu, Q. Meng, W. Xia, F. Qi, P. Zhu, X. Zou, T. Jiang, Y. Guo, J. van Wezel, A. Kogar, M.W. Zuerch, J. Zhang, Y. Zhu, and D. Xiang, *Ultrafast formation of topological defects in a 2D charge density wave*, Nature Physics **20**, 54 (2024).
8. J.S.H. Lee, T.M. Sutter, G. Karapetrov, P. Musumeci, and A. Kogar, *Topological phase transition to a hidden charge density wave liquid*, arXiv:2505.04867 (2025).

Nanoscale Microwave Impedance Microscopy of Complex Materials

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Keywords: Milli-Kelvin microscopy, microwave imaging, conductivity fluctuations, amorphous semiconductors, time-of-flight experiments

Research Scope

The goal of this DOE program is to investigate the response of complex quantum materials to multiple external stimuli with nanoscale spatial resolution. Specifically, the research team has been developing microwave impedance microscopy (MIM) with high spatial and temporal resolutions, as well as inside a dilution refrigerator with milli-Kelvin (mK) temperatures and high magnetic-fields. The successful implementation of mK-MIM has led to the visualization of edge channels in quantum anomalous Hall state and axion insulator state. The study of amorphous semiconductors with time-of-flight MIM has resulted in the understanding of conductivity fluctuations and charge dynamics in thin-film field-effect transistors. Our work is thus of great interest to energy-related science and technology.

Recent Progress

In the past two years, we have studied quantum anomalous Hall states by the dilution-refrigerator-based mK-MIM and amorphous In-Ga-Zn-O semiconductors by time-of-flight MIM. Details of the accomplishments are as follows.

Implementing MIM in a dilution refrigerator

The PI's group has implemented the mK-MIM inside a dilution refrigerator with an 8 T superconducting magnet (Publication #2). As shown in Fig. 1a, the cryostat is housed in a steel enclosure underneath the ground level. The entire structure rests on four pneumatic isolators that can effectively filter out floor vibrations. The PI has installed a helium reliquefier (Fig. 1b) to recondense the exhaust gas, which minimizes the liquid helium consumption and increases the run time to several months without the need for refill. The vibration level at the sample stage is below 1 nm when the reliquefier is off and 1 ~ 2 nm with reliquefier on, which is much better than that reported by other groups using closed-cycle dilution refrigerators for MIM¹. The height feedback control is based on a quartz tuning fork², with an etched tungsten wire mounted on one of the prongs as the MIM tip. The system can simultaneously track the surface and perform MIM experiment using the demodulated signals. Fig. 1c shows the topographic image of a monolayer WTe₂ sample encapsulated by top and bottom hBN flakes taken at the base temperature of 110 mK. The line profile in Fig. 1d indicates that the instrument can resolve the heights of a monolayer TMD (~ 1 nm) and interface bubble (~ 2 nm).

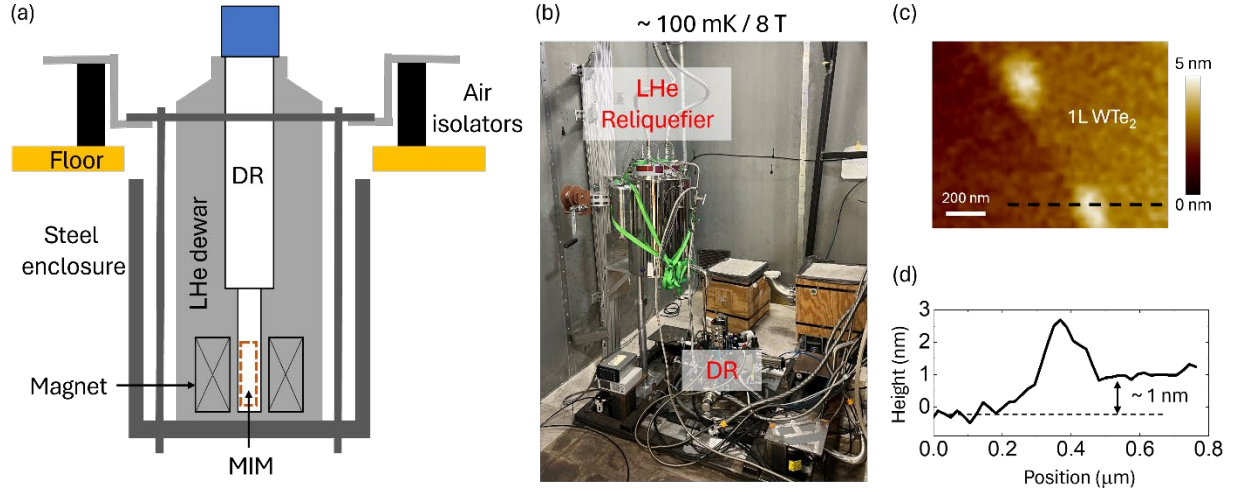


Fig. 1 (a) Schematics of the dilution refrigerator system with vibration isolation. (b) Photo of the apparatus and helium reliquefier. (c) Topographic image of a monolayer WTe_2 sample encapsulated by hBN flakes taken at 110 mK. (d) Profile along the dashed line in (c), showing the height of the monolayer as ~ 1 nm.

We demonstrated the local conductivity imaging on a magnetically (V and Cr) doped topological insulator $(\text{Bi, Sb})_2\text{Te}_3$ (BST). Figs. 2a and 2b show the B -field dependence of Hall (σ_{xy}) and longitudinal (σ_{xx}) conductivities, respectively. The quantization of σ_{xy} at $+e^2/h$ and the nearly zero σ_{xx} above 1 T are clear signatures of the Chern number $C = 1$ quantum anomalous Hall (QAH) state. As the B -field is swept toward the $C = -1$ QAH state, two prominent σ_{xx} peaks are observed, accompanied by two steps of change in σ_{xy} , first to zero and then to $-e^2/h$. In between the peaks, the minimum in σ_{xx} and the zero σ_{xy} plateau indicate the formation of an axion insulator state with antiparallel magnetization of the two doped layers.

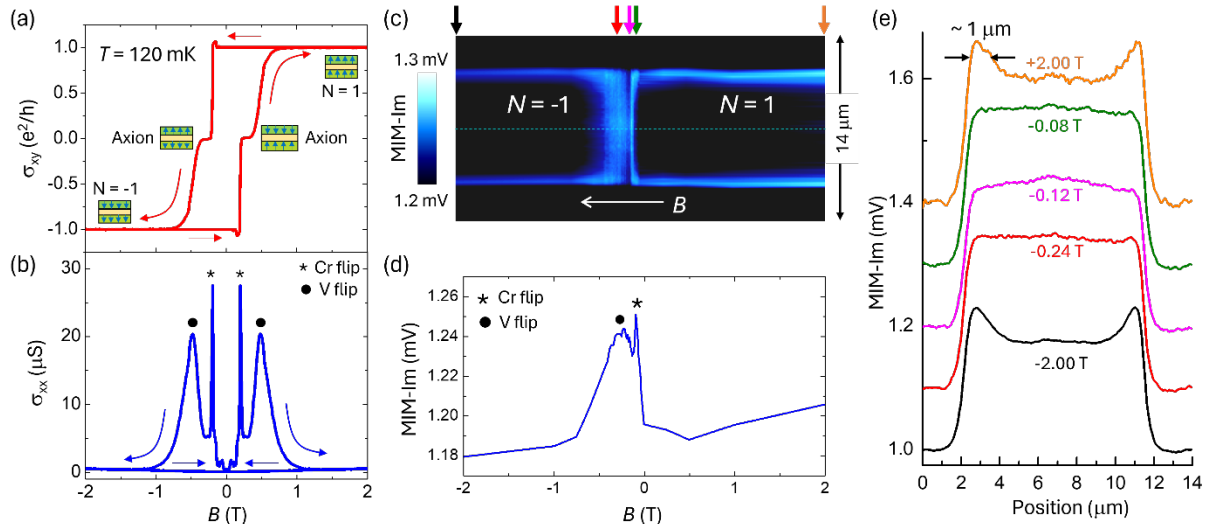


Fig. 2 (a) Magnetic field dependence of σ_{xy} and (b) σ_{xx} at $T = 120$ mK of a magnetically doped topological insulator. (c) MIM-Im single-line profile across the device from 2T to -2 T at 130 mK. (d) Field-dependent MIM-Im signals at the center of the Hall bar. The asterisks and dots denote topological phase transitions in the Cr-doped and V-doped BST layers, respectively. (e) Selected profiles at 5 representative fields.

Fig. 2c shows the field-dependent MIM-Im data across the device, with the signals along the center line plotted in Fig. 2d. The narrow and broad peaks correspond to the magnetization flipping of Cr- and V-doped BST layers, respectively, and the dip between them represents the axion insulator state. The characteristic line profiles at five different fields are shown in Fig. 2e. When the system is in the $C = 1$ QAH state, the MIM-Im profile exhibits two prominent peaks, i.e., the chiral edge channels. Around $B = -0.08$ T, the edge state disappears, and the sample is uniformly conductive. Beyond -1 T, the edge state reappears in the $C = -1$ data. In short, the mK-MIM is fully up and running for imaging under ultralow temperatures and strong B -fields.

Visualizing conductivity fluctuations in amorphous semiconductors

Charge transport in amorphous semiconductors³ is considerably more complicated than the process in crystalline materials due to abundant localized states. In addition to device-scale characterization, spatially resolved measurements are important to unveiling electronic properties. In this work (Publication #3), we imaged the evolution of local conductivity during the normal operation of amorphous In-Ga-Zn-O (a-IGZO) thin-film transistor (TFT) devices⁴ by MIM (Fig. 3a), which probes conductivity without Schottky barrier's influence. In the sub-threshold regime, we observed local conductivity fluctuations with an amplitude of 10-20% of the overall values. Autocorrelation analysis of MIM images in Fig. 3b indicates that the characteristic length scale of the spatial conductivity variation is ~ 200 nm, i.e., in the mesoscopic regime. Our imaging result is of great importance for both fundamental understanding and practical application of amorphous semiconductors.

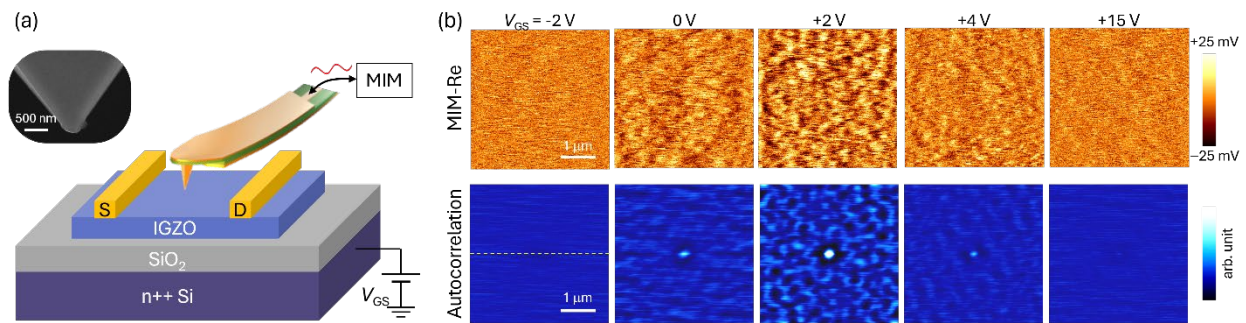


Fig. 3 (a) Schematic of MIM imaging on a back-gated a-IGZO TFT device. (b) Top: MIM-Re images on a-IGZO under different V_{GS} . Bottom: autocorrelation of the corresponding MIM images. The characteristic length scale of conductivity fluctuation from the autocorrelation analysis is ~ 200 nm.

Probing charge dynamics by time-of-flight MIM

Conventional studies of charge transport in a-IGZO usually involve steady-state or transient measurements on field-effect transistors. As shown in Fig. 4a, we carried out position-dependent time-of-flight experiments⁵ on a-IGZO devices by time-resolved MIM, which offer spatial and temporal information on the underlying transport dynamics (Publication #4). The spatiotemporal conductivity data can be nicely fitted to a two-step function, corresponding to two coexisting mechanisms with a typical time scale of milliseconds, as shown in Fig. 4b. The competition

between multiple-trap-and-release conduction through band-tail states and hopping conduction through deep trap states is evident from the fitting parameters, which is summarized in the diagram in Fig. 4c. Such understandings of the length scale and time scale of charge dynamics in a-IGZO are important for their device applications.

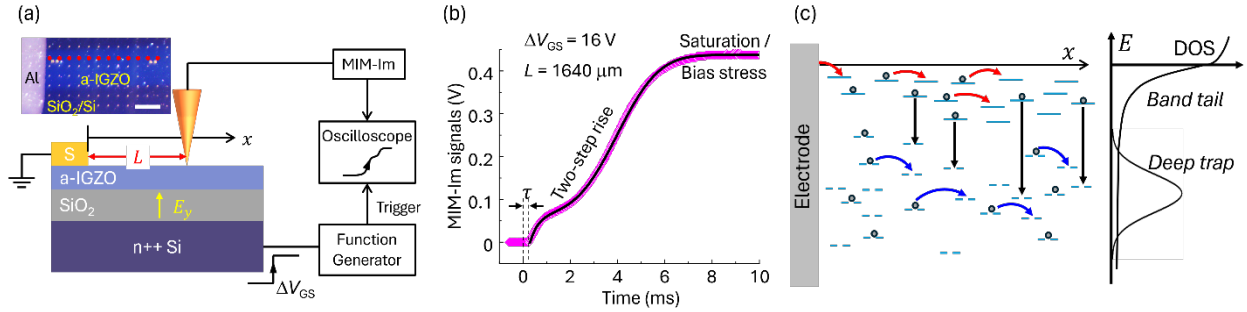


Fig. 4 (a) Schematic of the time-of-flight MIM setup and optical image of the a-IGZO sample. Scale bar: 500 μm. (b) Time evolution at $L = 1640$ μm from the electrode, showing the initial delay, two-step rise, saturation, and bias-stress effect. (c) Left: Schematic of distribution of in-gap states in a-IGZO with a source electrode. Right: Density of states in a-IGZO, consisting of an exponential band tail and a Gaussian-like localized band.

Future Plans

In the new cycle of this DOE program, the PI's group will utilize the mK-MIM to spatially probe topology and correlation in various 2D van der Waals heterostructures. For graphene-based devices, we plan to study the edge states at charge neutrality point and integer quantum Hall states, which will shed light on the complex quantum phases of graphene under strong magnetic fields. We will then investigate the edge and bulk states of interlayer excitonic insulator phase in quantum Hall bilayers, providing microscopic understanding of this macroscopic phase coherent system. For transition-metal dichalcogenide (TMD) devices, we will start from the imaging of strongly correlated states in twisted homo-bilayer TMDs. By controlling the material parameters and twist angles, we will compare the strengths of Mott-like states when different conduction valleys are occupied in the moiré superlattice structures. The magnetic-field dependence will also reveal the presence of nontrivial topology in the systems. We expect a highly fruitful program with mK-MIM studies in the next 2 years.

References

1. L.W. Cao, C. Wu, R. Bhattacharyya, R. Zhang, and M. T. Allen. "MilliKelvin microwave impedance microscopy in a dry dilution refrigerator." *Review of Scientific Instruments* **94**, 093705 (2023).
2. Y.-T. Cui, E. Y. Ma, and Z.-X. Shen. "Quartz tuning fork based microwave impedance microscopy." *Review of Scientific Instruments* **87**, 063711 (2016).
3. P.W. Anderson. "Model for the Electronic Structure of Amorphous Semiconductors". *Physical Review Letters* **34**, 953 (1975).
4. K. Nomura, H. Ohta, A. Takagi, T. Kamiya, M. Hirano, H. Hosono. "Room-temperature fabrication of transparent flexible thin-film transistors using amorphous oxide semiconductors". *Nature* **432**, 488 (2004).
5. R. Dost, A. Das, M. Grell. "Time-of-flight mobility measurements in organic field-effect transistors". *Journal of Applied Physics* **104**, 084519 (2008).

Publications

1. L. Caretta, Y.-T. Shao, J. Yu, A. B. Mei, B. F. Grosso, C. Dai, P. Behera, D. Lee, M. McCarter, E. Parsonnet, K.P. Harikrishnan, F. Xue, X. Guo, E. S. Barnard, S. Ganschow, Z. Hong, A. Raja, L. W. Martin, L.-Q. Chen, M. Fiebig, K. Lai, N. A. Spaldin, D. A. Muller, D. G. Schlom & R. Ramesh. “*Non-volatile electric-field control of inversion symmetry*” *Nature Materials* **22**, 207-215 (2023).
2. Z. Jiang, S. K. Chong, P. Zhang, P. Deng, S. Chu, S. Jahanbani, K. L. Wang, and K. Lai. “*Implementing microwave impedance microscopy in a dilution refrigerator*.” *Review of Scientific Instruments* **94**, 053701 (2023).
3. J. Yu, Y. Zhou, X. Wang, A. Dodabalapur, and K. Lai. “*Visualization of Mesoscopic Conductivity Fluctuations in Amorphous Semiconductor Thin-Film Transistors*.” *Nano Letters* **23**, 11749-11754 (2023).
4. J. Yu, Y. Zhou, X. Wang, X. Ma, A. Dodabalapur, and K. Lai. “*Probing Charge Dynamics in Amorphous Oxide Semiconductors by Time-of-Flight Microwave Impedance Microscopy*.” *ACS Applied Electronic Materials* **6**, 8448–8454 (2024).

New Cryo-EM Tools for Studying Dynamic Interfaces in Battery Materials

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Keywords: Battery interfaces, cryo-EM, solid electrolyte interphase, Li metal

Research Scope

Understanding the dynamic and non-equilibrium processes that occur during battery operation is crucial for accelerating the development of better batteries. Currently, these time-dependent and metastable battery states can only be studied by in situ or operando experiments, as ex situ techniques are limited to observing materials in their equilibrium state. While in situ tools shed light on how electrode morphologies and surface chemistries evolve during battery operation, important interfacial structures below length scales of ~ 50 nm are difficult to access, representing a critical blind spot for understanding nanoscale processes away from equilibrium.

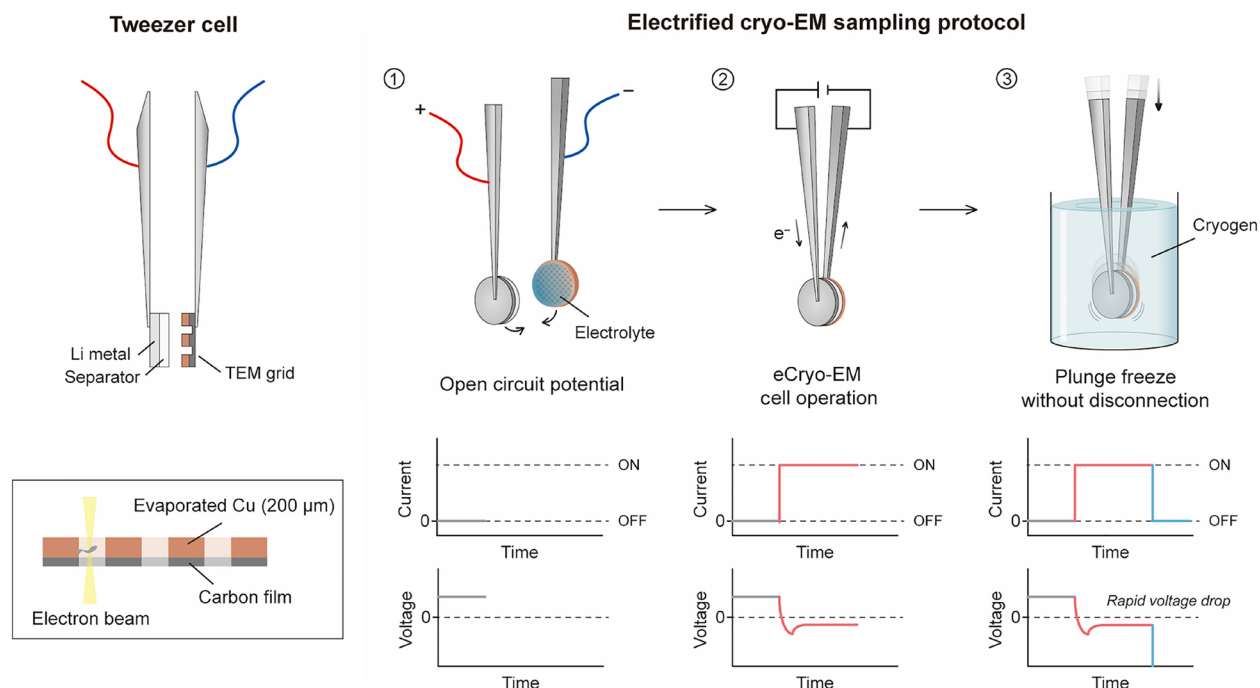


Fig. 1. Schematic diagrams illustrating the electrochemical tweezer cell design and eCryo-EM sample preparation procedure.

The solid electrolyte interphase (SEI), a nanometer-thick interfacial layer on lithium metal, plays a pivotal role in battery reversibility by mediating ion and electron transport. Despite its importance, the SEI remains one of the most enigmatic aspects of battery science due to limitations in characterizing its dynamic formation and evolution. Bridging this gap requires imaging tools

that can capture transient interfacial phenomena at nanometer resolution while the battery is actively cycling.

Recent Progress

Our team has developed a novel experimental platform, termed electrified cryo-EM (eCryo-EM), that kinetically traps and images battery interfaces under realistic electrochemical biasing. This platform utilizes a miniaturized, two-electrode tweezer-cell system that can be flash-frozen mid-operation, preserving metastable interfaces with nanometer fidelity. Using this approach, we have resolved early-stage SEI formation on Li metal, uncovering counterintuitive growth behaviors that challenge conventional paradigms. This allows us to uncover the SEI growth kinetics on metallic Li for the first time, which has remained elusive due to their high reactivity. Surprisingly, we discover that the transport properties through the SEI of both high performing and conventional electrolytes are within 10% of one another, suggesting similar passivating properties. Instead, their reactivity differs by a factor of three, which is likely the key reason for enhanced performance.

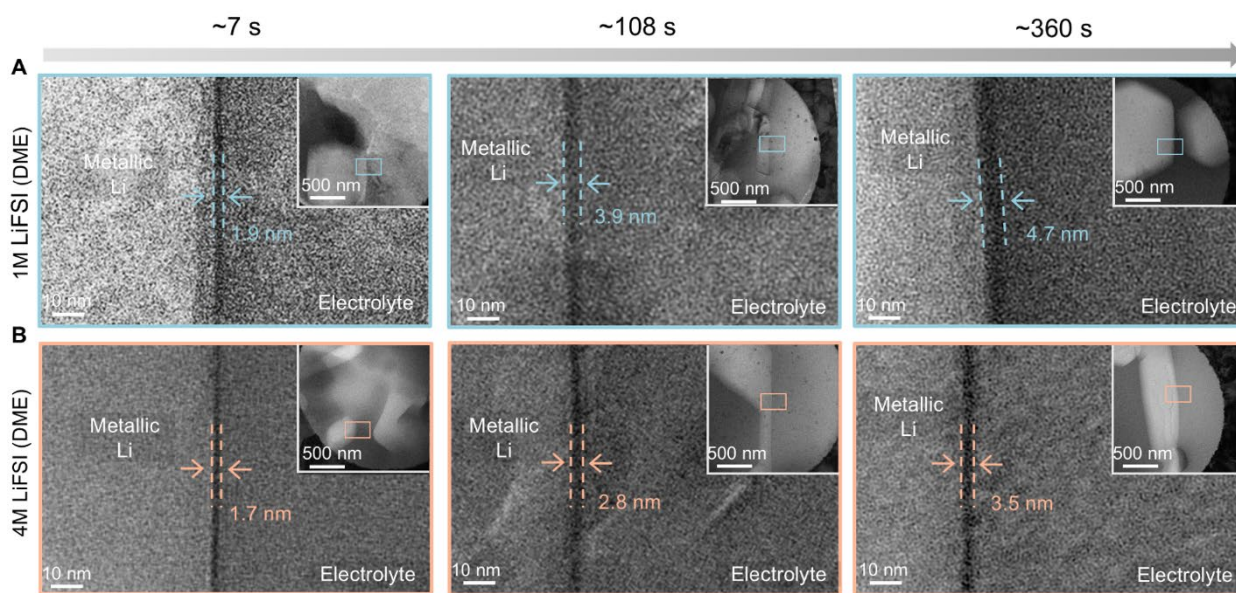


Fig. 2. eCryo-EM images of lithium deposited in 1M LiFSI in DME and 4M LiFSI in DME. The capacity is approximately $0.002 \text{ mAh cm}^{-2}$, 0.03 mAh cm^{-2} , and 0.1 mAh cm^{-2} from left to right.

Based on these findings, a key design principle to improve battery performance may be to decrease the reactivity of both solvent and salt molecular components. This refines previous semi-empirical approaches of fluorinating all electrolyte components or targeting anion-derived SEI films, opening an underexplored design space for improving battery performance. More broadly, eCryo-EM provides a general approach to study the dynamic nanoscale processes at electrified interfaces fundamental to all electrochemical devices (e.g., electrocatalysts, supercapacitors), introducing exciting opportunities for scientific exploration and discovery. This study establishes a foundation for the next generation of cryo-EM technologies, which may also have broad implications for

biology, where electrified interfaces are the basis of facilitating action potentials that enable communication between biological cells. Additionally, our innovations in cryo-EM have enabled recent progress described below:

Quantitative SEI Composition Mapping Reveals Dominance of Li₂O over LiF

While LiF has long been considered favorable for SEI design, our recent collaborative work challenges this paradigm by developing a quantitative titration framework to assess SEI composition across ten diverse electrolyte systems. We found that Li₂O, not LiF, is the most statistically correlated phase with high Coulombic efficiency, reaching >99% CE in fluorine-free electrolytes. Using cryo-EM, we imaged Li₂O domains ordered along the SEI, revealing a previously underappreciated chemical–structural functionality (*Nature Energy* **9**, 580, 2024). These findings suggest that oxygen-rich SEI architectures may be more beneficial for Li⁺ transport than previously assumed. Our Cryo-EM platform enabled direct imaging of these nanostructures, providing essential corroborative evidence to validate titration-based quantification.

Electric Field as a Tuning Knob for SEI Chemistry via EDL Engineering

Our team has uncovered that SEI structure and chemistry can be drastically modulated by tuning the electrical double layer (EDL) via electric field control. By comparing electrochemically formed SEIs (with an applied electric field) and chemically formed SEIs (without an applied field), we found that the electric field strongly influences which species in the EDL are decomposed into the SEI. Cryo-EM imaging revealed that chemically formed SEIs are 50% thinner, exhibit more uniform Li₂O-rich layering, and possess a hybrid mosaic–multilayer nanostructure (*Joule* **8**, 3038, 2024). These SEIs also demonstrated greater resistance to corrosion and improved Li reversibility. This work highlights the electric field as a new axis of control in SEI engineering—orthogonal to electrolyte formulation—and further highlights Cryo-EM as a powerful tool for resolving how subtle changes in interfacial conditions impact SEI formation.

Molecular Design of Miniature Solvation Structures for Uniform and Safe SEI Formation

A complementary strategy we explored involves rational electrolyte design to precondition the solvation environment of Li⁺ before interfacial decomposition occurs. In collaboration with researchers at KAIST, we introduced symmetric ionic plastic crystals (IPCs) that promote miniature anion–Li⁺ solvation clusters, reducing anion aggregation and enabling high mobility with reduced desolvation barriers. Cryo-TEM and 3D secondary ion mass spectrometry revealed that such electrolytes produce SEI films with highly uniform inorganic nanocrystals (LiF, Li₃N, Li₂O) embedded in amorphous organic layers. These SEIs are not only electrochemically stable but also physically robust under high-rate cycling and mechanical abuse, such as nail penetration tests. The ability to correlate solvation structures in bulk electrolytes with interphase morphology

at the nanometer scale further underscores the unique advantage of cryo-EM as a bridge between electrolyte chemistry and interfacial design (*Nature Energy* **10**, 502, 2025).

Future Plans

We aim to further expand the capabilities of electrified cryo-EM (eCryo-EM) by integrating high-speed plunge-freezing robotics and programmable electrochemical biasing. This advancement will allow for high-throughput trapping of electrode–electrolyte interfaces across a wide array of electrolyte chemistries, bias conditions, and timepoints. The resulting statistical dataset will uncover critical correlations between SEI growth kinetics, spatial heterogeneity, and electrolyte-driven decomposition pathways—enabling robust, ensemble-level insights beyond anecdotal single-particle analysis.

To move beyond 2D projections, we are developing time-resolved cryo-electron tomography (cryo-ET) protocols to reconstruct the 3D architecture of interphases with nanometer resolution. These volumetric datasets will be paired with electrochemical and transport modeling to understand how SEI porosity, tortuosity, and nanograin distributions affect ion conduction, mechanical integrity, and failure modes under different cycling protocols.

A second frontier involves applying eCryo-EM to new classes of buried electrochemical interfaces that remain poorly understood due to the limitations of conventional characterization. In solid-state batteries, for example, the buried interface between Li metal and solid electrolytes exhibits rapid interfacial degradation and filament growth that are challenging to capture with traditional tools. Likewise, multivalent systems such as Zn and Mg introduce unique interfacial chemistries—such as soluble SEI intermediates and high-field effects—that demand tailored imaging strategies. We have begun developing solid–solid freezing mounts and tailored sample transfer protocols to preserve these more reactive interfaces under bias.

Our long-term vision is to establish eCryo-EM as a generalizable framework for imaging non-equilibrium electrochemical phenomena, not only in batteries but also in emerging areas such as electrocatalysis and membrane separations for critical materials.

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. G. M. Hobold, C. Wang, K. Steinber, Y. Li, B. M. Gallant. *High lithium oxide prevalence in the lithium solid–electrolyte interphase for high Coulombic efficiency*, Nature Energy **9**, 580 (2024).
2. Y. Li, Y. Liu, Z. Zhang, W. Zhou, J. Xu, Y. Ye, Y. Peng, X. Xiao, W. Chiu, R. Sinclair, Y. Li, Y. Cui. *Electrified Operando-Freezing of Electrocatalytic CO₂ Reduction Cells for Cryogenic Electron Microscopy*, Nano Letters **24**, 10409 (2024).
3. X. Yuan, D. Chang, B. Liu, K. Liang, K. Liang, J. Yu, M. Mecklenburg, P. Sautet, Y. Li. *Engineering battery corrosion films by tuning electrical double layer composition*, Joule **8**, 3038 (2024).
4. J. Jang, C. Wang, G. Kang, C. Han, J. Han, J.S. Shin, S. Ko, G. Kim, J. Baek, H.T. Kim, H. Lee, C.B. Park, D.H. Seo, Y. Li, and J. Kang. *Miniature Li⁺ solvation by symmetric molecular design for practical and safe Li-metal batteries*, Nature Energy **10**, 502 (2025).
5. K. Liang, X. Yuan, X. Chen, B. Liu, J.T. Kim, J. Yu, D. Zhao, and Y. Li. *A Beginner’s Guide to Cryo-EM for Battery Research*, Nano Letters **25**, 7210 (2025).
6. C. Wang, J.T. Kim, X. Yuan, J.K. Kim, B. Liu, M.H. Kim, D. Zhao, M. Mecklenburg, and Y. Li. *Trapping and Imaging Dynamic Battery Nanointerfaces via Electrified Cryo-EM*, Science Advances **11**, eadv3191 (2025).

Visualizing Topological States at Dislocations in Fe-Chalcogenides and Symmetry-Breaking Electronic Orders in Kagome Magnet

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Keywords: Topological defect, edge and screw dislocations, Kagome magnet FeSn, Fe-chalcogenides, symmetry-mismatched MBE

Research Scope

Atomic-scale defects are increasingly recognized not simply as imperfections but as active quantum elements that can host robust, localized electronic states for quantum devices. Defects in topological materials further open a new frontier for defect-based quantum functionality. Here, real-space topological defects such as dislocations can host localized, symmetry-protected electronic states, which are dictated by both the Burgers vector of the defect (a real-space topological invariant) and the momentum-space topology of the bulk band structure. This convergence enables topological defects to serve as probes of band topology and as active platforms for localizing and manipulating quantum states. The objective of this part of the project is to synthesize topological and superconducting materials with controlled distribution of topological defects, including screw and edge dislocations, that can host topological defect-bound states and Majorana zero mode.

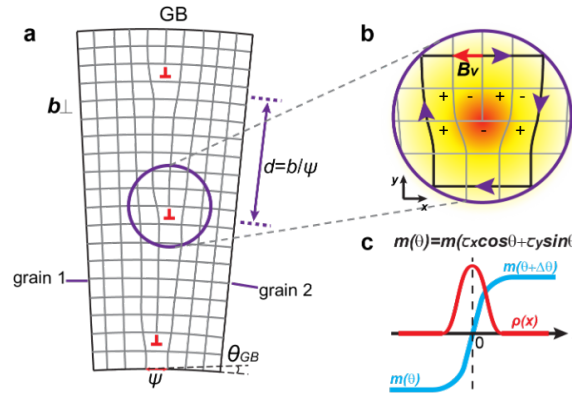


Figure 1. Dislocation bound states. a, Dislocation model of low-angle grain boundary. b, Topological states trapped at the core of an edge dislocation. c, Phase shift yields a sign-change in the Dirac mass $m(\theta)$ across the edge dislocation, and a local mode is represented in local density of states $\rho(x)$.

Recent Progress

We have synthesized tetragonal FeSe(001) films on the SrTiO₃(111) substrate via symmetry-mismatched van der Waals (vdW) epitaxy, which leads to a network of screw dislocations and grain boundaries composed of edge dislocation arrays. Using low-temperature scanning tunneling microscopy/spectroscopy, we have observed zero-dimensional states localized at both screw and edge dislocation cores. First-principles calculations further confirm that these bound states originate from the nontrivial bulk topology of the FeSe band structure.

1. Dislocation-bound states in FeSe/SrTiO₃(111)

As shown in Fig. 2(a), the tetragonal FeSe, in which Se-Fe-Se atomic layers form a unit cell along the [001] direction, exhibits intrinsically strong intralayer and weak interlayer vdW bonding. During MBE growth on the three-fold symmetric SrTiO₃(111) substrate (Fig. 2(a)), the epitaxial alignment of the four-fold tetragonal FeSe(001) on the substrate is fundamentally influenced by symmetry matching. High-symmetry directions of the FeSe lattice tend to align along a high-

symmetric direction of a substrate, so that the FeSe–SrTiO₃ system has the highest possible symmetry. This leads to three energetically equivalent orientations, each rotated relative to the substrate high symmetry axes (Fig. 2(a)). Consequently, a polycrystal will be formed by the coalescence of the misaligned 2D grains during growth, leading to two types of topological defects – spirals enabled by screw dislocations (Fig. 2(b)) and grain boundary (GB) composed of edge dislocations (Figs. 2(b-c)).

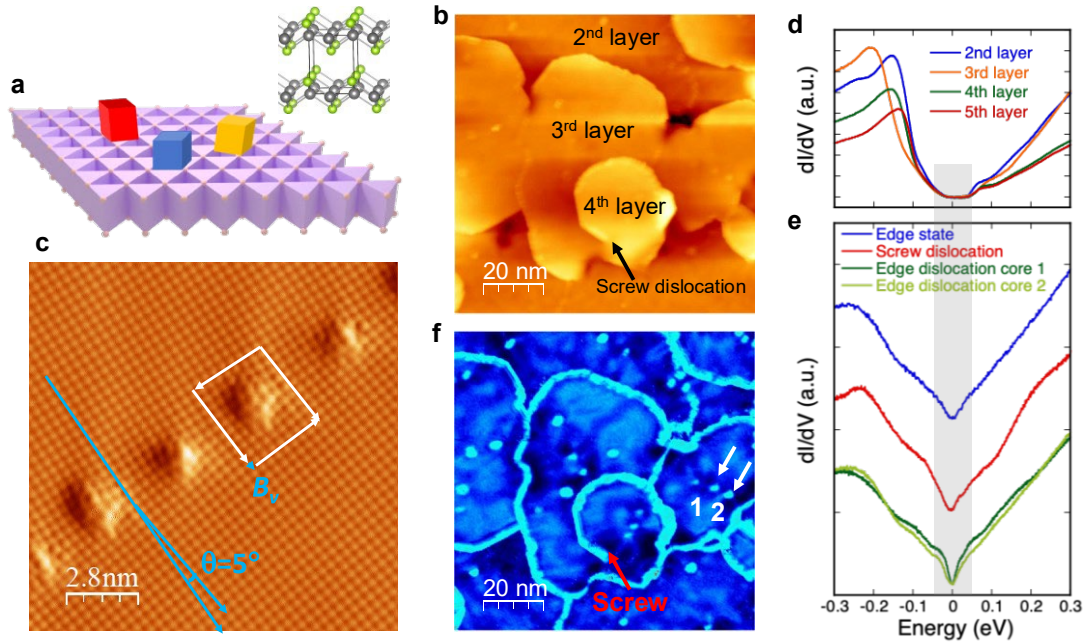


Figure 2. Symmetry mismatched vdW epitaxy and dislocation bound states in FeSe(001)/SrTiO₃(111). a, Three rotation grains of a vdW material with four-fold symmetry on three-fold symmetric substrate. b, STM image of the spiral growth of FeSe(001)/SrTiO₃(111). c, Atomic resolution STM image of a 5-degree grain boundary consisting of periodic edge dislocations. d, Layer-dependent dI/dV spectra. e, dI/dV spectra at screw and edge dislocation cores (e). f, dI/dV map at 50 meV, revealing higher LDOS at step edge and dislocation core.

The spiral growth produces terraces separated by single-layer steps. dI/dV measurements on the terraces consistently show a pronounced suppression in the differential conductance near the Fermi level, revealing an apparent energy gap of approximately $\Delta \approx 50$ meV (Fig. 2d), attributed to nematic ordering. This “gapped” behavior will serve as a baseline for comparison across structures. Near step edges, the dI/dV spectrum exhibits a distinct V-shaped (Fig. 2e), deviating sharply from the terrace spectra (Fig. 2d). Spatial mapping of the dI/dV (Fig. 2f) shows an enhanced local density of states (LDOS) near step edges, consistent with the presence of one-dimensional topological edge states we previously reported in FeSe multilayer films. Strikingly, similar V-shaped spectra and enhanced LDOS are observed at both edge and screw dislocation cores (Figs. 2(e-f)), implying a common origin for the defect-bound states. To further elucidate the nature of these localized states, we performed first-principles density functional theory calculations. The results confirm that the observed states stem from the nontrivial topology of the FeSe band structure. A manuscript is in preparation to report these findings.

2. Symmetry-breaking electronic orders in FeSn Kagome magnet

The Kagome lattice, a 2D network of corner-sharing triangles, provides an ideal platform to explore emergent quantum phenomena arising from geometric frustration, electron correlations, and spin-orbit coupling. In this work, we report the successful MBE growth of FeSn thin films on SrTiO₃(111) substrate, a model Kagome magnet composed of alternating Fe₃Sn Kagome layer and Sn₂ honeycomb layer. In situ STM reveals two distinct surface structures: a Sn-terminated honeycomb lattice and a Fe₃Sn-terminated Kagome lattice appearing as a close-packed triangular structure. dI/dV measurements reveal pronounced electronic nematicity, spontaneous breaking of the underlying rotational symmetry, indicative of strong correlation effects and electronic instabilities.

2.1 Strain induced giant periodic pseudo-magnetic field in epitaxial FeSn film on SrTiO₃(111)

The Sn-honeycomb layer, or stanene, has a quasi-2D electronic structure, similar to graphene. However, the stanene's Sn-Sn bond is weaker than the C-C bonding in graphene due to a larger bond length, thus facilitating a greater degree of its distortion or deformation. Under epitaxial strain, we discovered that the Sn honeycomb could be significantly distorted (Fig. 3), leading to periodic stripe modulations with a periodicity of 2.0 nm, ~ 3.8 a_{FeSn}. Such modulations also result in differential conductance peaks consistent with pseudo-Landau levels generated by pseudo-magnetic field of over 1000 T. These findings

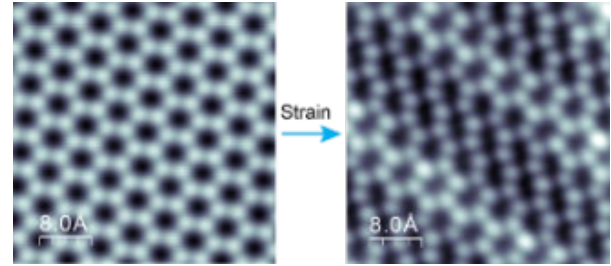


Figure 3. Epitaxial strain induced distortion of the Sn-honeycomb on the surface of FeSn/SrTiO₃(111). STM images of the undistorted (left) and edge dislocation at distorted (right) Sn-honeycombs.

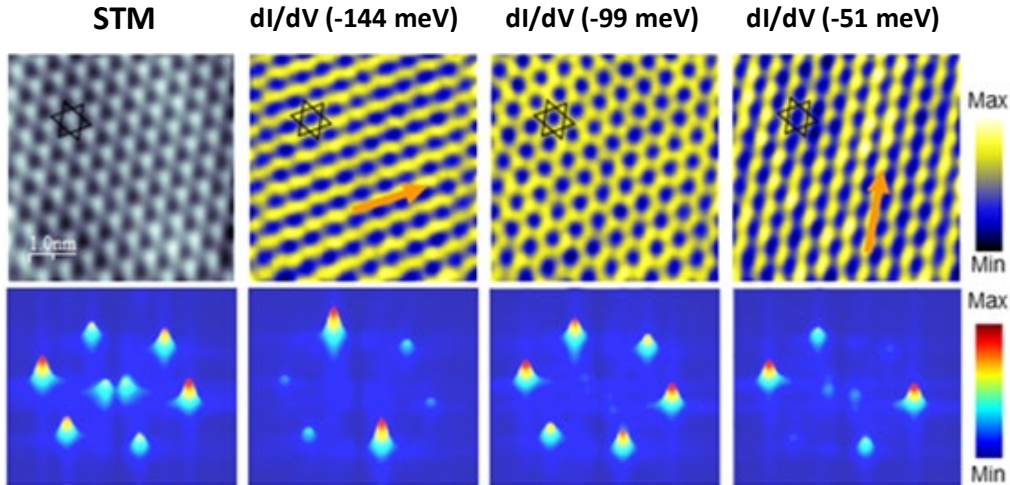


Figure 4. Stripes on the Kagome tunable by an applied in-plane magnetic field. Top panel: STM image and dI/dV maps at the energies indicated with an in-plane magnetic field $B = 2$ T. Bottom panel: FFT patterns from the image and dI/dV maps.

demonstrate the feasibility of strain engineering topological magnets at the nanoscale. The results have been published in *Nano Lett.* **23**, 2397 (2023).

2.2 Visualizing symmetry-breaking stripe order in epitaxial FeSn film

On the Fe₃Sn-termination, we further observed trimerization of the Kagome lattice, breaking its six-fold rotational symmetry while preserving the translational symmetry. This trimerized lattice also exhibits stripe modulations that are energy-dependent and tunable by an applied in-plane magnetic field, which are more pronounced in dI/dV maps. At -144 meV, the close-packed structure is modulated along one of the crystallographic directions, leading to substantially enhanced intensity at two of the peaks in the FFT pattern. Interestingly, a honeycomb structure appears at -99 meV, resulting in a symmetrical FFT pattern. Then, the structure reverts to be close packed at -51 meV, but with a stripe modulation rotated 60° from that at -144 meV. This stripe formation is again evident in the asymmetrical FFT patterns, indicating symmetry-breaking nematicity from the entangled magnetic and charge degrees of freedom in FeSn. The results have been published in *Nat. Commun.* **14**, 6167 (2023).

2.3 Anisotropic response of defect bound states to the magnetic field in epitaxial FeSn film

On both the Sn- and Kagome terminations, Sn-vacancy induces bound states that exhibit anomalous Zeeman shifts under a vertical field, where their energy increases linearly with field strength. With an in-plane field, the bound state energy shift further shows a two-fold oscillating behavior with the azimuth angle, demonstrating that charge ordering is strongly coupled to the magnetic field in Kagome magnet FeSn. The results have been published in *Nano Lett.* **25**, 4689 (2025).

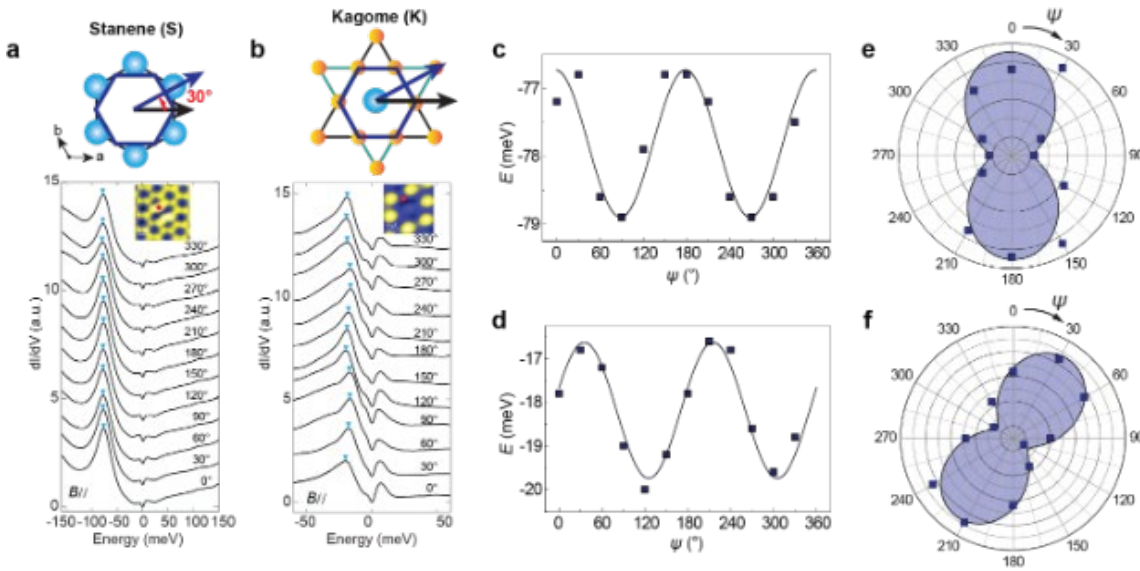


Figure 5. Two-fold oscillating behavior of the defect bound states in-plane magnetic field. a, dI/dV spectra under $B_{//}$ (1T). Inset: STM image of a Sn divacancy on the Sn layer. b, dI/dV spectra under $B_{//}$ (2 T). Inset: STM image of a Sn vacancy on the Kagome layer. c-d, The energy of the bound state shows oscillatory behavior as a function of ψ on both layers. e-f, Polar plots of the angle-dependent bound states on the Sn and Kagome layers.

Future Plans

By doping the FeSe multilayers to induce superconductivity, we will continue the systematic studies already underway to investigate the Majorana zero mode at topological defects. We will also probe the electronic properties of multi-twisted MoS₂ multilayers that we synthesized recently using chemical vapor deposition.

Publications supported by the DOE grant over the previous two years (2023 - 2025)

1. “Topological bound states at dislocations in epitaxial FeSe films”, Huimin Zhang, Basu Dev Oli, Zhengfei Wang, Michael Weinert, and Lian Li (to be published).
2. “Correlation Enhanced Electron-Phonon Coupling in FeSe/SrTiO₃ at a Magic Angle”, Qiang Zou, Antik Sihi, Basu Dev Oli, Mercè Roig, Daniel Agterberg, Michael Weinert, Lian Li, and Subhasish Mandal, Phys. Rev. Lett. (submitted) arXiv:2506.22435v1.
3. “Unraveling Enhanced Superconductivity in Single-layer FeSe through Substrate Surface Terminations”, Qiang Zou, Gi-Yeop Kim, Jong-Hoon Kang, Basu Dev Oli, Zhuozhi Ge, Michael Weinert, Subhasish Mandal, Chang-Beom Eom, Si-Young Choi, and Lian Li, Nano Lett. (under revision) arXiv:2502.16784.
4. “Anisotropic response of defect bound states to the magnetic field in epitaxial FeSn films”, Huimin Zhang, Zhengfei Wang, Michael Weinert, and Lian Li, Nano Lett. **25**, 4689 (2025).
5. “Highly Efficient Spin-Orbit Torque Switching using Bulk-Insulating Topological Insulator Bi₂Se₃”, Mehmet A. Noyan¹, Xiaohang Zhang, Jisoo Moon, Enrique Cobas, Mark Lohmann, Qiang Zou, Lian Li, Michael Weinert, Berend T. Jonker, Olaf M. J. van ‘t Erve, and Connie H. Li, Nano Lett. **25**, 6357 (2025).
6. “Discovery of room-temperature ferromagnetism in one-unit-cell FeSb/SrTiO₃(001) films with a Kagome lattice”, Huimin Zhang, Qinxin Liu, Liangzi Deng, Yanjun Ma, Samira Daneshmandi, Cheng Cen, Chenyu Zhang, Paul M. Voyles, Xue Jiang, Jijun Zhao, Ching-Wu Chu, and Lian Li, Nano Lett. **24**, 122 (2024).
7. “Visualizing symmetry-breaking electronic orders in epitaxial kagome magnet FeSn films”, H. Zhang, B. D. Oli, Q. Zou, X. Guo, Z. Wang, and L. Li, Nat. Commun. **14**, 6167 (2023).
8. “Giant periodic pseudo-magnetic fields in strained kagome magnet FeSn epitaxial films on SrTiO₃(111) substrate”, H. Zhang, M. Weinert, and L. Li, Nano Lett. **23**, 2397 (2023).
9. “Magnetic field-induced spin nematic phase up to room temperature in epitaxial antiferromagnetic FeTe thin films grown by molecular beam epitaxy”, Jisoo Moon, Qiang Zou, Huimin Zhang, Olaf M. J. van ‘t Erve, Nicholas G. Combs, Lian Li, and Connie H. Li, ACS Nano **17**, 16886 (2023).
10. “Deciphering alloy composition in superconducting single-layer FeSe_{1-x}S_x on SrTiO₃(001) substrates by machine learning of STM/S data”, Qiang Zou, Basu Dev Oli, Huimin Zhang, Joseph Benigno, Xin Li, and Lian Li, ACS Appl. Mater. Interfaces **15**, 22644 (2023).

Probing Unconventional Superconductivity with Advanced Tunneling Probes

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Keywords: Scanning tunneling microscopy, Josephson tunneling, multi-condensate superconductivity, odd-parity superconductivity, vortex

Research Scope

Topology and electron correlations in quantum materials have resulted in a plethora of exotic quantum phenomena. Of particular interest are unconventional superconductivity beyond the description of Bardeen–Cooper–Schrieffer theory, composite superconducting states resulting from interactions of primary orders, and competition among orders. We aim to explore exotic superconducting states by going beyond single-particle tunneling in conventional scanning tunneling microscopy (STM) because the ground state of a superconductor contains Cooper-pair condensates. Our strategy is to leverage multi-charge transport process in low-temperature atomic-scale microscopy including Josephson tunneling¹ and Andreev reflection², together with tunneling decay-rate imaging. So far, we have been exploring spectroscopic and real-space signatures of unconventional superconductivity and intertwined density waves in materials including UTe₂, FeSe, and Cs_xK_{1-x}V₃Sb₅ Kagome alloys. We have also been working on the development of new scanning probe microscopy (SPM) methods.

Recent Progress

In the past year, progress has been made towards visualizing signatures of sign-changing and odd-parity superconductivity using advanced SPM and developing new SPM methods enabling efficient measurements of tunneling decay rates. Three works are elaborated below.

1. Frustrated Josephson Coupling and Multi-condensate Visualization in FeSe (Publication 1)

In a Josephson junction involving multi-band superconductors, competition between inter-band and inter-junction Josephson coupling gives rise to frustration and spatial disjunction of superfluid densities among superconducting condensates³. Such frustrated coupling manifests as quantum interference of Josephson currents from different tunneling channels (Fig. 1a). In the simplest case, frustration happens between an s-wave superconductor interacting with a sign-changing $s^{\pm}$ -wave superconductor. Furthermore, depending on the relative inter-junction coupling strengths between the s-wave superconductor and the two bands, the junction may undergo a $0-\pi$ transition if the junction transparencies of each channel can be tuned. To our knowledge, direct observation of Josephson tunneling interference and visualizing multiple superconducting condensates at the atomic scale remains unachieved because such a technique does not exist. In this work, we explore these unconventional effects in the $s^{\pm}$ -wave superconductor FeSe. We use atomic-resolution

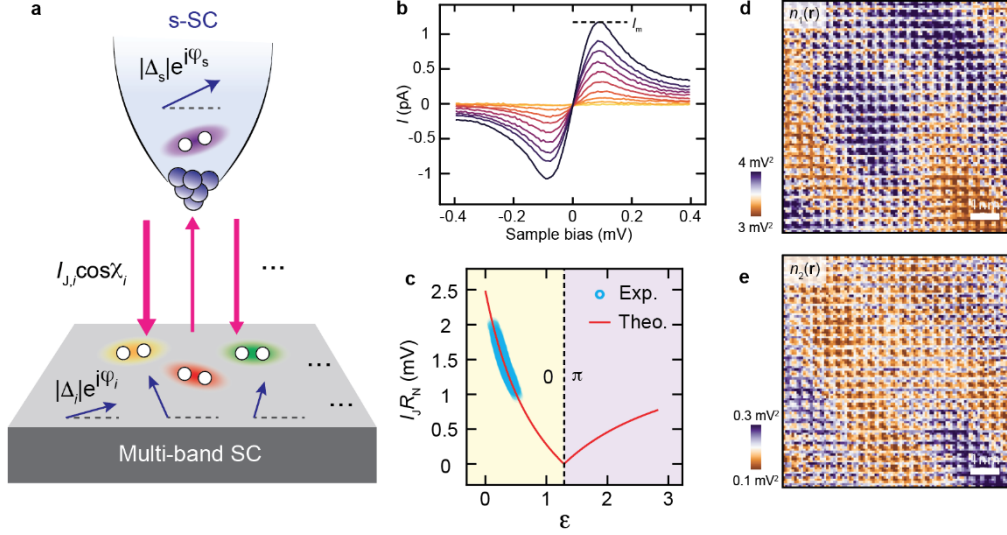


Figure 1. **a**, Schematic of Josephson tunneling interference between an *s*-wave superconductor (s-SC) and a multi-band superconductor due to the competition between inter-condensate and inter-junction phase differences. **b**, Josephson tunneling spectra between a Nb tip and FeSe at different R_N . **c**, The tendency of the junction towards a 0- π transition. **d,e**, Superfluid density of $n_1(\mathbf{r})$ and $n_2(\mathbf{r})$ of the two condensates. The cross-correlation between them is -0.72 .

scanned Josephson tunneling microscopy (SJTM) (Fig. 1b) for condensate-resolved imaging and junction tuning. We quantitatively demonstrate frustrated Josephson tunneling by examining two tunneling inequalities. The relative transparency of two parallel tunneling pathways is found tunable, revealing a tendency towards a 0- π transition (Fig. 1c). Simultaneous visualization of both superconducting condensates (Fig. 1d,e) reveals anti-correlated superfluid modulations, highlighting the role of inter-band scattering. Our study establishes SJTM as a powerful tool enabling new research frontiers of multi-condensate superconductivity.

2. Visualizing Unconventional Vortices and Vortex Core Bound States of UTe_2 (Publication 2)

Superconducting vortices can reveal electron pairing details and nucleate topologically protected states. Yet, vortices of bulk spin-triplet superconductors have never been visualized at the atomic scale. Recently, UTe_2 has emerged as a prime spin-triplet superconductor, but its superconducting order parameter is elusive, and whether time-reversal symmetry is broken remains unsettled⁴. In this work, we visualize vortices on the (011) surface of ultra-clean UTe_2 single crystals ($T_c = 2.1$ K) using milli-Kevn STM (Fig. 2a). We introduce $\frac{d^2I}{dV^2}$ imaging as an effective technique for vortex visualization in superconductors with substantial residual zero-energy density of states, as in UTe_2 . Anisotropic, crescent-shaped, single-flux-quantum vortices, with coherence lengths of ~ 12 nm (4 nm) parallel (perpendicular) to the **a**-axis, form a triangular vortex lattice (VL) under a small out-of-plane magnetic field (Fig. 2b). The invariance of vortex structures and VL under changes of field polarity and cooling history strongly supports time-reversal invariant superconductivity under zero field. At vortex cores (VCs), non-split, spectrally sharp zero-bias conductance peaks (ZBPs) persist up 8 T that are consistent with symmetry-protected Majorana

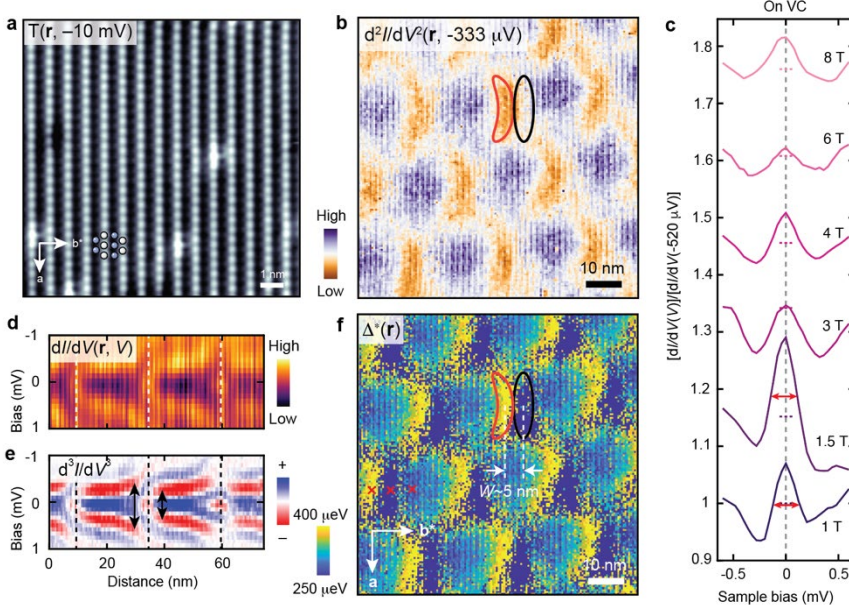


Figure 2. **a**, A typical topographic image of UTe_2 (011) surface. **b**, $d^2I/dV^2(\mathbf{r}, -333 \mu\text{V})$ image of the vortices under $B=4 \text{ T}$, showing a doublet structure of each vortex. **c**, Normalized differential conductance measured at the VCs showing prominent ZBPs up to 8 T. **d**, A series of $dI/dV(V)$ and **e**, d^3I/dV^3 spectra taken across three vortices showing enhanced gaps on the left side of VC.

zero modes in a topological vortex line (Fig. 2c). Close examination of vortex structures reveals a mirror-asymmetric doublet (Fig. 2d,e)—one with ZBPs and another with an enhanced superconducting gap (Fig. 2f), possibly originating from a field-induced multi-component order parameter. The interplay of anisotropic superconductivity, spin-triplet pairing, spin-orbit coupling, and $\mathbf{d}$ vector rotations under a magnetic field implies rich physics to be explored but also challenges for theoretical modeling. The exact forms of OPs and their vortex solutions under magnetic fields deserve future exploration.

3. Extracting Material Properties from STM Feedback Error Signals (Publication 3)

Imperfections in measurements, e.g., deviations and broadening, are not devoid of information; rather, they can reveal valuable physical properties and processes. STM leverages a negative feedback loop to regulate the tunneling current. Practically, current fluctuates around its setpoint and such deviations are considered insignificant and ignored in the past. In this work, we investigate the information embedded in these deviations and wonder if we can obtain tunneling process information and establish a new SPM modality by analyzing such ubiquitous error signals. Using Kagome alloys ($\text{Cs}_x\text{K}_{1-x}\text{V}_3\text{Sb}_5$) as a testbed where rich chemical and electronic heterogeneity exists down to the atomic scale, we observe an unexpected persistent DC current offset from its setpoint when the tunneling junction is periodically perturbed in the constant-current (C-C) mode with an active feedback loop (Fig. 3a). We demonstrate experimentally that such DC error signals encode the local tunneling barrier height ϕ_a or the square of the tunneling decay rate (d^2I/dz^2) under active tip-sample distance perturbation (Fig. 3b,c), and the square of local differential conductance $\left(\frac{dI}{dV}\right)^2$ under active bias voltage perturbation (Fig. 3d,e). The former is especially relevant for visualizing multi-quasiparticle tunneling process such as Andreev reflections¹ and Josephson tunneling², where the effective barrier height is scaled to $n^2\phi_a$ (here, $n=2$ for Josephson tunneling of Cooper pairs and Andreev reflection; $n>2$ for Josephson tunneling

of Cooper quartets and multiple Andreev reflections). Using phenomenological models, we reveal that such relationships result from the interplay of rectification and active feedback compensation in the C-C mode. Because no lock-in amplifiers are used, the experimental setup is simple and

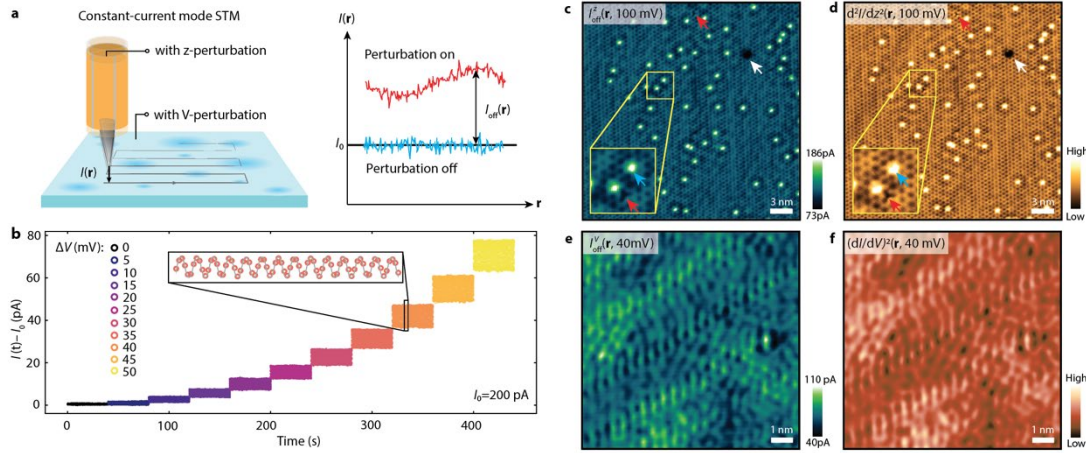


Figure 3. **a**, Schematics of the C-C mode STM under z - or V -perturbations and the resulting finite DC current error even with a closed feedback loop. **b**, The actual tunneling current error signal with active feedback as a function time under voltage perturbation. **c**, Simultaneously acquired $I^z_{\text{off}}(\mathbf{r})$ and **d**, $d^2I/dz^2(\mathbf{r})$ images. **e**, Simultaneously acquired $I^V_{\text{off}}(\mathbf{r})$ and **f**, $(dI/dV)^2(\mathbf{r})$ images on $\text{Cs}_{0.6}\text{K}_{0.4}\text{V}_3\text{Sb}_5$.

minimal, and the imaging can be performed rapidly and simultaneously with normal topographic imaging – the basic functionality of any STM. We further demonstrate evidence that the phenomenology can be generalized to other negative feedback systems. This new approach has the potential to broadly impact physical sciences by allowing rapid measurements without lock-in amplifiers. Especially, it will facilitate decay rate spectroscopy when multiple Andreev reflections take place for studying unconventional superconductivity.

Future Plans

In the near future, we will continue the characterization of odd-parity superconductivity in UTe_2 via vortex imaging, but now under different temperature and magnetic field directions. We also plan to search for new density waves and their spin signatures in UTe_2 and understand their coupling to superconductivity. We will further work on the characterization of density waves, nematicity, and chirality of a series of Kagome alloys, as well as the superconductivity therein.

References

1. Randeria, M. T., Feldman, B. E., Drozdov, I. K. & Yazdani, A. *Scanning Josephson spectroscopy on the atomic scale*. Phys. Rev. B **93**, 161115 (2016).
2. Ko, W., Lado, J. L. & Maksymovych, P. *Noncontact Andreev Reflection as a Direct Probe of Superconductivity on the Atomic Scale*. Nano Lett. **22**, 4042–4048 (2022).
3. Ota, Y., Machida, M., Koyama, T. & Matsumoto, H. *Theory of heterotic superconductor-insulator-superconductor Josephson junctions between single- and multiple-gap superconductors*. Phys. Rev. Lett. **102**, 237003 (2009).
4. Azari, N., M. Yakovlev, N. Rye, S. R. Dunsiger, S. Sundar, M. M. Bordelon, S. M. Thomas, J. D. Thompson, P. F. S. Rosa, & J. E. Sonier. *Absence of spontaneous magnetic fields due to time-reversal symmetry breaking in bulk superconducting UTe_2* . Phys. Rev. Lett. **131**, 226504 (2023).

Publications

1. N. Sharma, M. Toole, J. McKenzie, S. Ran, and X. Liu, *Atomic-scale frustrated Josephson coupling and multicondensate visualization in FeSe*. Nat. Mater. (2025), DOI: 10.1038/s41563-025-02290-y
2. N. Sharma, M. Toole, J. McKenzie, F. Cheng, S.M. Thomas, P.F.S. Rosa, Y.-T. Hsu, and X. Liu, *Observation of Persistent Zero Modes and Superconducting Vortex Doublets in UTe_2* . arXiv:2503.17450
3. N. Sharma, J. McKenzie, M. Toole, B. R. Ortiz, A. Capa Salinas, S. D. Wilson, and X. Liu, *Deriving Material Properties from Feedback Error Signals in Scanning Tunneling Microscopy*, Nano Letters **25**, 3309–3315 (2025)
4. Q. Gu, S. Wang, J. P. Carroll, K. Zhussupbekov, C. Broyles, S. Ran, N. P. Butch, S. Saha, J. Paglione, X. Liu, J.C. Séamus Davis, and D.-H. Lee, *Pair Wavefunction Symmetry in UTe_2 from Zero-Energy Surface State Visualization*, Science **388**, 938-944 (2025)

Inelastic Scattering of Structured Matter Waves for Quantum Materials Characterization

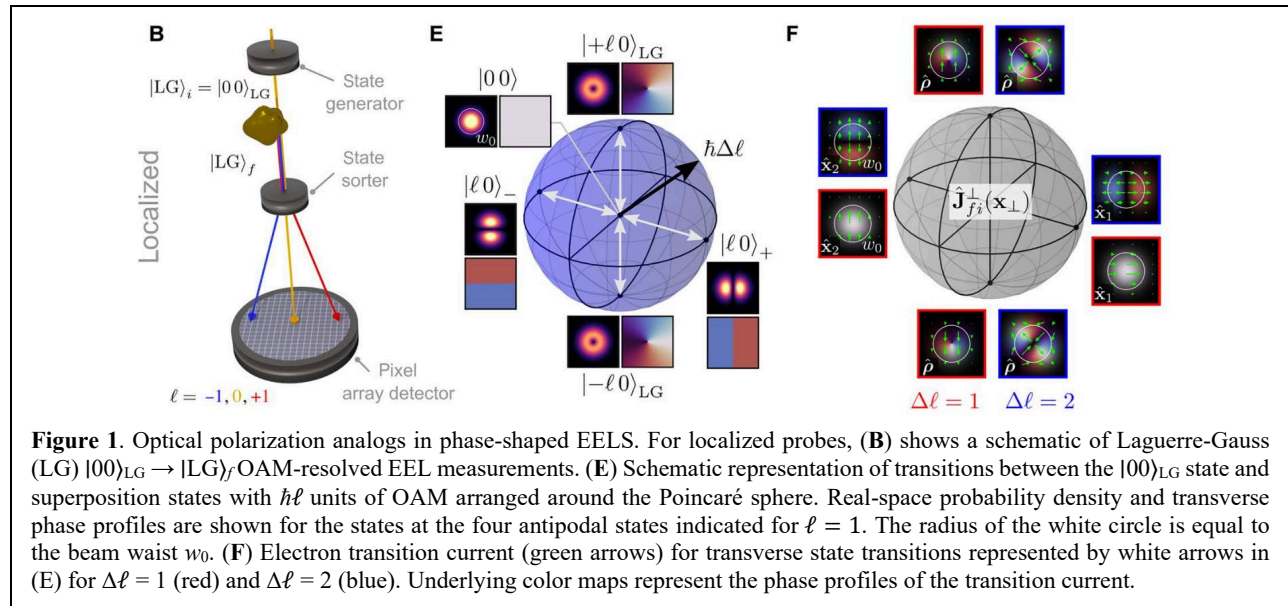
David J. Masiello
University of Washington

Keywords: structured electron beams, momentum- and pseudoangular momentum-resolved STEM EELS, high resolution EELS (HREELS), chiral phonons, surface lattice resonances

Research Scope

Alongside the recent proliferation of quantum materials comes the companion need to develop new measurement techniques for their characterization at their natural response scales in energy, length, momentum, and pseudoangular momentum (PAM). Advances in monochromation and aberration-correction technologies in scanning transmission electron microscopes (STEMs) now enable the investigation of low-energy excitations through inelastic free electron scattering approaching 1 meV, $0.01 \text{ \AA}^{-1}$, and 1 nm energy, momentum, and spatial resolutions, via electron energy-loss spectroscopy (EELS). The broad objective of this DOE ESPM funded research is the theoretical design of new classes of delocalized and localized electron probes endowed with precise symmetries to characterize the spatial-, energy-, momentum-, PAM-, and polarization-dependence of collective excitations in 2D and 3D periodic quantum materials and photonic crystals exhibiting chiral and topological character.

New collaborations with Sokrates Pantelides (Vanderbilt), Jordan Hachtel, (ORNL), Eric Hoglund (ORNL), Joshua Caldwell (Vanderbilt), Maureen Lagos (McMaster), Haihua Liu (Argonne), Jennifer Dionne (Stanford), Randall Goldsmith (Wisconsin), Ben McMorran (Oregon), and Dayne Swearer (Northwestern) have resulted in the course of this research.



Recent Progress

1. Optical polarization analogs in inelastic free-electron scattering

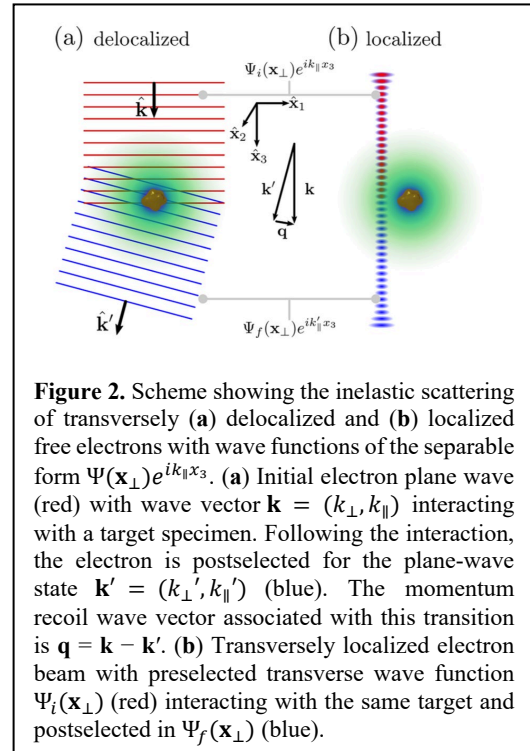
Marc R. Bourgeois, Austin G. Nixon, Matthieu Chalifour, David J. Masiello
Science Advances **9**, eadh2410 (2023)

Advances in the ability to manipulate free-electron phase profiles within the electron microscope have spurred development of quantum-mechanical descriptions of electron energy loss (EEL) processes involving transitions between phase-shaped transverse states. In this paper, we elucidated an underlying connection between two ostensibly distinct optical polarization analogs identified in EEL experiments using either focused or widefield geometries as manifestations of the same conserved scattering flux (**Fig. 1**). Our work introduced a procedure for probing general tensorial target characteristics including global mode symmetries and local polarization of both finite and periodically structured solid-state materials.

2. Inelastic scattering of transversely structured free electrons from nanophotonic targets: Theory and computation

Austin G. Nixon, Matthieu Chalifour, Marc R. Bourgeois, Michael Sanchez, and David J. Masiello
Physical Review A **109**, 043502 (2024), Editor's Suggestion

Recent advancements in abilities to create and manipulate the electron's transverse wave function within the TEM and STEM have enabled vectorially resolved electron- energy-loss (EEL) and - gain (EEG) measurements of nanoscale and quantum material responses using pre- and post-selected free-electron states. This newfound capability is prompting renewed theoretical interest in quantum-mechanical treatments of inelastic-electron-scattering observables and the information they contain. In this paper we presented a quantum-mechanical treatment of the inelastic scattering of free electrons between pre- and post-selected transverse states with fully retarded electron-sample interactions (**Fig. 2**) for both spontaneous EEL and continuous-wave laser-stimulated EEG measurements. General expressions for the state-resolved energy-loss and gain rates were recast in forms amenable to numerical calculation using the method of coupled dipoles. We numerically implemented our theory within the electron-driven discrete dipole approximation code (<https://github.com/MasielloGroup/e-dda>) and used it to investigate specific examples that highlight its versatility regarding the number, size, geometry, and material composition of the target specimen as well as its ability to describe matter-wave diffraction from finite nanoscopic targets.



3. Spectroscopy in Nanoscopic Cavities – Models and Recent Experiments

Marc R. Bourgeois, Feng Pan, Austin G. Nixon, C. Praise Anyanwu, Jennifer A. Dionne, Randall H. Goldsmith, and David J. Masiello

Annual Review of Physical Chemistry **75**, 509–534 (2024)

The ability of nanophotonic cavities to confine and store light to nanoscale dimensions has important implications for enhancing molecular, excitonic, phononic, and plasmonic optical responses. Spectroscopic signatures of processes that are ordinarily exceedingly weak such as pure absorption and Raman scattering have been brought to the single-particle limit of detection, while new emergent polaritonic states of optical matter have been realized through coupling material and photonic cavity degrees of freedom across a wide range of experimentally accessible interaction strengths. In this review article, we discussed both optical and electron beam spectroscopies of cavity-coupled material systems in weak, strong, and ultrastrong coupling regimes, thus providing a theoretical basis for understanding the physics inherent to each while highlighting recent experimental advances and exciting future directions.

4. Probing the Polarization of Low-Energy Excitations in 2D Materials from Atomic Crystals to Nanophotonic Arrays using Momentum-Resolved Electron Energy Loss Spectroscopy

Andrew W. Rossi, Marc R. Bourgeois, Caleb Walton, and David J. Masiello

Nano Letters **24**, 7748–7756 (2024)

Spectroscopies utilizing free electron beams as probes offer detailed information on the reciprocal-space excitations of 2D materials such as graphene and transition metal dichalcogenide monolayers. Yet, despite the attention paid to such quantum materials, less consideration has been given to the electron-beam characterization of 2D periodic nanostructures such as photonic crystals, metasurfaces, and plasmon arrays, which can exhibit the same lattice and excitation symmetries as their atomic analogues albeit at drastically different length, momentum, and energy scales. Because of their lack of covalent bonding and influence of retarded electromagnetic interactions, important physical distinctions arise that complicate interpretation of scattering signals. In this letter we presented a fully-retarded theoretical framework for describing the inelastic scattering of wide-field electron beams from 2D materials and applied it to investigate the complementarity in sample excitation information gained in the measurement of a honeycomb plasmon array in comparison to single monolayer graphene.

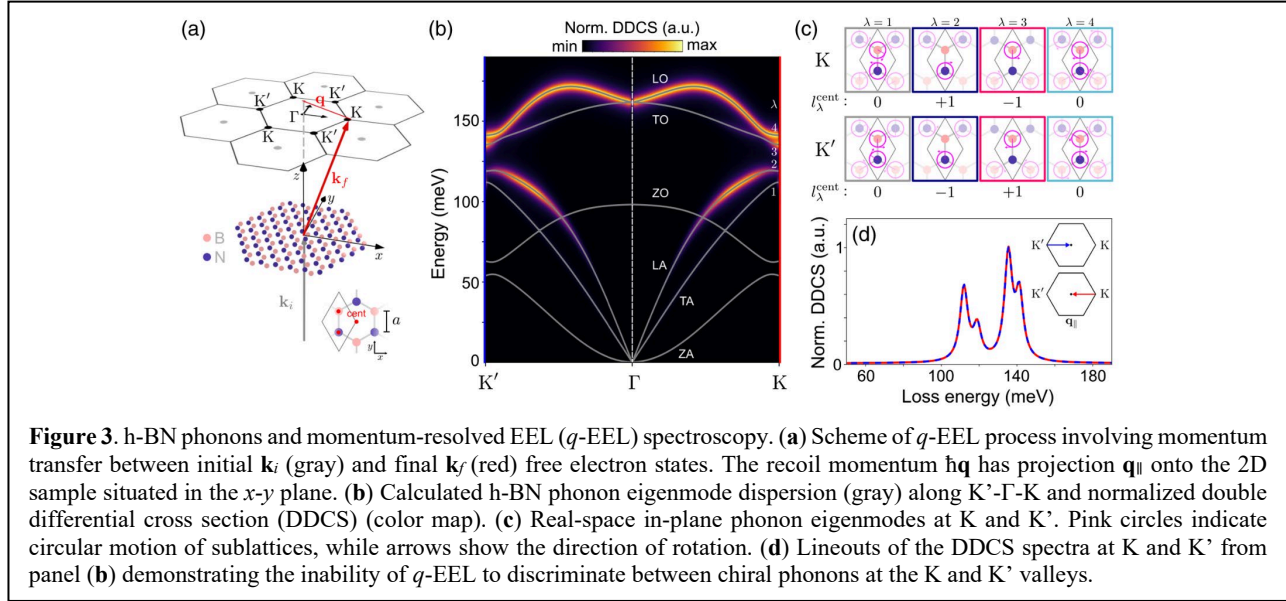
5. Strategy for Direct Detection of Chiral Phonons with Phase-Structured Free Electrons

Marc R. Bourgeois, Andrew W. Rossi, and David J. Masiello

Physical Review Letters **134**, 026902 (2025)

Chiral phonons possessing valley pseudoangular momentum (PAM) underlie a diversity of quantum phenomena of fundamental and applied importance, but are challenging to probe directly. In this letter we showed that deficiencies of typical momentum-resolved electron energy loss measurements that make it impossible to distinguish the PAM of chiral phonons can be overcome by introducing pinwheel free electron states with well-defined PAM (**Fig. 3**). Transitions between

such states generate 2D periodic arrays of in-plane field vortices with polarization textures tailored to selectively couple to desired chiral mode symmetries.



6. High-temperature phonons in h-BN: Momentum-resolved vibrational spectroscopy and theory

in collaboration with Sokrates T. Pantelides (Vanderbilt), Nion R&D (Kirkland, WA), et al.
in preparation (2025)

We recently developed a collaboration with Sokrates T. Pantelides, who has been investigating momentum-resolved vibrational spectroscopy in hexagonal boron nitride at temperatures of 300, 800, and 1300 K. By combining Pantelides' quantum mechanical density-functional-theory (DFT) calculations of temperature-dependent phonon self-energies with our treatment of the inelastic electron scattering cross section using the Born approximation we have elucidated the spectral signatures of temperature-dependent phonon energy shifts across multiple Brillouin zones (BZs). Specifically, we have applied this combined approach to temperature-dependent momentum-resolved vEELS of h-BN using data by the O. Krivanek team at Nion R&D. In addition to the inclusion of Umklapp processes within the theory both in the microscopic DFT and at the level of the electron kinematics, integration of the calculated inelastic scattering signal over the finite slit detection area $\Delta k_x \Delta k_y$ was found to be critical in interpreting the temperature-dependent measurements which are of finite resolution in momentum.

Future Plans

Future directions of this research will involve the theoretical development of phase and amplitude structured free electron probes for reciprocal-space excitation mapping using momentum- and PAM-resolved inelastic electron scattering measurements in high-resolution EELS (HREELS) and defect mapping with simultaneously high space-, momentum-, and PAM-resolution in 4D STEM EELS for studying the topology of 2D and 3D periodic quantum materials. Collaboration with experiment to implement these theoretical advances will be critical to our efforts.

References

1. M. R. Bourgeois, A. G. Nixon, M. Chalifour, D. J. Masiello, *Optical polarization analogs in inelastic free-electron scattering*, Science Advances **9**, eadh2410 (2023)
2. A. G. Nixon, M. Chalifour, M. R. Bourgeois, M. Sanchez, and D. J. Masiello, *Inelastic scattering of transversely structured free electrons from nanophotonic targets: Theory and computation*, Physical Review A **109**, 043502 (2024)
3. M. R. Bourgeois, F. Pan, A. G. Nixon, C. P. Anyanwu, J. A. Dionne, R. H. Goldsmith, and D. J. Masiello, *Spectroscopy in Nanoscopic Cavities – Models and Recent Experiments*, Annual Review of Physical Chemistry **75**, 509–534 (2024)
4. A. W. Rossi, M. R. Bourgeois, C. Walton, and D. J. Masiello, *Probing the Polarization of Low-Energy Excitations in 2D Materials from Atomic Crystals to Nanophotonic Arrays using Momentum-Resolved Electron Energy Loss Spectroscopy*, Nano Letters **24**, 7748-7756 (2024)
5. M. R. Bourgeois, A. W. Rossi, and D. J. Masiello, *Strategy for Direct Detection of Chiral Phonons with Phase-Structured Free Electrons*, Physical Review Letters **134**, 026902 (2025)

Publications

1. M. R. Bourgeois, A. G. Nixon, M. Chalifour, D. J. Masiello, *Optical polarization analogs in inelastic free-electron scattering*, Science Advances **9**, eadh2410 (2023)
2. A. G. Nixon, M. Chalifour, M. R. Bourgeois, M. Sanchez, and D. J. Masiello, *Inelastic scattering of transversely structured free electrons from nanophotonic targets: Theory and computation*, Physical Review A **109**, 043502 (2024)
3. M. R. Bourgeois, F. Pan, A. G. Nixon, C. P. Anyanwu, J. A. Dionne, R. H. Goldsmith, and D. J. Masiello, *Spectroscopy in Nanoscopic Cavities – Models and Recent Experiments*, Annual Review of Physical Chemistry **75**, 509–534 (2024)
4. A. W. Rossi, M. R. Bourgeois, C. Walton, and D. J. Masiello, *Probing the Polarization of Low-Energy Excitations in 2D Materials from Atomic Crystals to Nanophotonic Arrays using Momentum-Resolved Electron Energy Loss Spectroscopy*, Nano Letters **24**, 7748-7756 (2024)
5. M. R. Bourgeois, A. W. Rossi, and D. J. Masiello, *Strategy for Direct Detection of Chiral Phonons with Phase-Structured Free Electrons*, Physical Review Letters **134**, 026902 (2025)
6. K. Y. Lee, E. K. Beutler, T. Quispe-Crisolo, D. J. Masiello, and M. J. Lagos, *Substrate matters: Coupled phonon modes of a spherical particle on a substrate probed with EELS*, under review (2025)
7. M. Hershey, H. Liu, X. Guo, A. W. Rossi, M. R. Bourgeois, B. D. Clark, T. E. Gage, I. Arslan, D. J. Masiello, D. F. Swearer, *Probing plasmonic near-fields in oxide-modified aluminum nanocubes using photon-induced near-field electron microscopy*, under review (2025)
8. C. Whittier, T. Casagrande, M. Chalifour, K. Kelley, M. J. Tolchin, M. He, J. R. Nolen, J.-P. Maria, J. D. Caldwell, D. J. Masiello, N. D. Bassim, and M. J. Lagos, *Spatial Distribution and Sensitivity of Localized Plasmon Modes in Individual Infrared SPP/ENZ Resonators Probed via EELS*, under review (2025)
9. M. R. Bourgeois, A. W. Rossi, and D. J. Masiello, *Inelastic Scattering of Structured Matter Waves for Atomic- and Nano-Scale Materials Characterization*, ACS Nano invited Perspective in preparation (2025)

Ptychographic Atomic Electron Tomography: Mapping Heavy and Light Atoms in 3D

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Keywords: Ptychographic atomic electron tomography, nanocatalysts, high-entropy alloys, phase-change materials, and quantum emitters

Research Scope

The development of atomic electron tomography (AET) has revolutionized three-dimensional (3D) atomic-scale characterization, providing unprecedented insights into material properties at the fundamental level. Traditional AET primarily relies on annular dark-field (ADF) scanning transmission electron microscopy (STEM) tilt-series, combined with advanced tomographic reconstruction algorithms, to determine 3D atomic coordinates. We have recently made significant advancements in both methodology development and its application to critical materials science challenges, primarily supported by my DOE BES MSE grant. Specifically, we apply AET to

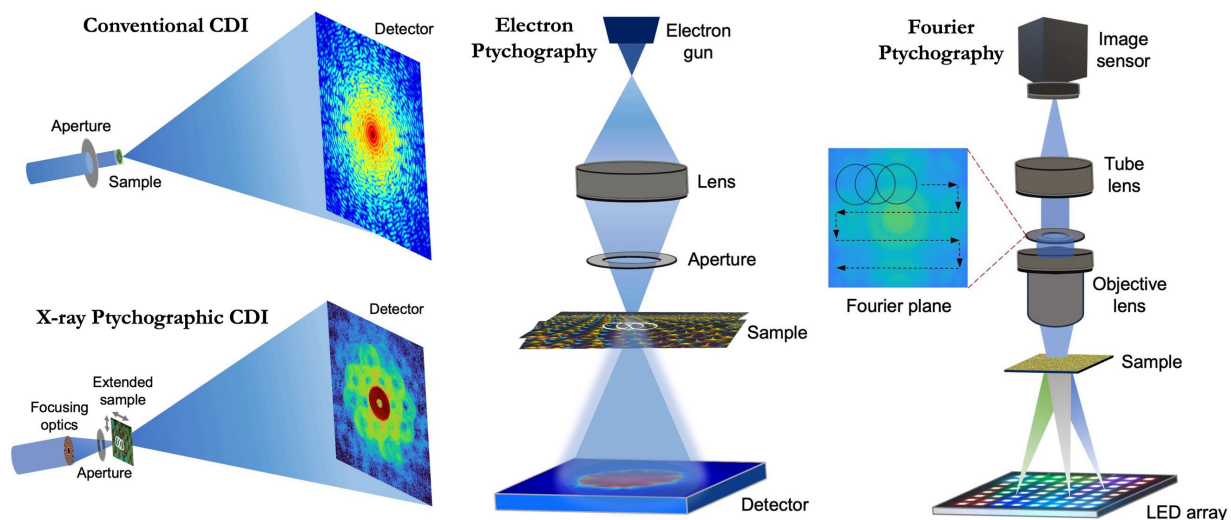


Figure 1. Schematics of representative CDI and modern ptychography methods. [J. Miao, *Nature* **637**, 281-295 (2025)]

determine the 3D atomic positions of medium- and high-entropy alloy nanoparticles, enabling a quantitative characterization of local lattice distortion, strain tensor, twin boundaries, dislocation cores, and chemical short-range order (CSRO). Notably, we observe CSRO-mediated twinning in these nanoparticles, representing the first experimental correlation between local chemical order and structural defects in any material. Additionally, we use AET to determine the 3D local atomic structure, surface morphology, and chemical composition of Pt alloy nanocatalysts for the electrochemical oxygen reduction reaction. The experimental 3D atomic structures are fed directly into first-principles-trained machine learning to identify the nanocatalysts' active sites. These predictions are subsequently validated by electrochemical measurements. Finally, we integrate ptychography with AET, named pAET, to precisely determine the 3D atomic coordinates of

individual carbon atoms in twisted bilayer graphene. This allows for a quantitative characterization of the 3D displacement vector field and interlayer modulation driven by van der Waals interactions. In 2025, Miao published a landmark *Nature* review that showcased the rapid advances in computational microscopy, covering coherent diffractive imaging and ptychography, and highlighted their transformative impact across diverse scientific disciplines (Fig. 1).

Building on our significant advances in AET and ptychography, we will investigate atomic-scale transition pathways in phase-change materials (GeTe, GeSb, GeBiTe) using in situ ptychographic experiments coupled with AET reconstructions. High-fidelity 3D atomic models will be analyzed to extract key structural parameters, enabling the identification of efficient phase-transition pathways and informing the design of energy-efficient phase-change memory materials. In parallel, we will advance pAET to map the 3D arrangement of Zn and O atoms, dopants, and vacancies in ZnO nanowires and nanoparticles, with the capability to detect substitutional dopants, vacancies, and donor-vacancy complexes. These materials will be synthesized via chemical vapor deposition and solution-based methods, then characterized for their optical and spin properties. High-resolution ptychographic tilt series will be acquired and reconstructed into detailed 3D atomic models. Automated atomic tracing and refinement will determine atomic identities, quantify local strain, and characterize bonding topology. By correlating the reconstructed defect structures with photoluminescence and spin measurements, we will elucidate the atomic origins of defect-related properties in ZnO and establish design principles for scalable, device-ready quantum emitters.

Recent Progress

3D imaging of individual carbon atoms

Carbon plays a foundational role in science and technology due to its diverse bonding configurations, structural versatility, and essential influence on the mechanical, chemical, electronic, and quantum properties of materials. However, directly imaging the three-dimensional (3D) coordinates of individual carbon atoms has remained a longstanding challenge. Using twisted bilayer graphene as a model system, we demonstrate pAET for determining the 3D atomic coordinates of individual carbon atoms with a precision of 0.11 Å. This precision enables detailed mapping of interlayer spacing variations modulated by local stacking configurations. Quantitative analysis of the 3D displacement vector field reveals the experimental observation of chiral lattice distortions driven by van der Waals interactions, including meron-like, anti-meron-

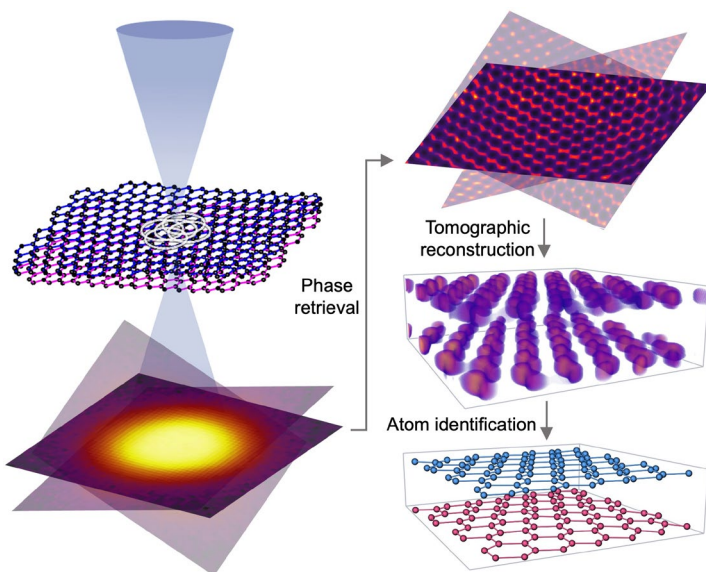


Figure 2. Schematic of the pAET workflow. A focused electron probe scans the sample, generating diffraction patterns that are processed to reconstruct phase images, which are then used for tomographic reconstruction, atom tracing, and position refinement.

like, and anti-skyrmion-like configurations. Furthermore, incorporating the experimentally determined 3D atomic coordinates into density functional theory (DFT) calculations uncovers an asymmetric electronic band structure with a 22 meV bandgap, in contrast to the gapless Dirac cone predicted by relaxed models. These findings provide direct insight into the coupling between 3D lattice deformation and electronic behavior in moiré-engineered carbon systems.

Atomic-scale identification of the active sites of nanocatalysts. Heterogeneous catalysts play a key role in the chemical and energy industries. To date, most industrial-scale heterogeneous catalytic reactions have relied on nanocatalysts. However, despite significant progress from theoretical, experimental and computational studies, identifying the active sites of alloy nanocatalysts remains a major challenge. This limitation is mainly due to an incomplete understanding of the 3D atomic and chemical arrangement of different constituents and structural reconstructions driven by catalytic reactions. Here, we use AET to determine the 3D local atomic structure, surface morphology and chemical composition of 11 Pt alloy nanocatalysts for the electrochemical oxygen reduction reaction (ORR). We reveal the facet, surface concaveness, structural and chemical order/disorder, coordination number, and bond length with unprecedented 3D detail. The experimental 3D atomic coordinates are used by first-principles trained machine learning to identify the active sites of the nanocatalysts, which are corroborated by electrochemical measurements. A striking feature is the difference of the ORR activity of the surface Pt sites on the nanocatalysts by several orders of magnitude. Furthermore, by analyzing the structure-activity relationship, we formulate an equation named the local environment descriptor to balance the strain and ligand effects and gain quantitative insights into the ORR active sites of the Pt alloy nanocatalysts. The ability to determine the 3D atomic structure and chemical composition of realistic nanoparticles coupled with machine learning could transform our fundamental understanding of the catalytic active sites and provide a guidance for the rational design of optimal nanocatalysts.

3D atomic positions and local chemical order in medium/high-entropy alloys. Medium- and high-entropy alloys (M/HEAs) mix several principal elements in near-equiatomic ratios, yielding exceptional properties but posing a central challenge: measuring 3D lattice distortion and local CSRO at the atomic level. We use AET to determine the 3D atomic positions and elemental identities in NiPdPt-based M/HEA nanoparticle catalysts, achieving 19.5 pm precision. Nanoparticles synthesized by carbothermal shock are imaged by ADF-STEM tilt series; reconstructions produce experimental 3D atomic models with single-phase fcc structure. In MEAs we resolve Ni, Pd, and Pt individually; in HEAs eight elements are grouped into three Z-contrast types. Comparing each atom and its nearest neighbors to an ideal fcc lattice, we map local lattice distortion: mean atomic displacements of $0.23 \pm 0.11 \text{ \AA}$, $0.26 \pm 0.12 \text{ \AA}$, $0.29 \pm 0.12 \text{ \AA}$, and $0.37 \pm 0.12 \text{ \AA}$ across representative particles. HEAs show larger, more heterogeneous distortion than MEAs, with local strain tensors spanning -8% to $+8\%$ in compression, tension, and shear. We identify twins, Shockley partials, and screw dislocations; HEAs display more diffuse twin boundaries and a higher dislocation propensity. CSRO analysis based on nearest-neighbor statistics reveals that in twin-free MEAs Ni and Pt tend to intermingle while Pd and Pt prefer to separate. In double-twinned MEAs these tendencies reverse and form elongated CSRO domains, indicating that CSRO mediates twin formation. We thus provide the first direct experimental link between local chemical order and structural defects in any alloy. These insights establish quantitative design handles, namely lattice distortion and CSRO, for optimizing mechanical and catalytic performance in M/HEAs.

Future Plans

Determining 3D atomic structure dynamics in phase-change materials. A central, long-standing question in the study of phase-change materials (PCMs) is how atoms rearrange in three dimensions during the reversible switching between amorphous and crystalline phases, a process that underpins their fast, stable performance in non-volatile memory. Previous diffraction-based investigations have yielded conflicting interpretations, ranging from minimal bond rupture between phases, to the presence of a metastable intermediate structure, to distortion-driven loss of long-range order. Because diffraction inherently produces 1D, ensemble-averaged information, it cannot directly resolve the local atomic rearrangements that occur during the transition. This limitation motivates the need for direct, high-precision, 3D atomic-scale observation.

We will address this challenge by applying pAET to measure temperature-dependent 3D atomic positions and chemical identities in representative PCM thin films, specifically GeTe, GeSb, and GeBiTe. These films, synthesized via atomic layer deposition, will incorporate 5 nm Au fiducial markers to enable robust tilt-series alignment. We will acquire 4D ptychographic tilt series over a $\pm 70^\circ$ range in 2.5° increments, first at 300 K and then at 350-550 K, spanning the ~ 450 K transition temperature. Multislice ptychography will be used to reconstruct high-fidelity phase images at each tilt, which will then be input into our in-house tomography algorithm for picometer-precision 3D reconstructions. From these reconstructions, we will extract quantitative measures of short- and medium-range order, bonding network topology, ring statistics, and defect populations. By comparing results across multiple annealing temperatures, we will map the atomic-level structural evolution and identify the specific rearrangements, bonding changes, and defect dynamics that drive the amorphous-to-crystalline transformation. This approach will yield the first direct experimental, 3D atomic-scale view of the phase transition in PCMs, providing a decisive test of competing theoretical models and revealing structure–property relationships critical for the design of faster, more energy-efficient memory and neuromorphic computing devices.

Deciphering the 3D structure of defect centers in ZnO. ZnO is a direct-band-gap II–VI semiconductor that exhibits bright near-band-edge emission from shallow donors such as Ga and In. These dopants can form defect centers with promising optical and spin properties, yet the 3D atomic structures of the underlying defects and impurity complexes remain unknown, limiting deterministic fabrication of quantum emitters. We will apply pAET to directly determine the 3D positions of individual Zn and O atoms in ZnO nanowires and nanoparticles, and to identify substitutional donors, vacancies, and donor-vacancy complexes. Samples will be synthesized by metal-organic chemical vapor deposition and solution methods, and pre-characterized for photoluminescence and spin properties. For each specimen, we will acquire ptychographic tilt series over $\pm 70^\circ$ in 2.5° increments. Multislice ptychography will recover high-fidelity phase images at each tilt, which will be reconstructed into 3D atomic models. Automated atomic tracing and refinement will assign atomic coordinates and chemical identities, enabling unambiguous

identification of Zn and O atoms, dopants, and vacancies, as well as precise quantification of local strain fields and bonding topology. Finally, we will correlate the reconstructed 3D defect structures with photoluminescence and spin measurements to establish direct structure–property relationships. This integrated approach will provide fundamental insights into the atomic origins of ZnO defect center properties and deliver design principles for scalable, device-ready quantum emitters.

Publications supported by the DOE BES MSE grant over the last two years

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1. N. Y. Kim, H. Zhong, J. Zhang, C. M. O’Leary, Y. Liao, J. Zou, H. Sha, M. Pham, W. Li, Y. Yuan, J.-H. Park, D. Kim, H. Jiang, J. Kong, M. Chi and J. Miao, “Three-dimensional imaging of individual carbon atoms”, submitted.
2. Y. Yang, J. Zhou, Z. Zhao, G. Sun, S. Moniri, C. Ophus, Y. Yang, Z. Wei, Y. Yuan, C. Zhu, Y. Liu, Q. Sun, Q. Jia, H. Heinz, J. Ciston, P. Ercius, P. Sautet, Y. Huang and J. Miao, “Atomic-scale identification of the active sites of oxygen reduction nanocatalysts”, *Nat. Catal.* **7**, 796–806 (2024).
3. C. M. O’Leary, H. Sha, J. Zhang, C. Su, S. Kahn, H. Jiang, A. Zettl, J. Ciston, and J. Miao, “Three-dimensional structure of buried heterointerfaces revealed by multislice ptychography”, *Phys. Rev. Applied* **22**, 014016 (2024).
4. S. Moniri, Y. Yang, J. Ding, Y. Yuan, J. Zhou, L. Yang, F. Zhu, Y. Liao, Y. Yao, L. Hu, P. Ercius and J. Miao, “Three-dimensional atomic structure and local chemical order of medium and high-entropy nanoalloys”, *Nature* **624**, 564–569 (2023).
5. M. Pham, Y. Yuan, A. Rana, S. Osher, and J. Miao, “Accurate real space iterative reconstruction (RESIRE) algorithm for tomography”, *Sci. Rep.* **13**, 5624 (2023).
6. D.J. Chang, C.M. O’Leary, C. Su, D.A. Jacobs, S. Kahn, A. Zettl, J. Ciston, P. Ercius, and J. Miao, “Deep-Learning Electron Diffractive Imaging”, *Phys. Rev. Lett.* **130**, 016101 (2023).

Partially supported by our DOE BES MSE grant

7. J. Miao, “Computational microscopy with coherent diffractive imaging and ptychography”, *Nature* **637**, 281–295 (2025).
8. J. Teeter, N. Y. Kim, T. Debnath, N. Sesing, T. Geremew, D. Wright, M. Chi, A. Z. Stieg, J. Miao, R. K. Lake, T. Salguero, and A. A. Balandin, “Achieving the 1D Atomic Chain Limit in Van der Waals Crystals”, *Adv. Mater.* **36**, 2409898 (2024).
9. H.-Y. Chao, K. Venkatraman, S. Moniri, Y. Jiang, X. Tang, S. Dai, W. Gao, J. Miao, and M. Chi, "In Situ and Emerging Transmission Electron Microscopy for Catalysis Research", *Chem. Rev.* **123**, 8347–8394 (2023).
10. J.-H. Park, A.-Y. Lu, M.M. Tavakoli, N.Y. Kim, M.-H. Chiu, H. Liu, T. Zhang, Z. Wang, J. Wang, L.G.P. Martins, Z. Luo, M. Chi, J. Miao, and J. Kong, "Revealing Variable Dependences in Hexagonal Boron Nitride Synthesis via Machine Learning", *Nano Lett.* **23**, 4741–4748 (2023).
11. N.Y. Kim, S. Cao, K.L. More, A.R. Lupini, J. Miao, and M. Chi, “Hollow Ptychography: Toward Simultaneous 4D Scanning Transmission Electron Microscopy and Electron Energy Loss Spectroscopy”, *Small* **19**, 2208162 (2023).
12. A. Rana, C.-T. Liao, E. Iacocca, J. Zou, M. Pham, X. Lu, E.-E. C. Subramanian, Y.H. Lo, S.A. Ryan, C.S. Bevis, R.M. Karl Jr., A.J. Glead, J. Rable, P. Mahale, J. Hirst, T. Ostler, W. Liu, C.M. O’Leary, Y.-S. Yu, K. Bustillo, H. Ohldag, D.A. Shapiro, S. Yazdi, T.E. Mallouk, S.J. Osher, H.C. Kapteyn, V.H. Crespi, J.V. Badding, Y. Tserkovnyak, M.M. Murnane, and J. Miao, “Three-dimensional topological magnetic monopoles and their interactions in a ferromagnetic meta-lattice”, *Nat. Nanotechnol.* **18**, 227–232 (2023).

Nano-Polaritonics in layered van der Waals heterostructures

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Keywords: Scanning Near-Field Optical Microscopy, Infrared and Terahertz Frequencies, Low-Dimensional Quantum Materials, Nanoscale Optical Imaging & Spectroscopy

Research Scope

Understanding light-matter interactions at the nanoscale and in the long-wavelength infrared (IR) and terahertz (THz) regimes is essential for uncovering emergent quantum phenomena in low-dimensional materials, including layered and twisted van der Waals (vdW) heterostructures¹. This research aims to advance nano-optical science by developing and applying IR/THz scanning near-field optical microscopy (SNOM) to probe fundamental quasiparticle excitations and their nano-optical response functions with nanometer resolution.

A primary challenge in long-wavelength optics is the diffraction limit, leaving conventional IR/THz spectroscopies to spatial resolution of 100-1000 μm – far too coarse to resolve the critical phenomena occurring at the nanoscale. Equally important yet largely unmet is the challenge of extending scanning nano-optical studies to uncharted conditions such as cryogenic base temperatures, ultrahigh vacuum (UHV), and high magnetic fields. These frontiers remain largely unexplored across the broader research community worldwide.

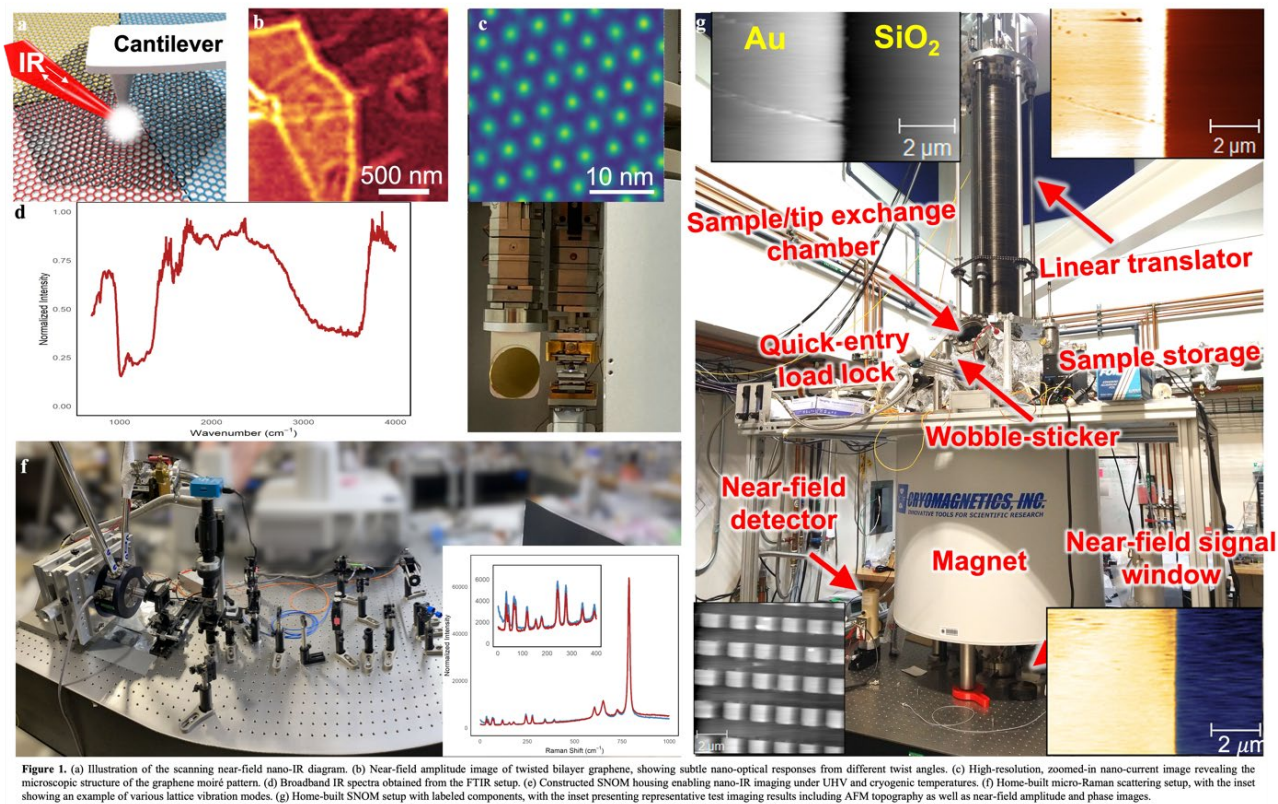
This project seeks to address these challenges by enabling studies of surface polaritonic modes – plasmons, phonons, and magnons in 2D vdW materials, where strong IR/THz coupling to collective charge or lattice dynamics supports a full suite of such excitations. This opens the door to inquiry into fundamental physics through polaritonic observation and control^{2,3}. In doing so, these efforts are expected to uncover novel quantum optical phenomena, with promising implications for energy harvesting, quantum sensing, and quantum communications.

Recent Progress

New instrument developments: We have recently established a multimodal infrared optical imaging and spectroscopy platform that integrates scanning near-field optical microscopy (SNOM), broadband Fourier-transform infrared (FTIR) spectroscopy, and micro-Raman scattering spectroscopy (Fig. 1). This highly complementary combination enables high-sensitivity, nanoscale-resolved studies of IR/THz light-matter interactions in quantum materials under diverse spatial, spectral, and environmental conditions.

Beyond these fully operational (SNOM + FTIR + Raman) platforms, the centerpiece of our recent effort is a fully home-built SNOM instrument (Fig. 1) capable of operating at cryogenic temperatures, under UHV, and in high magnetic fields – a capability set not available in any commercial system. The complete mechanical and optical construction is finished, and we are troubleshooting a recently identified AFM tip scanning interruption issue while optimizing

stability and performance. Once fully tested, this instrument will enable nanoscale optical investigations under previously inaccessible experimental conditions.



New experimental results: Rhombohedral stacking order in multilayer graphene has a profound impact on its electronic properties. In particular, the electronic characteristics of trilayer graphene are highly sensitive to its stacking sequence, especially the Bernal (ABA) and rhombohedral (ABC) configurations. While substantial progress has been made in understanding the electronic behavior of these stackings through charge transport studies, their local optical properties remain comparatively underexplored.

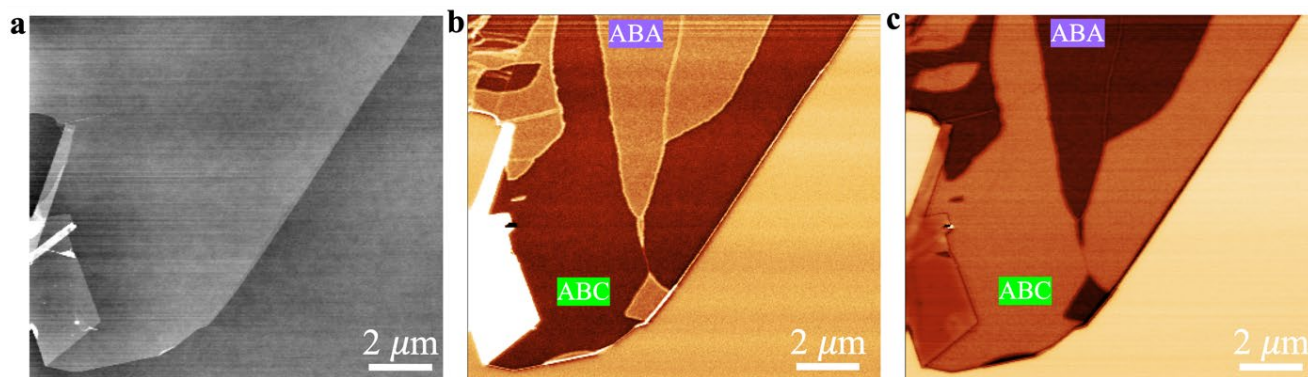


Figure 2. (a) AFM topography image of multi-layer graphene transferred onto a SiO₂/Si substrate. (b&c) Corresponding scanning near-field images: near-field amplitude (b) and near-field phase (c). Distinct regions with varying near-field contrast are clearly visible in both regimes, corresponding to different graphene stacking orders - rhombohedral (ABC) and Bernal (ABA) stacking.

We investigate the influence of stacking order on the local optical response of trilayer graphene, focusing on ABA and ABC domains within the same flake (Fig. 2). By employing SNOM imaging and spectroscopy, we probe the nanoscale-resolved optical conductivity of these domains well beyond the diffraction limit. Our preliminary results reveal that inter-band transitions, arising from the distinct electronic band structure of ABC-stacked graphene, lead to markedly different infrared responses over a broad range of carrier doping levels, in stark contrast to adjacent ABA-stacked regions. Supported by tight-binding calculations, these results offer new insights into the local plasmonic behavior of rhombohedral stacking, opening possibilities for stacking-order-engineered nanophotonic and nano-polaritonic applications.

Beyond plasmonic excitations in graphene family, low-symmetry van der Waals transition-metal oxides host a rich variety of lattice-vibration–driven anisotropic phonon-polaritonic modes. These modes, originating from strong coupling between infrared light and crystal lattice vibrations, offer a complementary route for manipulating light at deeply subwavelength scales. Twist engineering of layered polar dielectrics introduces a powerful degree of freedom for tailoring polariton propagation, confinement, and directional control.

We have recently investigated twisted α -V₂O₅/ α -V₂O₅ heterostructures, where a controlled rotational misalignment is introduced between two stacked layers³. Using SNOM, we experimentally verified that twisting can precisely control the propagation direction of polaritonic wavefronts, and we demonstrated the realization of canalized beam orientations. These twisted heterostructures were fabricated entirely in-house for the first time during this summer, marking a key technical milestone for our laboratory. Building on this capability, multiple related projects are now underway, including twisted α -V₂O₅/ α -MoO₃ systems and the integration of 2D oxide layers onto arbitrary target substrates (Fig. 3). Together, these efforts aim to establish twist-engineered oxide heterostructures as a versatile platform for controlling phonon polaritons and advancing nanoscale light–matter interaction research.

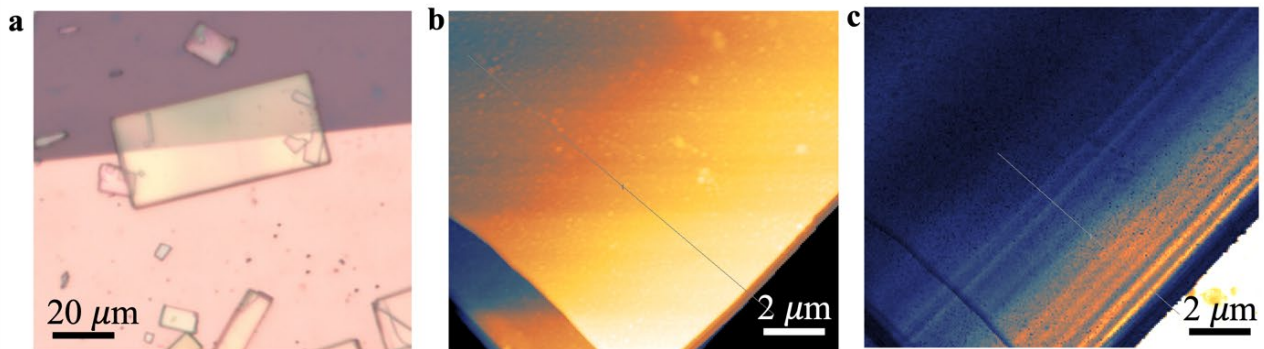


Figure 3. Optical image of as-fabricated V₂O₅ layers placed on a gold edge using the 2D transfer method, with the flake intentionally positioned so that half rests on gold and half on the Si substrate (a). AFM topography of the same device (b) shows no visible contrast from the underlying gold edge. The corresponding near-field image (c) reveals propagating phonon–polaritonic modes, with a clear change in wave periodicity across the gold edge, highlighting the pronounced effect of dielectric screening on shaping the nano-polaritonic wavefront.

Future Plans

Moving forward, we will continue developing our multimodal scanning near-field optical instruments and use nano-polaritonics as a local, non-invasive probe to explore the underlying physics of quantum materials. By harnessing various polaritonic modes, we aim to directly access local optical conductivity and response functions at deeply subwavelength scales. This approach is expected to reveal spatially varying and topologically non-trivial local features beyond the reach of conventional far-field optics. Some of our key research goals include:

Probing excitonic excitations in multilayer graphene systems (e.g., AB-BA bilayers, rhombohedral stacks) with tunable band gaps via electrostatic gating. This may enable detection of corner or edge excitonic modes as well as excitonic defect responses⁴. Additionally, we will investigate stacking-order domain boundaries in multilayer graphene, which can host topologically non-trivial and strain-induced localized states.

Investigating twisted graphene systems across a broad range of twist angles. While small-angle twisted graphene has been extensively studied, large-angle configurations - where intervalley Umklapp scattering dominates - remain less explored. These regimes may host novel phases such as higher-order topological insulators and chiral topological semimetals⁵. Through precision 2D transfer fabrication, near-field imaging, and theoretical modeling, we aim to systematically characterize these intriguing phenomena in the nanoscale.

Exploring monolayer Kagome metals like FeSn, the CsV₃Sb₅ family and related compounds, which exhibit rich phenomena including flat bands, Dirac fermions, charge-density-wave order, magnetism and strong correlations. Accessing them in the ultrathin limit may enable opening new avenues in correlated topological physics and spin-orbit torque applications.

Utilizing our new capability to fabricate twisted transition metal oxide heterostructures (e.g., V₂O₅/MoO₃) to study interlayer nano-polaritonic coupling and interactions. We will begin with anisotropic phonon polaritonic modes under different twist configurations. These structures offer a new platform for controlling polariton propagation direction, wavefront symmetry, and canalized beam orientation, and may open routes to hybrid polaritonic devices integrating phononic and plasmonic functionalities.

References

1. D. N. Basov, A. Asenjo-Garcia, P. J. Schuck, X. Zhu, and A. Rubio, *Nanophotonics in van der Waals materials*, *Nanophotonics* 10, 549–577 (2021).
2. G. X. Ni, A. S. McLeod, Z. Sun, L. Wang, L. Xiong, K. W. Post, S. S. Sunku, B.-Y. Jiang, J. Hone, C. R. Dean, M. M. Fogler, and D. N. Basov, *Fundamental limits to graphene plasmonics*, *Nature* 557, 530 (2018).
3. H. Shiravi, W. Zheng, Y. He, S. Ran, D. A. Rhodes, L. Balicas, H. D. Zhou, G. X. Ni, *Twist-Engineered Phonon Polaritons in α -V₂O₅*, *Opt. Lett.* **50**, 2986-2989 (2025).
4. H. Davenport, F. Schindler, and J. Knolle, *Berry Curvature of Low-Energy Excitons in Rhombohedral Graphene*, arXiv:2508.03290 (2025).

5. Li, J., Chen, C., & Yao, W. *Topological domain-wall states from Umklapp scattering in twisted bilayer graphene*. arXiv:2508.03761 (2025).

Publications

1. L. Zhang, G. X. Ni, J. He, G. Gao. *Above room temperature multiferroic tunnel junction with the altermagnetic metal CrSb*, Phys. Rev. B. **112**, 064401 (2025).
2. H. Shiravi, W. Zheng, D. A. Rhodes, L. Balicas, H. D. Zhou, G. X. Ni. *Tunable Polariton Canalization in Natural van der Waals Oxide*. Under Review in Adv. Opt. Mater. (2025).
3. L. Zhang, Y. Liu, J. Ren, G. Ding, X. Wang, G. X. Ni, G. Gao, Z. Cheng. *Intercalation-altermagnet-driven ferrimagnetic-ferroelastic multiferroics and anomalous and spin transport*. arXiv: 2506.18531 (2025).
4. Z. Dai, B. Cheng, R. Jing, L. Wehmeier, Z. Ji, D. N. Basov, G. X. Ni, M. K. Liu. *Magnetic field driven emergent phenomena: Insights from magneto-optics and nanoscopy*. Submitted to Prog. Quantum Electron. (2025).
5. H. Shiravi, W. Zheng, Y. He, S. Ran, D. A. Rhodes, L. Balicas, H. D. Zhou, G. X. Ni. *Twist-Engineered Phonon Polaritons in α -V₂O₅*. Opt. Lett. **50**, 2986-2989 (2025).
6. H. Shiravi, G. X. Ni. *Significantly enhanced near-field coupling via tip engineering*. Opt. Lett. **50**, 590-593 (2025).
7. Q. Xu, H. Siddiquee, S. Gould, J. A. Zhu, D. A. Martinez, C. Broyles, G. X. Ni, T. Kong, S. Ran. *Tunable giant anomalous Hall effect in the Kondo-lattice ferromagnet UBiTe*. Phys. Rev. B. **110**, 165162 (2024).
8. H. Shiravi, A. Gupta, B. R. Ortiz, S. Cui, B. Yu, E. Uykur, A. A. Tsirlin, S. D. Wilson, Z. Sun, G. X. Ni. *Plasmons in the Kagome metal CsV₃Sb₅*. Nature Commun. **15**, 5389 (2024).
9. S. Cui, C. Jiang, Z. Zhan, T. Wilson, N. Zhang, X. Xie, S. Yuan, H. Wang, C. Lewandowski, G. X. Ni. *Nanoscale Optical Conductivity Imaging of Double-Moiré Twisted Bilayer Graphene*. Nano. Lett. **24**, 11490-11496 (2024).
10. M. Papaj, G. X. Ni, C. Lewandowski. *Visualizing structure of correlated ground states using collective charge modes*. arXiv: 2310.19771 (2024).

Unveiling the Atomic Vibrational Anisotropy and Electron-Phonon Coupling via Momentum-Selective Electron Microscopy

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Keywords: Monochromated Electron energy-loss spectroscopy, phonon anisotropy, perovskite oxides, electron-phonon coupling, superconductivity

Research Scope

Studying individual vibrational modes is essential for understanding optical, thermal, and superconducting phenomena in a wide range of crystalline materials and their heterostructures. At the atomic level, vibrational trajectories, known as thermal ellipsoids, exhibit significant anisotropies due to local symmetries and are traditionally analyzed using optical and diffraction methods. However, the limited spatial and energy resolutions of these techniques result in measurements averaged over large crystal volumes and the entire phonon spectra, preventing a detailed understanding of individual phonon mode contributions to thermal and photonic responses as well as electron-phonon coupling (EPC) at interfaces. State-of-the-art monochromated electron energy-loss spectroscopy (EELS) in scanning transmission electron microscopy (STEM) enables nanoscale phonon spectroscopy with energy resolutions of just a few meV. We have developed and employed a series of space- and angle-resolved vibrational EELS methods to probe vibrational modes and map phonon dynamics at nanoscale interfaces. In this project, we further expanded the capabilities of vibrational EELS and developed a novel momentum-selective EELS (**q**-selective EELS) method to extract vibrational spectra with atomic displacements along specific crystallographic orientations. We demonstrated its application through two case studies: the local atomic vibrational anisotropies dictated by local symmetries in perovskite oxides and the EPC at an insulator/superconductor interface.

Recent Progress

1. Revealing polarization-induced atomic vibrational anisotropies by q-selective EELS.

Phonon anisotropy gives rise to the orientation dependency of dielectric, thermal, and optical properties of materials. At the atomic level, the vibration of individual atoms and thermal ellipsoids could exhibit strong anisotropies due to the local point group symmetry. Owing to the combined capabilities of few-meV energy resolution and sub-nm spatial resolution, the state-of-the-art monochromated EELS can probe local phonon modes at various crystalline imperfections. We further designed a **q**-selective EELS approach with a desired momentum exchange for revealing the frequency-linked vibrational anisotropies of individual oxygen atoms in a centrosymmetric cubic-phase SrTiO₃ (STO).

A 50-unit-cell (u.c.) thick freestanding STO films were used in this study to achieve high quality vibrational EELS hyperspectral imaging datasets with atomic resolution. The $\mathbf{q}$ -selective EELS experiments were conducted by controlling the displacement vector ($\mathbf{D}_{\text{EEA}}$) of the EELS entrance aperture (EEA) as shown in Fig. 1a, which is analogous to the dark-field or off-axis vibrational EELS conditions. The background subtracted vibrational spectrum of STO in Fig. 1b contains all major phonon modes of STO from 10 to 110 meV, consistent with the calculated phonon density of states (PhDOS). We collected multiple atomic resolution $\mathbf{q}$ -selective EELS spectrum mapping datasets with momentum exchange along either [100] or [001] directions of the STO lattice as shown in Figs. 1c and 1d. After alignment and summation, we achieved the energy-filtered vibrational signals from 10 to 110 meV for both X' shift and Y' shift as shown in Figs. 1e and 1f, respectively. The atomic feature shown in each mapping result changes from Sr atoms in 10–20 meV, to a mixture of Ti and O atoms in medium energy ranges, and to certain O atoms in the highest energy ranges, in good agreement with corresponding results simulated from a modified frequency-resolved frozen phonon multislice method.

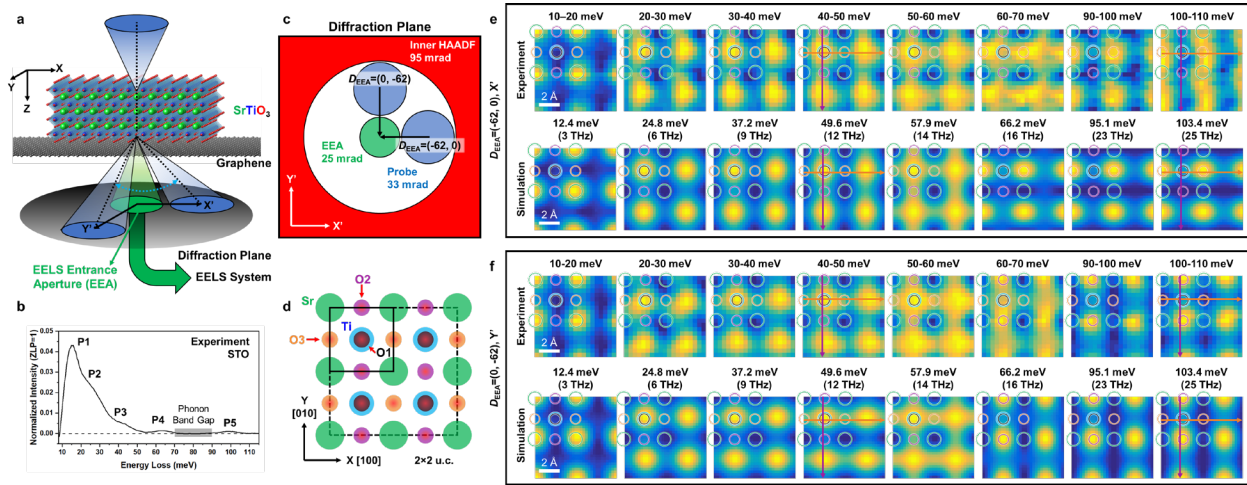


Fig. 1. Atomic resolution vibrational signal mapping of STO with two orthogonal displacement directions of EEA ($\mathbf{D}_{\text{EEA}}$). (a) Schematic of a $\mathbf{q}$ -selective EELS setup. The convergence semi-angle of the electron probe is 33 mrad (blue circle) with a spatial resolution of 1.5 Å. The collection semi-angle of EELS entrance aperture (EEA) is 25 mrad (green circle) and the diffraction pattern is displaced by 62 mrad away from the center of EEA. (b) A background-subtracted vibrational spectrum of STO averaged from a 2 nm × 2 nm region. (c) Diffraction plane showing the movable probe, a fixed EEA, and a high angle annular dark-field (HAADF) detector. (d) Atomic structure along [001] direction. (e) Experimental and simulated vibrational signal mapping in different energy ranges with $\mathbf{D}_{\text{EEA}} = (-62, 0)$ or X' shift. (f) Experimental and simulated vibrational signal mapping in different energy ranges with $\mathbf{D}_{\text{EEA}} = (0, -62)$ or Y' shift.

More intriguingly, we discerned two types of oxygen atoms exhibiting contrasting vibrational anisotropies below and above 60 meV due to their frequency-linked thermal ellipsoids. Figures 2a and 2b present the comparison between line profiles along horizontal and vertical directions. For X' shift, apical oxygen (O2) atoms have brighter intensities than equatorial oxygen (O3) atoms in the map of 40–50 meV, while O2 atoms are much dimmer than O3 in the map of 100–110 meV. In contrast, the intensity modulations are reversed for Y' shift. By considering the scattering

probability of vibrational EELS, the momentum exchange along X' (Y') direction will selectively excite the X (Y) component of atom projected PhDOS. For example, O2 atoms possess more phonon states of X component than O3 atoms below 60 meV, but less phonon states above 60 meV as shown in Fig. 2c. Such differences for both X and Y components can be used to explain the observed intensity modulations in Fig. 1. The anisotropy of oxygen atomic vibrations can be visualized by plotting the thermal ellipsoids as shown in Figs. 2d and 2e. Theoretical modeling further points out that the thermal vibrations of oxygen atoms transform from oblate ellipsoids at low energies to prolate ones at high energies, both possessing much stronger anisotropies than the averaged one extracted from traditional measurements in literature.

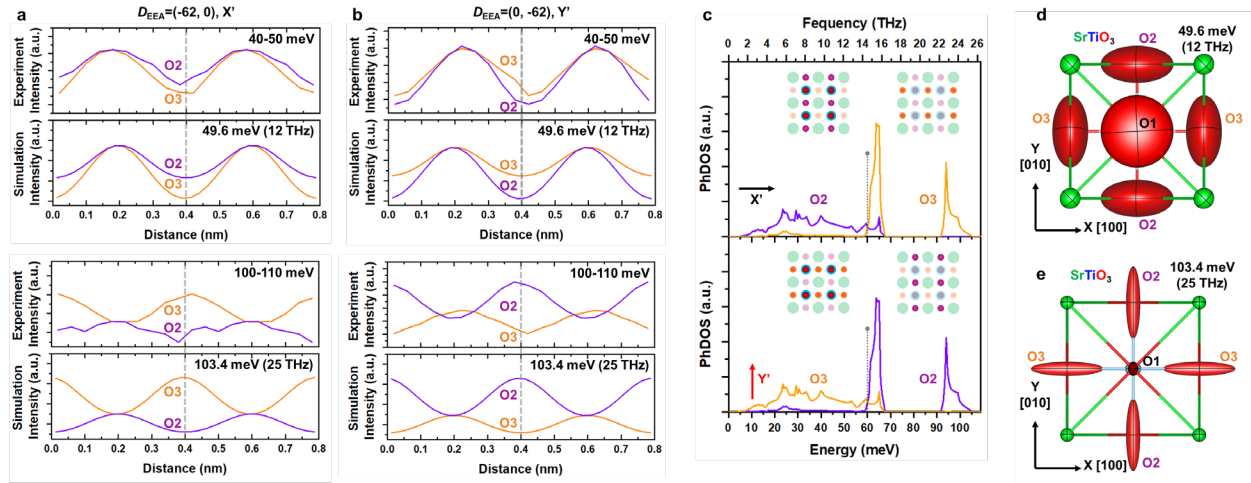


Fig. 2. Momentum-selective excitation of oxygen vibrations and thermal ellipsoids. (a, b) Line profiles of vibrational signals in chosen energy ranges along horizontal (orange) and vertical (purple) directions as indicated in Fig. 1 for both X' shift (a) and Y' shift (b). (c) Projected PhDOS of O1, O2, and O3 atoms along X' (upper) and Y' (lower) directions. The O1 curve overlaps with the O2 (O3) one in the upper (lower) panel. Insets illustrate the intensity modulation of vibrational signals at different oxygen atoms below and above 60 meV. (d, e) [001]-projected thermal ellipsoids representing anisotropy of individual mean-squared displacements of all atoms at 49.6 meV (12 THz, d) and 103.4 meV (25 THz, e), respectively. The amplitude of displacement is exaggerated for visual clarity.

Collecting high quality vibrational EELS datasets is often challenging and requests extremely long acquisition time due to the ultralow beam current of the monochromated electrons. As a result, atomic resolution vibrational signal mapping can be prone to failure on ferroelectric oxides due to sample drift and charging issues. To address these problems, we introduced a multi-frame EELS mapping technique to mitigate these issues by employing newly designed post-processing algorithms to reconstruct high-quality vibrational signal mapping datasets. With the aid of this multi-frame EELS and post-acquisition analysis, we further applied the $\mathbf{q}$ -selective EELS approach to distinguish the altered vibrational anisotropies of apical and equatorial oxygen atoms in a non-centrosymmetric tetragonal-phase BaTiO₃ (BTO) as schematically shown in Fig. 3a.

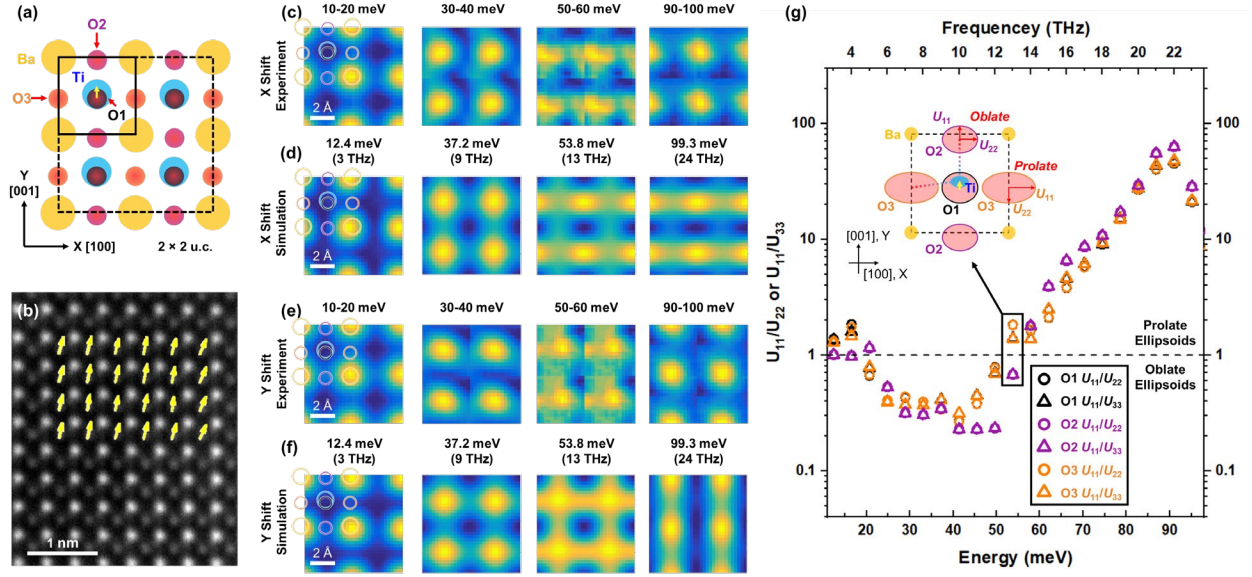


Fig. 3. Atomic resolution q-selective vibrational signal mapping of BTO. (a) Atomic structure of BTO along [010] direction. (b) A HAADF-STEM image of BTO overlapping with polarization vectors. (c-f) Experimental and simulated vibrational signal maps in different energy ranges for X and Y shifts. (g) The variation of aspect ratio (U_{11}/U_{22} or U_{11}/U_{33}) of thermal ellipsoids of oxygen atoms in BTO at different energies. The inset schematically illustrates that apical (O2) and equatorial oxygen (O1 and O3) atoms exhibit dissimilar thermal ellipsoids at 53.8 meV (13 THz).

Figure 3b presents an atomic resolution HAADF STEM image of a 50 uc tetragonal BTO freestanding film with an in-plane polarization. Using the multi-frame EELS method, we collected atomic resolution vibrational EELS hyperspectral imaging datasets along X and Y directions on the BTO region with a polarization vector parallel to Y direction. After drift correction and data summation, we obtained energy-filtered vibrational signal maps averaged across multiple BTO unit cells in various energy intervals as shown in Figs. 3c and 3e. The atomic feature changes from pure Ba atoms in 10–20 meV, to Ti in 30–40 meV, then to a mixture of Ti and O atoms in 50–60 meV, and to pure O atoms in 90–100 meV, in agreement with both simulated PhDOS and even quantitatively matching with simulated vibrational signal maps in Figs. 3d and 3f obtained from a modified frequency-resolved frozen phonon multislice method. The signal maps of 90–100 meV exhibit different patterns as brighter O3 (equatorial oxygen) atoms for X shift and brighter O2 (apical oxygen) atoms for Y shift. Unexpectedly, the 50–60 meV maps show asymmetric modifications of vibrational signal intensities. We then figured out that it arises from the polarization-induced shortening of O2-Ti bonds. Figure 3g plots the aspect ratios of anisotropic displacement parameters of three oxygen atoms along O-Ti direction (U_{11}) and in the O-Ba plane (U_{22} or U_{33}), which can be used to estimate the anisotropy of oxygen thermal ellipsoids. At 53.8 meV, O2 and O3 atoms exhibit oblate and prolate ellipsoids respectively, leading to the asymmetric modifications of oxygen vibrational signals between X and Y shifts. These modifications are strongly associated with the ferroelectricity of the BTO. This approach opens new avenues for visualizing phonon eigenvectors at specific crystallographic sites, offering a fresh

perspective on investigations into dielectric, optical, thermal, mechanical, and superconducting properties with unparalleled spatial and energy resolution [1].

2. Revealing exotic phonon modes and electron–phonon coupling at FeSe/SrTiO₃ superconducting interface

The superconducting transition temperature (T_C) of one unit cell FeSe films on SrTiO₃ substrates (1 uc FeSe/STO) was reported to be 65 K and higher than the bulk FeSe in the absence of oxide substrates. The electron-phonon coupling (EPC) at the 1 uc FeSe/STO interface is thought to play a vital role in enhancing superconductivity. The underlying mechanism of remarkable T_C increases in this heterostructure remains elusive. A critical factor is the coupling with interfacial bosonic modes, as indicated by the replica electron bands, which are thought to stem from oxygen optical phonons in STO. Despite extensive studies on electronic and atomic structures, there is still a lack of direct experimental evidence of the local phonon modes at the interface and their correlation with EPC and T_C enhancement. Here, we aim to answer this question by probing atomic level phonon variations at the 1 uc FeSe/STO interface with the newly developed **q**-selective EELS approach.

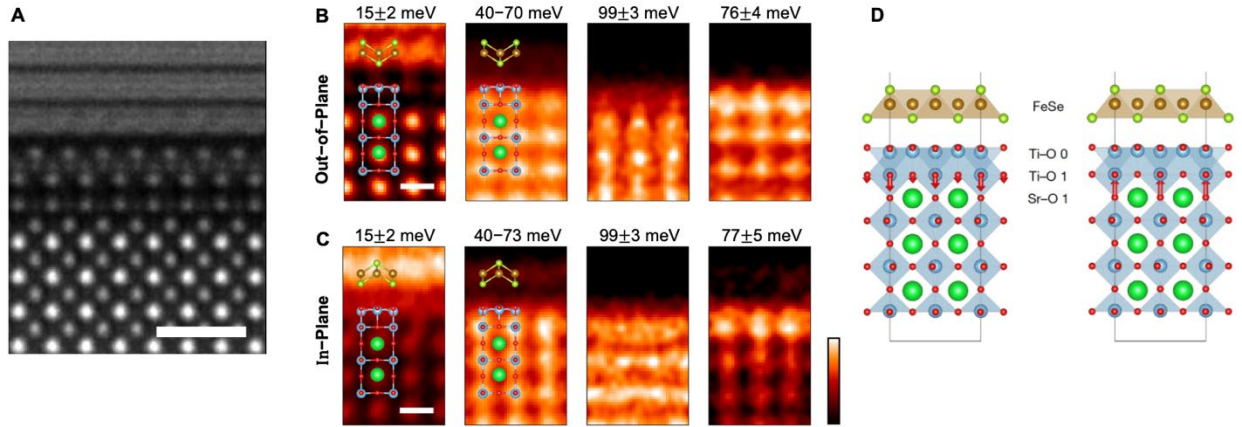


Fig. 4. Atomically resolved phonon spectral imaging of 1 uc FeSe/STO interfaces. (A) A HAADF STEM image of a Te capped 1 uc FeSe/STO sample. Scale bars = 10 Å. (B, C) Vibrational signal maps from out-of-plane and in-plane acquisitions in different energy ranges. Scale bars = 4 Å. (D) The atomic displacement patterns at the Γ point for the two optical phonon modes with strong contribution to EPC.

1 uc FeSe films were grown on doped STO substrates using molecular beam epitaxy (MBE). Figure 4a displays an atomic resolution HAADF STEM image on a cross-sectional 1 uc FeSe/STO specimen with Te protection capping layers. There is an extra atomic layer of TiO_x between the 1 uc FeSe film and the TiO₂ terminated STO substrate. We performed **q**-selective EELS experiments to detect the atomically resolved vibrational spectra by displacing the diffraction pattern along out-of-plane (OOP) and in-plane (IP) directions. Figures 4b and 4c show the energy-filtered vibrational signal maps in several representative energy ranges. There are extra optical phonon modes in the energy range of 75–88 meV with a primary mode at 76 meV. These modes are characterized as OOP vibrations of oxygen atoms in the interfacial TiO_x layer and the apical oxygen in STO. Our

first-principles calculations figured out that such modes give rise to the enhancement of EPC strength, especially at the high-energy (HE) mode of 78.0 meV and low-energy (LE) mode of 65.7 meV as shown in Fig. 4d and the opening of superconducting gap (Δ) of 1 uc FeSe/STO. Simulation results also confirmed that the eigen-displacements of both LE and HE modes drive OOP motions of oxygen atoms near the interface.

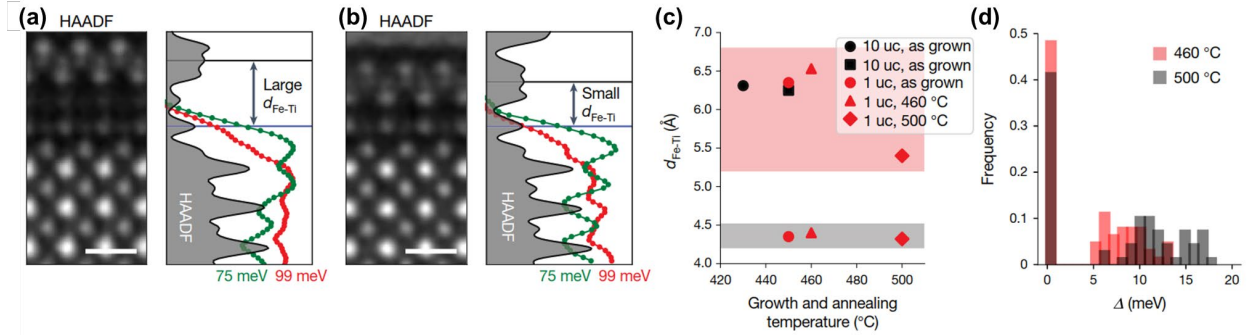


Fig. 5. Influence of interlayer spacing on phonons and superconductivity. (a) A HAADF STEM image of 1uc FeSe/STO interface with a large interlayer spacing and the intensity line profiles of 75 and 99 meV signals. (b) A HAADF STEM image with a small interlayer spacing and phonon line profiles. (c) The interlayer spacing ($d_{\text{Fe-Ti}}$) measured from various samples with different growth and annealing temperatures. (d) Statistical distribution of Δ values measured at 5 K from 1 uc FeSe/STO samples with different annealing temperatures. Scale bars, 5 Å.

To further correlate the interface structure and phonons with superconducting properties, we performed the same STEM imaging and vibrational EEL spectroscopy and measured the superconducting gap (Δ) using *in-situ* scanning tunneling microscopy and spectroscopy (STM-STS) at 5 K on several FeSe/STO samples prepared with varying growth and annealing temperatures. Because both STEM-EELS and STM-STS are local probes, we performed multiple measurements in the same region with both techniques. STEM imaging found that there are either large interlayer spacing ($d_{\text{Fe-Ti}}$) values of more than 6 Å in Fig. 5a or small $d_{\text{Fe-Ti}}$ values of nearly 4.3 Å in Fig. 5b. As summarized in Fig. 5c, thick (10 uc) FeSe films grown on STO substrate only exhibit large $d_{\text{Fe-Ti}}$. For the annealed 1 uc FeSe/STO samples, both small and large $d_{\text{Fe-Ti}}$ interfaces coexist. Specifically, the small $d_{\text{Fe-Ti}}$, double-TiO_x structure predominates in the 1 uc FeSe/STO samples annealed at a high temperature of 500 °C. Meanwhile, the measured Δ in Fig. 5d denotes that the mean and largest Δ both increase with the annealing temperature. Thus, the correlation between the smaller $d_{\text{Fe-Ti}}$ and larger Δ in the 500 °C annealed 1 uc FeSe/STO samples indicates that the EPC is rather short ranged, highlighting the importance of interface homogeneity for the high T_c of 1 uc FeSe/STO. These findings shed light on the microscopic origin of the interfacial EPC and offer insights into achieving large and consistent T_c enhancement in FeSe/STO and potentially other superconducting systems [2].

Future Plans

Our $\mathbf{q}$ -selective EELS method provides a powerful tool for element-resolved and atomic site-specific analysis of phonon eigenvectors in complex perovskite oxides and their heterostructures

and can be generally utilized to investigate the anisotropic phonon behaviors in diverse materials. The ability to map vibrational anisotropy with unprecedented spatial and energy resolution opens avenues for further studies on ferroelectric phase transitions, the origins of ferroelectricity, and the role of apical oxygen sites in modifying exchange interactions in high-temperature superconductors. For instance, the local vibrational anisotropy of apical oxygen in cuprates and emerging nickelates would be revealed by our method and be used to understand the interaction between electrons and phonons and even the underlying superconducting mechanisms. Furthermore, exploring $\mathbf{q}$ -selective EELS signals with certain momentum exchanges could enable precise measurements of polarization vectors and associated oxygen-octahedra distortion for more displacive ferroelectrics. We will select the $\langle 111 \rangle$ directions to facilitate the study of spontaneous polarization in BiFeO₃ in a pseudo-cubic phase.

References

1. X. Yan, P. M. Zeiger, Y. Huang, H. Sun, J. Li, C. A. Gadre, H. Yang, R. He, T. Aoki, Z. Zhong, Y. Nie, R. Wu, J. Rusz, X. Pan. Atomic-Scale Imaging of Frequency Dependent Phonon Anisotropy. *Nature* **2025**, in press.
2. H. Yang, Y. Zhou, G. Miao, J. Rusz, X. Yan, F. Guzman, X. Xu, X. Xu, T. Aoki, P. Zeiger, X. Zhu, W. Wang, J. Guo, R. Wu, X. Pan. Phonon modes and electron–phonon coupling at the FeSe/SrTiO₃ interface. *Nature* **2024**, 635, 8038, 332–336. Doi: 10.1038/s41586-024-08118-0

Publications

1. H. Yang, Y. Zhou, G. Miao, J. Rusz, X. Yan, F. Guzman, X. Xu, X. Xu, T. Aoki, P. Zeiger, X. Zhu, W. Wang, J. Guo, R. Wu, X. Pan. Phonon modes and electron–phonon coupling at the FeSe/SrTiO₃ interface. *Nature* **2024**, 635, 8038, 332–336. Doi: 10.1038/s41586-024-08118-0
2. X. Yan, P. M. Zeiger, Y. Huang, H. Sun, J. Li, C. A. Gadre, H. Yang, R. He, T. Aoki, Z. Zhong, Y. Nie, R. Wu, J. Rusz, X. Pan. Atomic-Scale Imaging of Frequency Dependent Phonon Anisotropy. *Nature* **2025**, in press.
3. C. Addiego, W. Gao, H. Huyan, X. Pan. Probing charge density in materials with atomic resolution in real space. *Nature Reviews Physics* **2023**, 5, 117–132. Doi: 10.1038/s42254-022-00541-4
4. C. Addiego, J. A. Zorn, W. Gao, S. Das, J. Guo, C. Qu, L. Zhao, L. W. Martin, R. Ramesh, L.-Q. Chen, X. Pan. Multiscale electric-field imaging of polarization vortex structures in PbTiO₃/SrTiO₃ superlattices. *APL Materials* **2023**, 11, 5, 051106. Doi: 10.1063/5.0146713
5. H. Huyan, Z. Wang, L. Li, X. Yan, Y. Zhang, C. Heikes, D. G. Schlom, R. Wu, X. Pan. Dislocation-Assisted Quasi-Two-Dimensional Semiconducting Nanochannels Embedded in Perovskite Thin Films. *Nano Letters* **2023**, 23, 12, 5409–5416. Doi: 10.1021/acs.nanolett.2c03404
6. X. Yan, J. Li, L. Gu, C. A. Gadre, S. L. Moore, T. Aoki, S. Wang, G. Zhang, Z. Gao, D. N. Basov, R. Wu, X. Pan. Curvature-Induced One-Dimensional Phonon Polaritons at Edges of Folded Boron Nitride Sheets. *Nano Letters* **2022**, 22, 23, 9319–9326. Doi: 10.1021/acs.nanolett.2c02879

7. S. Cai, C. Guo, B. Niu, L. Xie, C. Addiego, D. Wu, P. Wang, S. P. Lau, H. Huang, X. Pan. In Situ Observation of Domain Wall Lateral Creeping in a Ferroelectric Capacitor. *Advanced Functional Materials* **2023**, 33, 50, 2304606. Doi: 10.1002/adfm.202304606
8. S. Cai, Y. Lun, D. Ji, P. Lv, L. Han, C. Guo, Y. Zang, S. Gao, Y. Wei, M. Gu, C. Zhang, Z. Gu, X. Wang, C. Addiego, D. Fang, Y. Nie, J. Hong, P. Wang, X. Pan. Enhanced polarization and abnormal flexural deformation in bent freestanding perovskite oxides. *Nature Communications* **2022**, 13, 5116. Doi: 10.1038/s41467-022-32519-2
9. Q. Qian, H. Ren, J. Zhou, Z. Wan, J. Zhou, X. Yan, J. Cai, P. Wang, B. Li, Z. Sofer, B. Li, X. Duan, X. Pan, Y. Huang, X. Duan. Chiral molecular intercalation superlattices. *Nature* **2022**, 606, 7916, 902–908. Doi: 10.1038/s41586-022-04846-3
10. Z. Zhao, Z. Liu, A. Zhang, X. Yan, W. Xue, B. Peng, H. L. Xin, X. Pan, X. Duan, Y. Huang. Graphene-nanopocket-encaged PtCo nanocatalysts for highly durable fuel cell operation under demanding ultralow-Pt-loading conditions. *Nature Nanotechnology* **2022**, 17, 9, 968–975. Doi: 10.1038/s41565-022-01170-9
11. H. Yang, P. M. Zeiger, A. Konečná, L. Han, G. Miao, Y. Zhou, Y. Huang, X. Yan, W. Wang, J. Guo, Y. Nie, R. Wu, J. Rusz, X. Pan. Inelastic electron scattering at large angles: the phonon polariton contribution. arXiv:2401.04719, **2024**.
12. X. Wang, C. A. Gadre, R. Yang, W. Zou, X. Bin, C. Addiego, T. Aoki, Y. Quan, W.-T. Peng, Y. Huang, C. Du, M. Xu, X. Yan, R. Wu, S. P. Ong, B. Liao, P. Cao, X. Pan. Atomic-scale tunable phonon transport at tailored grain boundaries. arXiv:2405.07464, **2024**.

Combining quantum calculations and electron microscopy to unveil nanostructure properties

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Keywords: STEM, vEELS, DFT, machine learning, vEELS simulations

Research Scope

The focus of this research is to highlight the power of combining density-functional-theory (DFT) calculations with scanning transmission electron microscopy (STEM) and STEM-based electron-energy-loss spectroscopy (EELS) to unveil the structural, electronic, magnetic, vibrational, and optical properties of complex materials and nanostructures. In the last 2-3 years, the advent of high-energy-resolution EELS enabled vibrational EELS (vEELS) for phonons and phonon polaritons. Theoretical research is conducted collaboratively with experimentalists in the U.S. and abroad. Recently, machine-learning potentials have been adopted as a powerful extension of DFT. A new objective has been added to use theory, nanophotonics experiments (**Joshua Caldwell** of Vanderbilt University), and vEELS (**Jordan Hachtel**, ORNL) to bridge Maxwellian theories of phonon polaritons and DFT. In another recent component, we pursued calculations of vEELS beyond the vibrational density of states (vDOS), both in house and in collaboration with **David Masiello** of the University of Washington in Seattle, who is funded by this DOE Program and has been developing such methodologies.

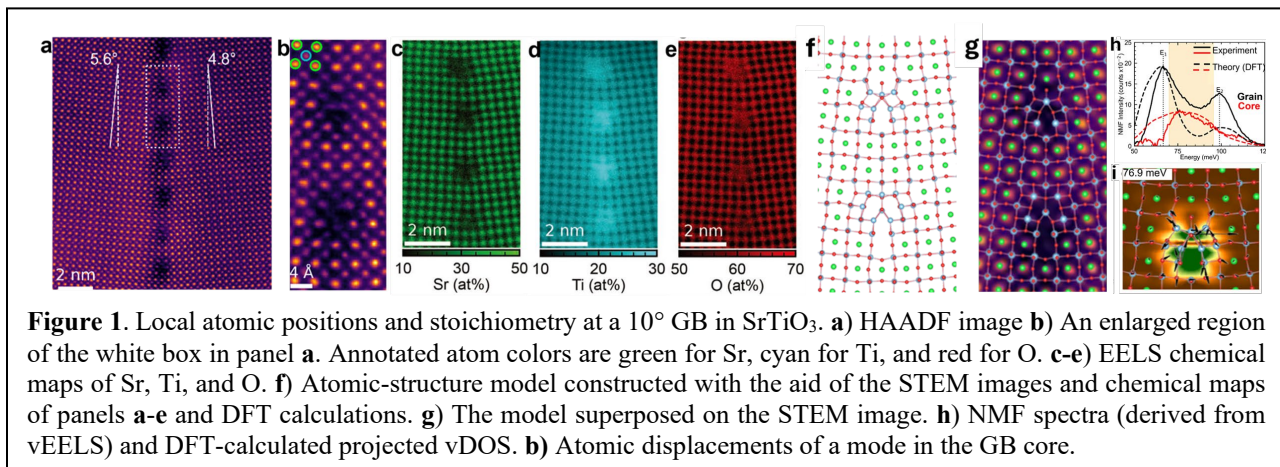
Recent Progress

A few of the most interesting projects, either completed or in progress are highlighted in this section.

Probing vibrational states in the core of a low-angle tilt grain boundary in a complex oxide¹

Key collaborators: STEM microscopists Jordan Hachtel (ORNL) and Eric Hoglund (U of VA). Theory by De-Liang Bao -- Advanced Materials 2023

This work is the first demonstration of combining STEM imaging, STEM-based vEELS maps, and theory to probe directly phonons in a grain boundary (GB) core, 10° tilt GB in SrTiO₃. **Figures 1a-e** show STEM images and vEELS maps of the GB that were combined with DFT calculations to construct the model shown in **Figs. 1f-g**. This model was used for DFT calculations of

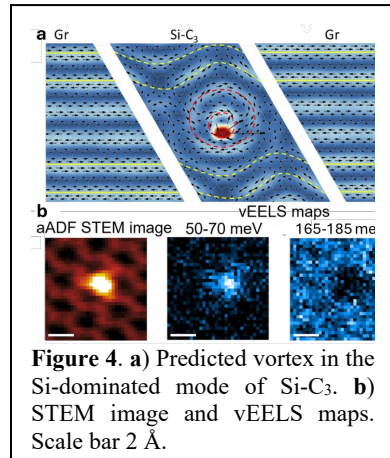
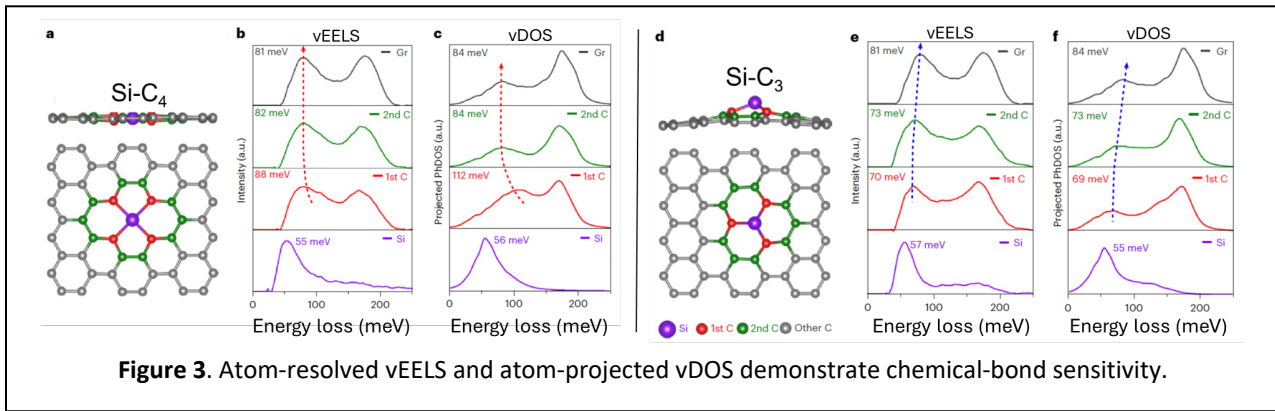


vibrational densities of states (vDOS) in the grain and the GB-core regions, in overall good agreement with the vEELS (**Fig. 1h**). It is clear that the phonon spectra in the GB-core and grain regions are quite different, while comparison of the vEELS with theory enables the conclusion that the core vibrational modes are spatially localized: their energies lie within a gap in the grain phonon bands (beige shaded energy range); the localization of a such mode is manifest in **Fig. 1i**.

Atom-by-atom vEELS with chemical-bond sensitivity² – Vibrational vortices at point defects³

Key collaborator: STEM microscopist Wu Zhu (University of the Chinese Academy of Sciences, Beijing); theory by D. L. Bao – Nature Materials 2023.

This paper reported the first single-atom vEELS with chemical-bond sensitivity by examining two known configurations of Si impurities in graphene: Si bonded to four C atoms (Si-C₄) and Si bonded to three C atoms (Si-C₃), shown in schematics in **Figs. 3a** and **3d**. Atom-resolved vEELS for the two defects, shown in **Figs. 3b,e**, and atom-projected vDOS, shown in **Figs. 3c,f**, are in excellent agreement. The Si-C₃ and Si-C₄ spectra feature distinct evolutions from Si to successive color-coded C-atom rings, reflecting their chemical bonding.



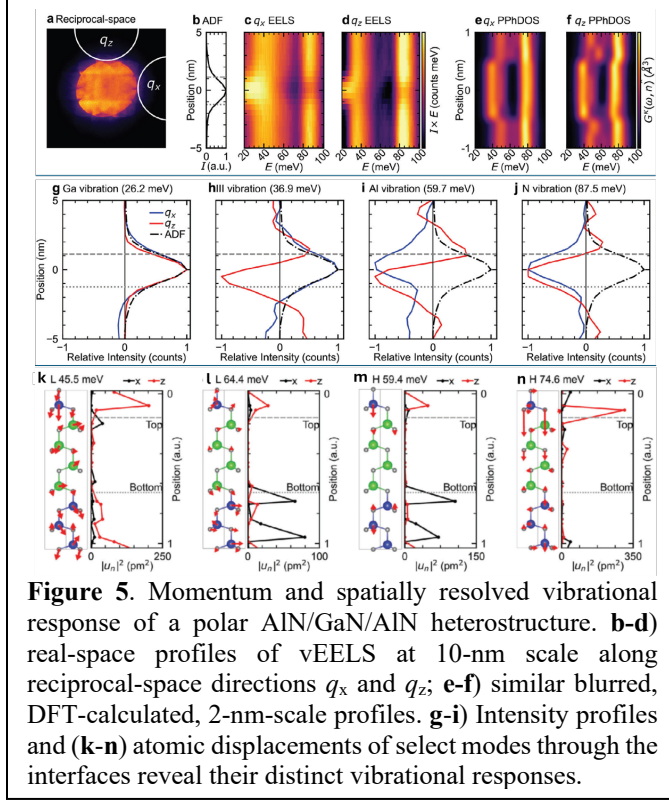
In **Fig. 4**, we demonstrate how theory can go beyond experiments to predict phenomena that currently are not observable.³ The calculated atomic displacements for the 55-meV, Si-dominated mode of Si-C₃ (**Fig. 3f**) reveal a vortex pattern (**Fig. 4b**), driven by large Si displacements. Experimental efforts to obtain a vEELS map by adding the signal over a small energy range (**Fig. 4a**) does not have the necessary resolution. Theory established that such vortices appear in Si-C₄ as well as in heavy impurities in h-BN, e.g., P at N sites and Al at B sites.

Non-equivalent atomic vibrations at interfaces in a polar superlattice⁴

Key collaborators: Microscopists Eric Hoglund and Jordan Hachtel (ORNL); theory by Harrison Walker – Advanced

Materials 2024.

This project combines spatial and momentum resolution in vEELS to determine both the angular and spatial dependence of phonon modes, together with DFT calculations, to demonstrate distinct vibrational responses at the isomorphic but non-equivalent interfaces in a polar superlattice. **Figures 5a-f** demonstrate the complementarity of experimental data and theory by comparing spectra obtained from orthogonal momentum conditions with direction projected vDOS; **Figures**



g-j (vEELS) and **Figs. k-n** (theory) demonstrate distinct vibrational responses at non-equivalent interfaces and showcase both the directionality and participating species of a mode at a given energy. Thus, we demonstrate STEM-EELS possesses sensitivity to both the displacement vectors and frequencies of phonons with atomic resolution. In a parallel pursuit, we employed DFT-based machine-learned potentials and determined that the thermal conductances of nonequivalent GaN/AlN interfaces differ by up to 10%, which can be increased or decreased by intermixing (X. Zhang et al., to be published).

Distinctive vibrational spectral patterns in chiral polar vortex lattices.

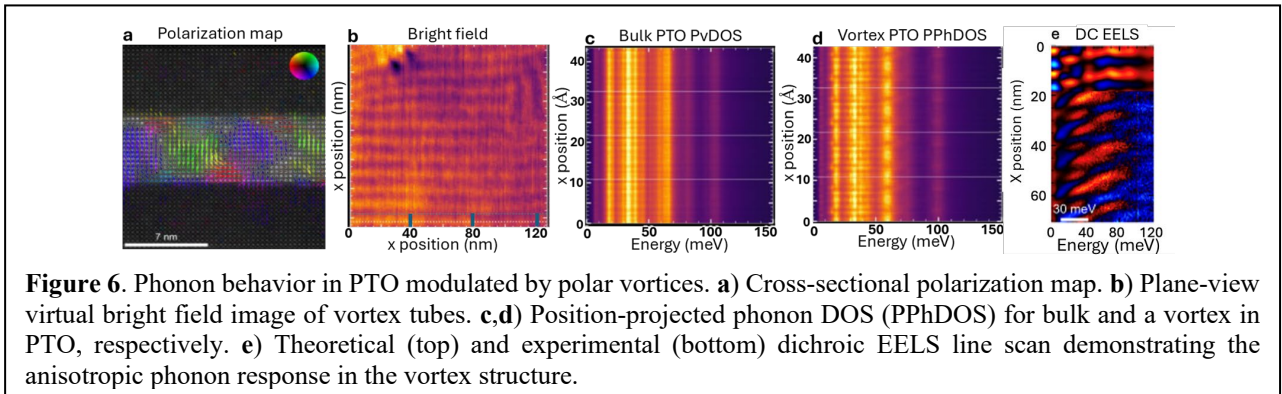
Key collaborators and theory as above. Paper in final stage of preparation.

Polar vortex lattices have been known to

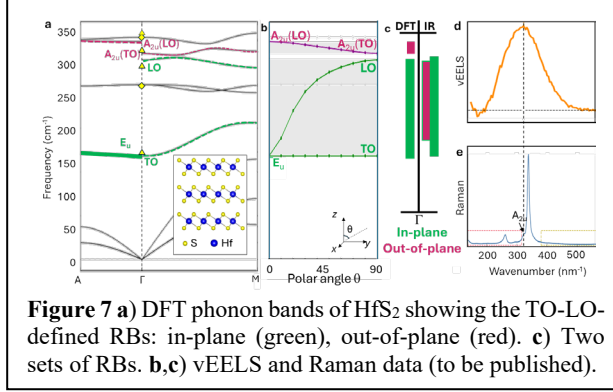
form in the PbTiO_3 parts of $\text{PbTiO}_3/\text{SrTiO}_3$ superlattices. Here we again use momentum-resolved vEELS with nanometer spatial resolution to unveil emergent vibrational patterns across the vibrational spectrum. We further employ DFT-based machine-learning molecular dynamics simulations to unveil the underlying phonon structure. We demonstrate that the vortex-lattice periodicity and the lack of inversion symmetry of the vortex ferroelectric ordering impart their symmetries onto collective vibrations and produce distinctive spectral "swoops" that are present in both experiment and theory. Key results are shown in **Fig. 6**, establishing a relationship between polar topologies and phonon behavior.

The role of DFT in phonon-polariton theory.

Key collaborators: Joshua Caldwell (Vanderbilt), Jordan Hachtel (ORNL), Alex Paarmann (Berlin), Thomas Beechem (Purdue U.); theory: De-Liang Bao – paper in preparation.



Phonon polaritons (PhPs) have had a resurgence in the last decade, as modern photonics techniques and vEELS achieved major advances. PhP theory is derived from Maxwell's equations with only input the solids's dielectric tensor $\epsilon(\omega)$. Typically, "experimental" $\epsilon(\omega)$ fitted to infrared reflectance or ellipsometry data are used. A role for DFT calculations in PhP research has not been articulated adequately in the literature. We have found significant connections, catalyzed by $\epsilon(\omega)$.



In uniaxial materials such as h-BN and 2D dichalcogenides, $\epsilon(\omega)$ is diagonal. The two components, $\epsilon_{\parallel}(\omega)$ and $\epsilon_{\perp}(\omega)$, can be expressed in terms of the TOLO formula, which features a resonance at $\omega = \omega_{\text{TO}}$, and a frequency ω_0 defined by $\epsilon(\omega_0) = 0$, which coincides with ω_{LO} . The energy ranges $\omega_{\text{TO}} - \omega_{\text{LO}}$ define the Reststrahlen Bands (RBs) where hyperbolic polaritons propagate, the focus of both photonics and EELS experiments. If, however, light impinges at a

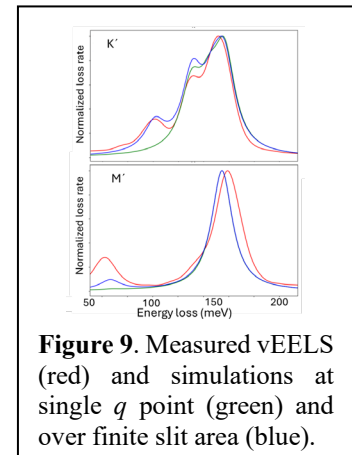
polar angle θ (tilt from the z axis), the TOLO formula does not apply. One can rotate $\epsilon(\omega)$, but phonon connection is lost. Phonon dispersions for HfS₂ are shown in **Fig. 7a,b**. The ω_0 defined by the rotated $\epsilon(\omega)$, do not correspond to phonon frequencies, which has implications for the measured phonon spectra and polaritons.

In the case of HfS₂, we found that the DFT-derived out-of-plane RB disagrees with the IR-derived RB (**Fig. 7c**). Recently collected photonics polaritonic data by the Caldwell team can be explained only by the latter (to be published). Out-of-plane vEELS (Hachtel) and Raman data (Beechem) have confirmed the DFT-calculated phonon frequencies (**Fig. 7d,e**), leaving open questions that call for further investigations.

Advances in simulating vEELS beyond DOS

In-house by Harrison Walker in collaboration with Thomas Pfeifer (ORNL) and, separately, by A. O'Hara with David Masiello of the U. of Washington and the Neon, Inc., team. Papers in preparation.

Our work has thus far been based on comparing vEELS with calculated DOS, which has limitations, especially in dealing with momentum resolved EELS as discussed earlier. Walker and Thomas adopted an approach developed by J. Castellanos-Reyes, P. Zeiger and J. Rusz in 2025, using molecular dynamics simulation to acquire time-dependent atomic configurations that are fed into frozen-phonon multislice simulations to obtain the scattering probabilities of transmitted electrons. These time-dependent probabilities can be Fourier transformed to the frequency space and compared with measured spectra. The technique has been tested for model Si and AlN systems, revealing an important role for selection rules in the scattering amplitudes, and in the acquisition of polarization-selective signals. Furthermore, thickness-dependent sensitivity effects have been identified by sampling the upper surface of a film at a disproportionate level. This effect can yield sensitivity to through-plane vibrational modes, which may be measured experimentally if sufficient sensitivity can be achieved.



We recently initiated a collaboration with **David Masiello**, who has been developing alternative approaches to simulating vEELS using the Born approximation, which requires the dynamical matrix. We have applied this approach to high-temperature momentum-resolved vEELS of h-BN using data by the O. Krivanek team at Neon because the Stokes approach proved inadequate. Key new ingredients are inclusion of Umklapp terms and integration of the inelastic scattering signal over a finite momentum range Δq . In **Fig. 9**, we show typical results for momentum transfer to two points outside the first Brillouin zone.

1. E. Hoglund, D.-L. Bao, A. O'Hara, T. Pfeifer, Md S. B. Hoque, S. Makarem, J. M. Howe, S. T. Pantelides, P. E. Hopkins, and J. A. Hatchel, "Direct visualization of localized vibrations at complex grain boundaries", *Advanced Materials* **35**, 2208920 (2023).
2. M. Xu, D.-L. Bao, A. Li, M. Gao, D. Meng, A. Li, S. Du, G. Su, S. J. Pennycook, S. T. Pantelides, and W. Zhou, "Single-atom vibrational spectroscopy with chemical-bonding sensitivity", *Nature Materials* **22**, 612 (2023).
3. D.-L. Bao, M. Xu, A.-W. Li, G. Su, W. Zhou, S. T. Pantelides, "Phonon vortices at heavy impurities in two-dimensional materials", *Nanoscale Horizons* **9**, 248-253 (February 1, 2024).
4. E. R. Hoglund, H. A. Walker, Md. K. Hussain, D.-L. Bao, H. Ni, A. Mamun, J. Baxter, J. D. Caldwell, A. Khan, S. T. Pantelides, P. E. Hopkins, J. A. Hachtel, "Non-equivalent atomic vibrations at interfaces in a polar superlattice", *Advanced Materials* **36** 2402925 (2024).

Other Publications

1. Md S. Bin-Hoque, E. R. Hoglund, B. Zhao, D.-L. Bao, H. Zhou, S. Thakur, E. Osei-Agyemang, K. Hattar, E. A. Scott, M. Surendran, J. A. Tomko, J. T. Gaskins, K. Aryana, S. Makarem, A. Alwen, A. M. Hodge, G. Balasubramanian, A. Giri, T. Feng, J. A. Hachtel, J. Ravichandran, S. T. Pantelides, P. E. Hopkins, "Ruddlesden-Popper chalcogenides push the limit of mechanical stiffness and glass-like thermal conductivity in single crystals", *Nature Communications* **16**, 6104 (2025).
2. C. Brahms, L. Zhang, X. Shen, U. Bhattacharya, M. Recasens, J. Osmond, T. Grass, R. W. Chhajlany, K. A. Hallman, R. F. Haglund, S. T. Pantelides, M. Lewenstein, J. C. Travers, A. S. Johnson, "Decoupled few-femtosecond phase transitions in vanadium dioxide", *Nature Communications* **16**, 3714 (2025).
3. Q. Y.-P. Wang, X.-L. Shi, X. X. Li, E. Zhao, Z.-G. Chen, J. Zou, K. Leng, Y. Cai, L. Zhu, S. T. Pantelides, J. Lin, "Constrained patterning of orientated metal chalcogenide nanowires and their growth mechanism", *Nature Communications* **15**, 60744 (2024).
4. H. A. Walker, E. R. Hoglund, D.-L. Bao, Md K. Hussain, H. Ni, A. Mamun, J. Baxter, A. Khan, J. D Caldwell, P. E Hopkins, J. A. Hachtel, S. T. Pantelides, "Integration of machine-learned force fields for phonon DOS in nanoscale heterostructures", *Microscopy and Microanalysis* **30**, ozae044.212 (2024).
5. M. J. Swamynadhan, A. O'Hara, S. Ghosh, S. T. Pantelides, "Engineering collinear magnetization in hexagonal LuFeO_3 and magnetoelectric control of skyrmions in hexagonal 2D epilayers", *Advanced Functional Materials* **34**, 2400195 (2024).
6. X. Zhang, Y.-T. Zhang, Y.-P. Wang, S. Li, S. Du, Y. Y. Zhang, S. T. Pantelides, "Structural and mechanical properties of monolayer amorphous carbon and boron nitride", *Physical Review B* **109**, 174106 (2024).
7. S. T. Pantelides, "Combining electron microscopy with atomic-scale calculations—A personal perspective", *Chinese Physics B* **33**, 120704 (2024).
8. N. G. Richardson, A. O'Hara, and S. T. Pantelides, "Generation of out-of-plane ferroelectric behavior in a one-atom-thick monolayer", *2D Materials* **11**, 035019 (2024).
9. J. Matson, S. Wasserroth, X. Ni, M. Obst, K. Diaz-Granados, G. Carini, E. M. Renzi, E. Galiffi, T. G. Folland, L. M. Eng, J. M. Klopff, S. Mastel, S. Armster, V. Gambin, M. Wolf, S. C. Kehr, A. Alù, A. Paarmann, J. D. Caldwell, *Nature Communications* **14**, 5240 (2023).
10. S. Li, Y.-P. Wang, S. Ning, K. Xu, S. T. Pantelides, W. Zhou, J. Lin, "Revealing 3D ripple structure and its dynamics in freestanding monolayer MoSe_2 by single-frame 2D atomic image reconstruction", *Nano Letters* **23**, 1298 (2023).

Quantum-Coherent Manipulation of Two-Level Systems via Wavefunction Engineering in a Scanning Electron Microscope

William Putnam, University of California, Davis

Keywords: electron microscopy, light-matter interaction, quantum information

Research Scope

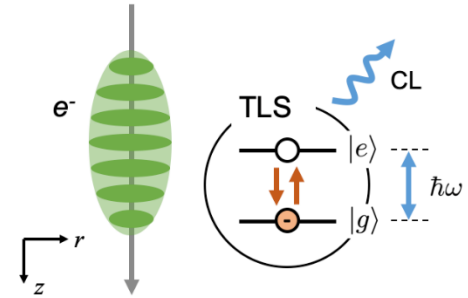
Two-level systems are ubiquitous in materials science and physics. For example, the fundamental building block of a quantum computer, the *qubit*, is a two-level system. Two-level systems are manipulated with oscillating electromagnetic waves. However, such electromagnetic control has limitations; for instance, the diffraction limit restricts the spatial localization of these controlling waves. In this project, we will explore the manipulation and control of two-level systems in an entirely new way, with engineered electron wavefunctions in a scanning electron microscope (SEM).

Future Plans

Our hypothesis is that by using engineered, modulated electron wavefunctions, we can coherently control two-level systems (TLSs), specifically quantum defects. Furthermore, this control should occur at the nanometer spatial scale and potentially the attosecond temporal scale. In essence, our hypothesis is the hypothesis of *free-electron-bound-electron resonant interactions* (FEBERI). FEBERI was proposed in 2020 [1], and these interactions have yet to be demonstrated experimentally.

The physics underlying FEBERI is illustrated in Fig. 1. A modulated, bunched electron packet passes near a TLS. The electron packet has density modulations that match the period of the TLS resonance, $2\pi/\omega$. Additionally, the electron carries an evanescent near field, and this near field (just like the electron density) is modulated with a period of $2\pi/\omega$. As the electron passes the TLS, this near field couples to the TLS and can control and manipulate the TLS just like a normal electromagnetic wave, albeit with the potentially $\approx 1\text{-nm}^2$ transverse spot size of the electron. The passing electron can thereby drive a population transfer from the ground to the excited state. Importantly, this population transfer can be detected via enhanced fluorescence, that is, from enhanced cathodoluminescence (CL). In our experiments, CL

(a) ELECTRON AND TLS



(b) PHASE-LOCKED ELECTRONS

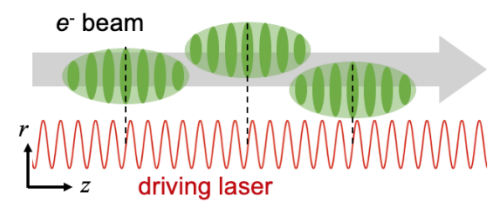


Figure 1: Two-level systems and FEBERI. (a) A two-level system (TLS) interacting with an electron wavefunction that has been bunched by a modulating laser. The density modulation of the electron matches the resonant frequency of the TLS, ω . The electron drives population transfer in the TLS yielding enhanced cathodoluminescence (CL). (b) Multiple electrons modulated by the same laser will be locked in phase (by the long-coherence length laser) even if they arrive at different times; so, multiple electrons can coherently excite a

will be our primary experimental probe. (We should note that, more generally, the electron density modulations can be a *subharmonic* of the TLS resonance, *i.e.*, a frequency of ω/n , for integer n .)

Our experiments will take place in a customized scanning electron microscope (SEM). The SEM will consist of a continuous electron current that passes through a modulating “membrane”. The membrane will likely be a silicon nitride membrane, which has been shown to support near fields that can accelerate and decelerate passing electrons [2]. In our initial experiments, the membrane will be illuminated by a picosecond-duration laser with a wavelength of ≈ 1200 nm. (This laser pulse train will be derived from a Cr:ZnSe/S, mid-infrared laser system.) Passing the membrane, an electron packet will receive momentum kicks from the illuminating laser light. With our high-current SEM, we can ensure, with high probability, that a passing electron will always encounter a laser pulse. As the electron propagates, the modulated momentum will cause parts of the electron packet to accelerate and parts to decelerate. This acceleration and deceleration will reshape the electron wavefunction into a series of ultrashort (≈ 1 -fs duration) packets [3]. In the microscope, this modulated electron wavefunction will interact with a sample consisting of TLSs. Specifically, in our first experiment, we will use NV centers. NV⁰ centers in diamond have a long-lifetime (>10 -ns) transition around 575 nm. This transition will be excited by the second harmonic content of the bunched electron wavefunction. The resulting fluorescence from the NV-center sample will be collected in a standard cathodoluminescence system.

This project will consist of three bold goals. First and foremost, we will study the current-scaling of the cathodoluminescence. If our hypothesis, that is, the FEBERI hypothesis, is correct, we should see that the CL signal will scale with the *square* of the number of electrons. This is because we anticipate that the electrons will *coherently* transfer population from the ground state to the excited state. These experiments will require careful tuning of our engineered electron wavefunctions; additionally, we will require TLSs, like NV centers, with coherence times long enough to interact with multiple electron packets. Second, we will use our specialized SEM to study the spatial dependence of the coupling to the TLS. Specifically, we will position our electron probe at different locations surrounding our quantum defects and study the spatial profile of the coupling at nanometer-scale resolution. Third, we will simultaneously drive our TLS sample with an exciting optical signal. By adjusting the phase of this signal, relative to our modulating laser light, and probing with our modulated electrons, we will study the sub-cycle, *i.e.* attosecond, dynamics of the population transfer in our TLSs.

References

1. A. Gover and A. Yariv, *Free-Electron-Bound-Electron Resonant Interaction*, Phys. Rev. Lett. **124**, 064801 (2020).
2. D. Nabben, J. Kuttruff, L. Stolz, A. Ryabov, and P. Baum, *Attosecond Electron Microscopy of Sub-Cycle Optical Dynamics*, Nature **619**, 63 (2023).
3. A. Feist, K. E. Echternkamp, J. Schauss, S. V. Yalunin, S. Schafer, and C. Ropers, *Quantum coherent optical phase modulation in an ultrafast transmission electron microscope*, Nature **521**, 200 (2015).

Nano-optical imaging, spectroscopy, and control of quantum materials

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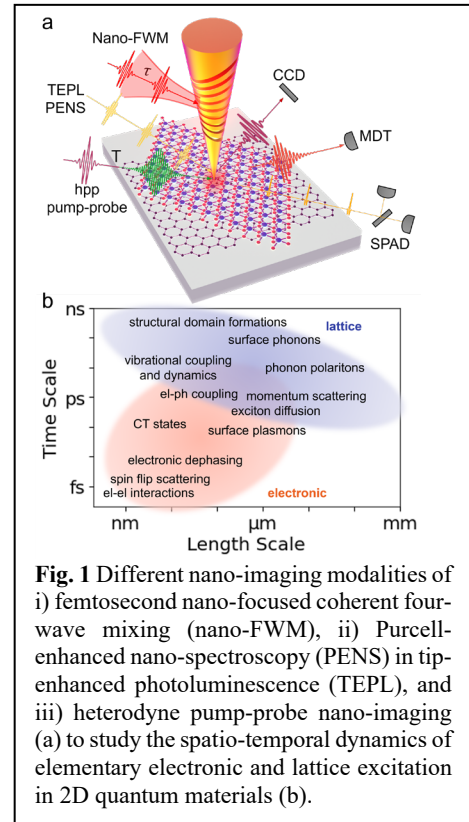
Keywords: Optical nano-imaging, ultrafast spectroscopy, quantum dynamics, 2D materials

Research Scope: Optical nano-probe imaging of 2D quantum materials. The combination of scanning probe microscopy with optical spectroscopy provides for deep sub-diffraction ***nano-imaging and -spectroscopy*** to resolve the microscopic origin of a macroscopic material response otherwise obscured by spatial and ensemble averaging in conventional far-field spectroscopy. Beyond identifying underlying heterogeneities, many phenomena in nano- and meta-materials, quantum nano-devices, or quantum phases in novel Moiré superlattices are by their very nature nanoscale phenomena which can only *meaningfully be understood if studied with nano-localized spectroscopy*.

The fascinating properties of ***2D quantum materials*** and their heterostructures from superconductivity to 2D magnetism and topological phases emerge from *coupling* between the many degrees of freedom tunable by, e.g., choice of material, layer stacking, relative orientation, gating, or strain. However, understanding and controlling the interplay of many *intra- and interlayer interactions* that gives rise to the complex quantum phases has remained a major experimental challenge.

The goal of this project is to resolve the competing coupling mechanisms in these materials through ***ultrafast nano-imaging*** and ***nano-cavity enhanced spectroscopy*** (Fig. 1). Here we *actively perturb* the material response via nano-cavity Purcell enhancement, nano-localized force and strain control, near-field momentum, coherent and collective excitation, and far-from equilibrium pump-pulse excitation. This allows for the *selective modification* of one or more of the resonance excitations to *disentangle coupled* internal parameters and resolve their relative contributions to the system response that are difficult or impossible to separate otherwise. We are therefore not merely extending far-field spectroscopy to nanoscale resolution, rather we are redefining how near-field enhancement and localization, momentum, and tip-induced strain can be used to *selectively* probe quantum dynamics inaccessible to far-field techniques.

Recent Progress: By controlling tip-sample distance together with tip plasmon and optical antenna resonances we deterministically modify mode volume and near-field coupling strength. In particular, in ***tip-enhanced nano-cavity spectroscopy*** and imaging, the Purcell-enhanced radiative emission allows for quantum state interference and emission control. In its implementation in linear *tip-enhanced photoluminescence (TEPL)*, *nonlinear two-photon photoluminescence (2PPL)*, and *coherent FWM*, we disentangle and even control competing relaxation pathways otherwise difficult to separate with conventional spectroscopy techniques. This allowed us to resolve *coherent dynamics*, *intra- and inter-layer coupling* and scattering, and *substrate interactions* in 2D quantum and complex materials. Specifically, we established ultrafast pump-



probe nano-imaging with far from equilibrium excitation [2,4,8]. In applications to graphene, transition metal dichalcogenides (TMD), and corresponding heterostructures, we were able to resolve the coupled few-fs dynamics between bright, interlayer, and even spin- or momentum-dark excitons [3], resolved interlayer energy transfer dynamics [5], the heterogeneity of ultrafast coherent exciton dynamics [1,7,9], gate tuning hybrid plasmon and phonon polaritons [6], and achieved electric field control of chirality [10]. In the following we highlight four examples:

1. Ultrafast exciton dynamics in WSe₂: decoherence and heterogeneity [9]. In order provide further insight into the exciton dynamics in TMDs associated with intra- and interlayer coupling and the role of heterogeneities, in this work we perform spatio-temporal adiabatic nano-focused FWM imaging of the exciton coherence in WSe₂.

No ultrafast nanoimaging experiments have yet addressed the relationship between exciton coherence and spatial heterogeneity at room

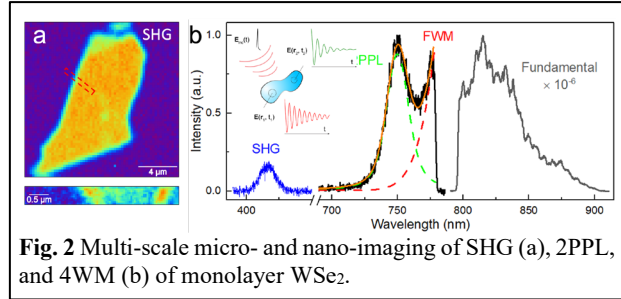


Fig. 2 Multi-scale micro- and nano-imaging of SHG (a), 2PPL, and 4WM (b) of monolayer WSe₂.

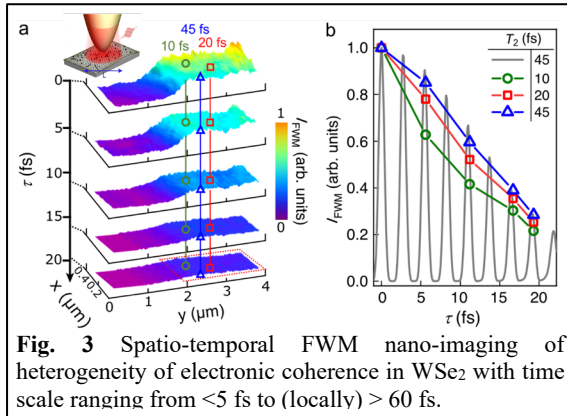


Fig. 3 Spatio-temporal FWM nano-imaging of heterogeneity of electronic coherence in WSe₂ with time scale ranging from <5 fs to (locally) > 60 fs.

defect and disorder induced localization protecting coherence. The ongoing correlative multi-dimensional coherent spectroscopy as well as Moiré confined excitons will further address these outstanding questions.

2. Interlayer coupling and dynamics [8]. In the combination of *tip-enhanced nano-cavity* spectroscopy with *adiabatic nonlinear nano-imaging* we extended our previous development of *nanocavity clock spectroscopy (NCS)* into the nonlinear optical regime, as a universal nano-optical approach to *distinguish and resolve intra- and inter-layer coupling* in 2D heterostructures.

In layer stacked 2D van der Waals heterostructures the mechanisms underlying *interlayer coupling*, including charge and energy transfer, are still not clear, particularly their sensitivity to spatial heterogeneities in the form of defects, edges, grain

temperature. Here, we performed the first **spatio-spectral and spatio-temporal coherent FWM nano-imaging** (Fig. 2). In two-pulse correlation nano-FWM imaging, we probe the electronic coherence in monolayer WSe₂ with simultaneous nm-spatial and fs-temporal resolutions. We observe **room-temperature dephasing times** of the nonlinear polarization ranging from $\lesssim 5$ fs to $\gtrsim 45$ fs (**Fig. 3**), locally even exceeding >60 fs. While this demonstrates a high sensitivity with respect to defects, the longest coherence times exceed what is expected theoretically, suggesting the possibility of

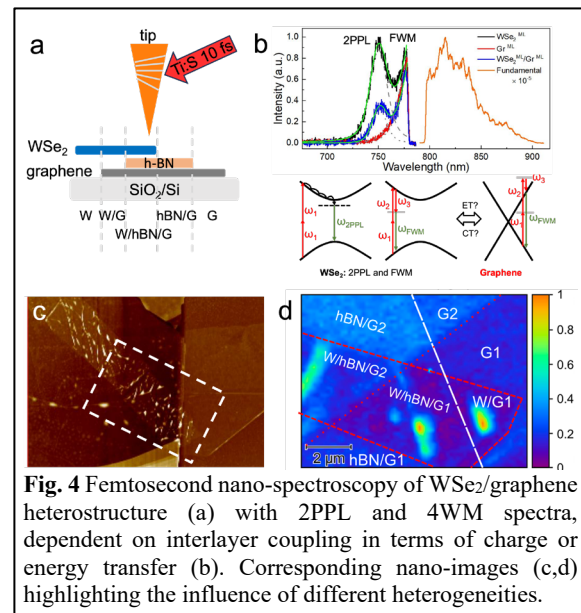


Fig. 4 Femtosecond nano-spectroscopy of WSe₂/graphene heterostructure (a) with 2PPL and 4WM spectra, dependent on interlayer coupling in terms of charge or energy transfer (b). Corresponding nano-images (c,d) highlighting the influence of different heterogeneities.

boundaries or strain. Given the limited spatial resolution of previous approaches, it raises questions about the role of spatial heterogeneities and the distinction between interlayer charge and energy transfer.

Here, we perform spatio-spectral tip-enhanced nanoimaging of coherent FWM and incoherent 2PPL in WSe₂/graphene (**Fig. 4**). We observe a high degree of spatial heterogeneity associated with folds, wrinkles, bubbles, and other defects, which we resolve with ≈ 50 nm spatial resolution. We *isolate the homogeneous response* in clean sampling regions and distinguish between charge versus energy transfer by inserting hexagonal boron nitride (hBN) as an interlayer spacer, selectively blocking the charge transfer channel. Based on the identification of energy transfer controlling the FWM response, we then take advantage of NCS as a tool to *separate competing relaxation pathways* through their selective and tip-sample distance-dependent modification in z-scan nano-spectroscopy (**Fig. 5**). From the *multispectral nano-FWM and 2PPL*, we then quantify the energy transfer time as $\tau \approx 0.35$ ps.

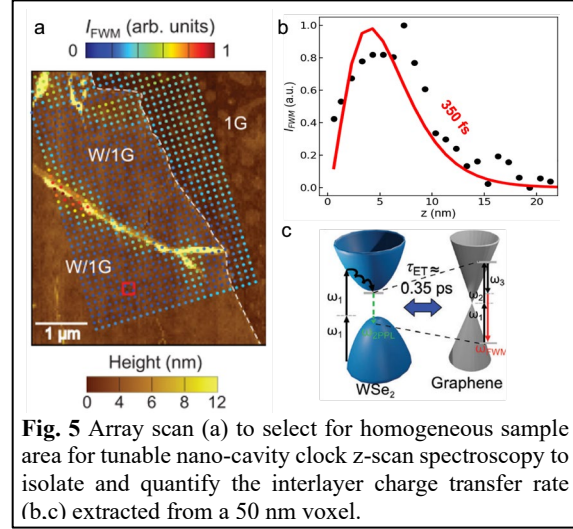


Fig. 5 Array scan (a) to select for homogeneous sample area for tunable nano-cavity clock z-scan spectroscopy to isolate and quantify the interlayer charge transfer rate (b,c) extracted from a 50 nm voxel.

Our results are consistent with an Auger-type process as a form of dipole (WSe₂) – monopole (graphene) interaction in agreement with recent ARPES work performed on a judiciously prepared one-off sample. In contrast, our complementary approach based on **nano-cavity clock spectroscopy** is broadly applicable to micro- to nano-scale samples structures, and able to quantify complex and competing dynamics of multi-excitonic systems which we investigate currently.

3. Second-harmonic generation (SHG) [3]: To gain further insight into the ultrafast relaxation dynamics in TMDs, we perform ultrafast circular polarization SHG pump-probe microscopy. Building on our previous work on SHG nano-crystallography in MoS₂ and in order to extend specificity with respect to *spin degrees of freedom*, we now resort to the sensitivity of SHG with respect to *time-reversal symmetry* using circular polarized excitation.

Strong spin-orbit coupling and the broken inversion symmetry in TMD monolayers couple the electron spin to the valley pseudospin giving rise to inequivalent K and K' points of opposite order with spin-split valence and conduction bands (**Fig. 6**).

Applied to monolayers of WSe₂, in femtosecond SHG pump-probe microscopy (**Fig. 6a,b**), with K valley-selective circular pump excitation and K' valley-selective circular probe SHG we resolve two time constants of ~ 40 fs and ~ 270 fs (**Fig. 6c**). We attribute these times, respectively, to the fast formation of momentum-dark excitons by spin-

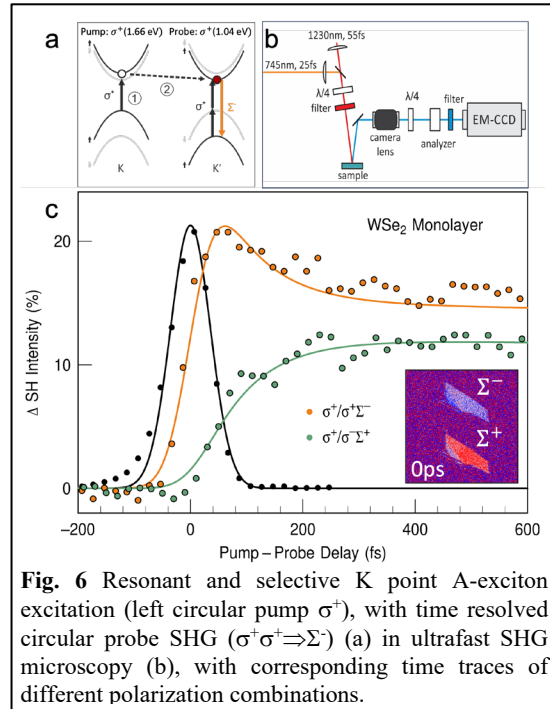


Fig. 6 Resonant and selective K point A-exciton excitation (left circular pump σ^+), with time resolved circular probe SHG ($\sigma^+ \sigma^+ \rightarrow \Sigma^-$) (a) in ultrafast SHG microscopy (b), with corresponding time traces of different polarization combinations.

conserving scattering and the slower formation of spin-dark excitons by spin flip scattering induced by strong electron-phonon coupling.

4. Gate-tuning MoO₃/graphene IR s-SNOM [6]: Gate-modulation of hybrid plasmon-phonon polaritons (HPPPs) of single-layer α -MoO₃ with graphene allows for tuning the infrared nano-photonic response of nano-focusing and negative refraction. In IR nano-imaging we resolved and gate-modulated wavelength, amplitude, and dissipation rate of the HPPPs in both single-layer and twisted bilayer α -MoO₃/graphene heterostructures (**Fig. 7**). In theory collaboration with Andrea Alù (CUNY) we could assign the behavior to an intricate interplay of gate-dependent in-plane and out-of-plane components of the HPPP complex momentum associated with the dependent optical conductivity of monolayer graphene.

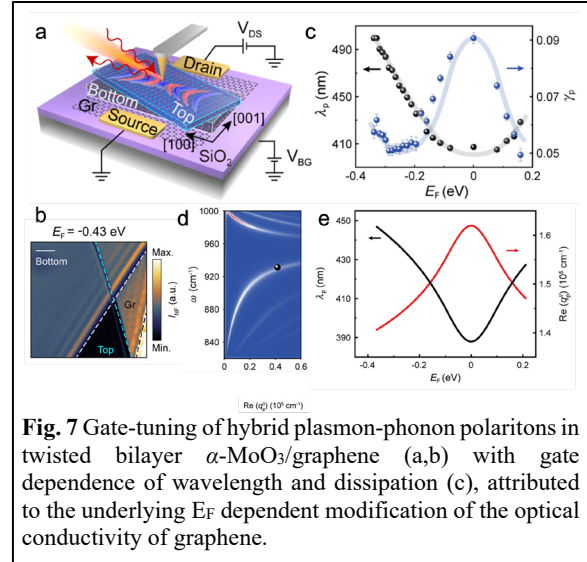


Fig. 7 Gate-tuning of hybrid plasmon-phonon polaritons in twisted bilayer α -MoO₃/graphene (a,b) with gate dependence of wavelength and dissipation (c), attributed to the underlying E_F dependent modification of the optical conductivity of graphene.

Future Plans: In ongoing and future experiments we will image and resolve i) competing quantum dynamics of *intra- and interlayer excitons* in transition metal dichalcogenides (TMDs) monolayers and their heterostructures through active control of radiative and non-radiative rates in Purcell-enhanced nano-imaging (PENS), ii) *exciton coherence, localization, and nonlocality* in correlative few-femtosecond four-wave mixing (nano-FWM) spatio-temporal nano-imaging in TMDs and graphene, and iii) far-from-equilibrium *interfacial thermal transport* and *intra-excitonic 1s2p* transitions in heterodyne pump IR-probe nano-imaging.

Publications (supported by BES, past 2 years)

- [1] B. G. Whetten, E. S. Kane, A. Belyanin, and M. B. Raschke, *Nonlinear nano-imaging of ultrafast coherence and coupled quantum dynamics*, Annalen der Physik, (in preparation, invited review).
- [2] R. Wilcken, B. L. Esses, and M. B. Raschke, Pump-probe nano-imaging: ultrafast movies resolving far-from-equilibrium and excited state dynamics in functional materials, Nature Reviews Methods Primers (submitted).
- [3] M. Axt, B. G. Whetten, G. Mette, M. B. Raschke, J. GÜdde, and U. Höfer, Ultrafast intervalley exciton scattering in monolayer WSe₂ probed by circular dichroism pump-probe second-harmonic microscopy, (submitted).
- [4] Z. Zhao, V. Kravtsov, Z. Wang, Z. Zhou, L. Dou, D. Huang, Z. Wang, X. Cheng, M. B. Raschke, and T. Jiang, Applications of ultrafast nano-spectroscopy and nano-imaging with tip-based microscopy, eLight **5**, 1 (2025).
- [5] W. Luo, R. Song, B. G. Whetten, V. Kravtsov, D. Huang, X. Cheng, T. Jiang, A. Belyanin, T. Jiang, and M. B. Raschke, Nonlinear nano-imaging of interlayer coupling in 2D graphene-semiconductor heterostructures, Small **20**, 2307345 (2024).
- [6] Z. Zhou, ... , M. B. Raschke, Andrea Alù, A. and T. Jiang, Gate-tuning hybrid polaritons in twisted α -MoO₃/graphene heterostructures, Nano Lett. **23**, 11252 (2023).
- [7] J. Zhu, Ultrafast nano-movie of graphene, Nature Nanotechnol. **18**, 1263 (2023).
- [8] M. B. Raschke, M. Schubert, P. Narang, and A. Paarmann, Optical nanoprobe imaging and spectroscopy, Appl Phys. Lett. **123**, 230401 (2023).
- [9] W. Luo, B. G. Whetten, V. Kravtsov, A. Singh, Y. Yang, D. Huang, X. Cheng, T. Jiang, A. Belyanin, M. B. Raschke, Ultrafast nano-imaging of electronic coherence of monolayer WSe₂ Nano Lett. **23**, 1767 (2023).
- [10] P. Behera, M. A. May, et al., Electric field control of chirality in a ferroelectric vortex phase, Science Advances **8**, eabj8030 (2022).

Scanning Thermal Microscopy for Probing Nanoscale Energy Transport, Dissipation and Quantum Friction

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Keywords: Scanning Thermal Microscopy, Calorimetric Scanning Probes, Near-Field Radiation, Internal Cooling, Thermoelectrics

Research Scope

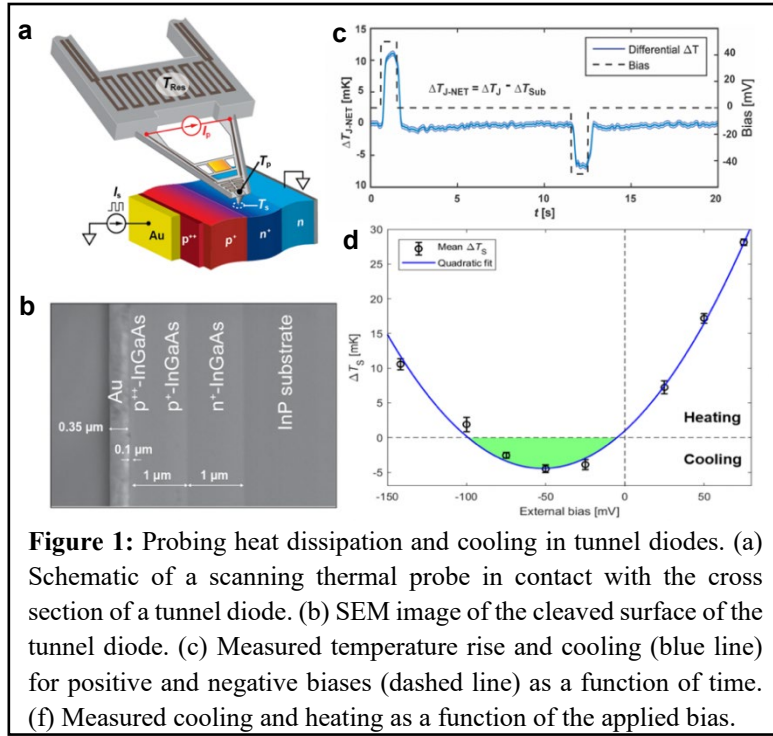
In this work we significantly advance scanning probe microscopy and thermometry tools and employ them to answer a number of crucial questions related to energy transport in nanoscale devices and gaps. Our recent advances in scanning thermal microscopy have demonstrated how temperature fields can be probed quantitatively with nanometer spatial resolution and millikelvin temperature resolution. By leveraging these advances, we have recently studied how quantum mechanical tunneling can be engineered for achieving internal cooling in electronic devices. Further, we have leveraged custom developed scanning thermal probes to explore how transport of thermal energy via evanescent electromagnetic modes (near-field thermal radiation) can result in extremely large heat fluxes. Recently, via careful experiments, we established the upper limits to achievable enhancements via such evanescent modes. Further, we performed first experiments to quantify near-field thermal radiation at cryogenic temperatures and its use for thermal management. Finally, we have explored how the thermoelectric properties of molecular junctions can be controlled via quantum interference effects.

Recent Progress

Observation of Internal Cooling in Tunnel Diodes (A. Reihani *et al.*, Phys. Rev. Lett. (2024)):

In recent work we developed novel scanning thermal microscopy tools that enable temperature measurements with nanometer spatial resolution and millikelvin thermal resolution and obtained first direct quantitative measurements of the cross-sectional temperature profiles of fully functional, cleaved InGaAs-based tunnel diodes. Tunnel diodes represent the first quantum-electron devices that were developed and for decades have been widely used in high-speed electronics. These applications exploit the property of a negative slope in the current-voltage curve resulting from the existence of a range of voltage biases for which tunneling is suppressed following a bias range for which tunneling is strongly favored. However, there has been little research on the energy conversion processes associated with electron transport in Esaki diodes. In recent joint work, we demonstrated that energy filtering associated with tunneling results in electronic cooling that is capable of suppressing the temperature of the semiconductor lattice. Specifically, we showed that localized refrigeration can be realized in a semiconductor diode fabricated in III-V semiconductor materials with cooling power densities of $\sim 5 \text{ W/cm}^2$, comparable to the power density encountered in photovoltaic and integrated circuit applications.

In Fig. 1 we show the schematic of a cleaved tunnel diode being probed using a scanning thermal probe (Fig. 1a) along with an SEM image (Fig. 1b) of the cleaved device used in our experiments.



(2022); S. Yan *et al.*, *Phys. Rev. Lett* (2023); Y. Luan *et al.*, *To be submitted*): Groundbreaking theoretical work pertinent to radiative heat transfer in nanoscale gaps (i.e., in the near-field) was first reported by Polder and Van Hove (Polder and Van Hove, *Phys. Rev. B* (1971)), when they quantitatively predicted, using the theory of fluctuational electrodynamics (FED), the heat transfer rates between planar metallic surfaces. From this work two seminal conclusions were drawn that suggested (1) that, upon decreasing the gap-size from microns to ~ 100 nm, heat transfer rates would increase exponentially with reduced gap size by several orders of magnitude — even exceeding the far-field Blackbody limit — due to contributions from evanescent modes and (2) that for gap-sizes below 100 nm the heat flux increases rather slowly with decreasing gaps (i.e. saturates) due to the presence of a characteristic cut-off wave vector. Despite the central importance of these theoretical predictions for the overall understanding of near-field radiative heat transfer, no consistent, replicated experimental evidence has been established, rather a number of contradictory measurements have been reported, some going as far as seriously challenging the validity of the theory of fluctuational electrodynamics.

Recently (R. Mittapally *et al.*, *Nano Lett.* (2022)), we explored the following questions regarding nanoscale radiative heat transfer (RHT): 1) What are the theoretical limits to nanoscale radiative heat transfer rates, and 2) Can the theoretically predicted limits be experimentally confirmed and how close, in magnitude, can real devices match the predictions for a given class of materials? Specifically, we first established a theoretical framework that allows us to explore the limits to near-field RHT for phonon polaritonic materials. By optimizing for maximum RHT over the space of practical polaritonic materials, we showed that properly chosen materials can increase the RHT approximately 5-fold compared to SiO_2 (the material which up to now was believed to support the highest RHT rate) at a given gap size. Next, we experimentally probed near-field RHT in three carefully selected material systems—doped Si, Al_2O_3 and MgF_2 that closely approximate the theoretically predicted optimal properties—using specifically designed and meticulously micro-

In one of our experiments, the local temperature change in tunnel junctions was measured by applying three-level voltage pulses. The measured temperature change of the tunnel diode region, obtained after suitable averaging, is also shown in Fig. 1c. Additional experiments were also performed to understand the bias dependence of cooling (see Fig. 1d). Our data reveal for the first time that internal refrigeration (cooling) can be achieved in carefully engineered tunnel diodes and can locally cool the lattice, offering a new approach for cooling semiconductor devices.

Probing Energy Transport via Photons in Nanoscale Gaps (R. Mittapally *et al.*, *Nano Lett.*

transport can dramatically enhance heat transfer we could also demonstrate how thermal transport can be tuned by taking advantage of superconducting phase transitions to enable the development of thermal diodes. This work (Y. Luan, *et al.*, “A Cryogenic Near-Field Thermal Diode Using Superconducting Phase Transitions”) is now being submitted for review and publication.

Probing the Effect of Quantum Interference Effects on Thermoelectric Properties (*H. Xu et al., JACS (2023)*; *S. Yan et al., Nanoscale (2024)*): In recent years, the development and study of molecular junctions has seen renewed interest for two reasons: (1) Molecular junctions may lead to the development of new organic-based, thermoelectric devices. (2) Due to their structure featuring discrete energy levels molecular junctions allow to test and to verify the theories of quantum physics.

In the work of *H. Xu et al., (JACS (2023))*, we systematically explored the effect of quantum interferences on thermoelectric properties of molecular junctions. We designed and synthesized two new classes of porphyrins, P1 and P2 and their Zn complexes, Zn–P1 and Zn–P2. Past theory suggests that P1 and Zn–P1 feature destructive quantum interference in single-molecule junctions with gold electrodes and may thus show high thermopower, while P2 and Zn–P2 do not. Our detailed experimental single-molecule break-junction studies of conductance and thermopower revealed that the electrical conductance of the P1 and Zn–P1 junctions is relatively close, and the same holds for P2 and Zn–P2, while there is a 6-fold reduction in the electrical conductance between P1 and P2 type junctions. Further, we observed that the thermopower of P1 junctions is slightly larger than for P2 junctions, while Zn–P1 junctions show the largest thermopower and Zn–P2 junctions show the lowest. However, the predicted large difference in conductance and thermopower values between Zn–P1 and Zn–P2 derivatives, suggested in previous model calculations, is not supported by our experimental and theoretical findings, highlighting the need for improved approaches for predicting thermoelectric properties of molecular junctions.

In a recent work (*S. Yan et al., Nanoscale (2024)*), we investigated how electron-donating and electron-withdrawing substituents and their positions could influence both the electrical conductance and thermopower on a organic framework and to see if these properties could be improved compared to the parent *meta*-OPE that we previously investigated. We also explored how the substituents affect the destructive interference. We found one combination of substituent and position that increased the generation of thermopower in the Au–*meta*-OPE3–Au single molecular junctions by almost 50% compared the parent unsubstituted Au–*meta*-OPE3–Au single molecular junction. Interestingly, at the same time, that junction showed the lowest electric conductance, showing that within a series of derivatives differentiating in the type and position of one substituent, it is possible to tune the electric conductance and thermopower separately.

Future Plans

In the future we plan to employ scanning thermal microscopy tools to obtain insights into thermal transport in electronic and phononic devices. Specifically, we will seek to understand how phonon transport can be tuned by nanoscale manipulation of the structure of devices. Further, we will seek to develop novel scanning calorimetric techniques to understand heat transport and cooling at the atomic and molecular scales. Finally, we will develop new approaches to systematically quantify quantum friction—a topic that is of intense theoretical interest and vigorously debated, but with very little experimental data to date.

Publications

1. Y. Luan, S. Yan¹, J. Guan, A. Majumder, Y. Isshiki, Z. Wang, R. Mali, R. Yu, S. Fan, P. Reddy, and E. Meyhofer, “A Cryogenic Near-Field Thermal Diode Using Superconducting Phase Transitions” (to be submitted)”
2. A. Reihani, Z. Li, J. Guan, Y. Luan, S. Yan, J. Xue, E. Meyhofer, P. Reddy and R. J. Ram, “Cooling of Semiconductor Devices via Quantum Tunneling” *Physical Review Letters* **133**, 266301 (2024)
3. J. W. Lim, A. Majumder, R. Mittapally, A-R. Gutierrez, Y. Luan, E. Meyhofer and P. Reddy, “A nanoscale photonic thermal transistor for sub-second heat flow switching” *Nature Communications* **15**, 5584 (2024)
4. Y. Luan, S. Yan, K. Panda, A. Majumder, J. Guan, R. Mittapally, E. Meyhofer and P. Reddy, “The Metal–Insulator Transition in Vanadium Oxide Nanofilms Enables Microkelvin-Resolution Thermometry” *Nano Letters* **24**, 7048 (2024)
5. S. Yan, Y. Luan, H. Xu, H. Fan, L. Martin, A. K. Gupta, H. Linke, E. Meyhofer, P. Reddy, F. Pauly, K. Wärmarm, “How substituents tune quantum interference in meta-OPE3 molecular junctions to control thermoelectric transport” *Nanoscale* **16**, 13905 (2024)
6. S. Yan, Y. Luan, J. W. Lim, R. Mittapally, A. Reihani, Z. Wang, Y. Tsurimaki, S. Fan, P. Reddy and E. Meyhofer, “Surface phonon polariton-mediated near field radiative heat transfer at cryogenic temperatures” *Physical Review Letters* **131**, 196302 (2023)
7. H. Xu, H. Fan, Y. Luan, S. Yan, L. Martin, R. Miao, F. Pauly, E. Meyhofer, P. Reddy, H. Linke, K. Warnmark, “Effect of Destructive Quantum Interference on the Electrical Conductance and Thermopower of Molecular Junctions Containing Centrally Substituted meta-OPE3 Derivatives” *Journal of American Chemical Society* **43**, 23541 (2023)
8. R. Mittapally, J. W. Lim, E. Meyhofer, P. Reddy and E. Meyhofer “Quantifying the Spatial Distribution of Radiative Heat Transfer in Sub-Wavelength Planar Nanostructures” *ACS Photonics* **10**, 2474 (2023)
9. A. Majumder, D. Thompson, P. Reddy, and E. Meyhofer, “Quantifying the Spatial Distribution of Radiative Heat Transfer in Sub-Wavelength Planar Nanostructures” *ACS Photonics* **4**, 1144 (2023)
10. R. Mittapally, J. W. Lim, L. Zhang, O. D. Miller, P. Reddy, and E. Meyhofer, “Probing the limits to near-field heat transfer enhancements in phonon-polaritonic materials” *Nano Letters* **23**, 2187 (2023)

Programming and imaging active defect arrays in layered materials via atomic lock-on

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Keywords: Scanning transmission electron microscopy, beam-induced modification, optically active defects, CrSBr, van der Waals semiconducting magnet

Research Scope

The research scope of this project is to develop a quantitative understanding of electron beam-solid interactions in a magneto-correlated material, CrSBr, and then use programmed beam motions to form arrays of functional defects in the material. This research direction is motivated by the importance of creating atomic configurations with precisely defined structure and composition, as a key objective for enhancing the properties and functionality of materials. This is especially relevant in electronic materials, where individual defects with few-level electronic states that are able to emit single photons offer a foundation for quantum photonic hardware. Even more exciting possibilities are presented by large arrays of closely spaced, identical defects, as they can act as strongly correlated physical systems through interactions between the structures. Practical use of individual defect engineering to form large-scale quantum systems is currently limited by the challenges of reproducibility and scalability in creating and measuring such arrays. Our research is based on an electron microscopy strategy to manipulate large numbers of individual atoms, aided through deep learning-driven precision in electron beam control. We are using this approach to create arrays of specific defects that are intended to program new functionality in thin CrSBr crystals. We are simultaneously extending our beam-patterning experiments to image and quantify the kinetics and mechanisms that control larger scale structural transformations of CrSBr.

Recent Progress

In the first year of the project we focused on measuring beam-solid interactions in CrSBr and developing our beam steering capabilities to enable formation of large arrays of customizable defects in the material. We selected CrSBr for our experiments because its stability in air coupled with its highly anisotropic electronic and magnetic properties make it a suitable host for quantum phenomena [1, 2]. Furthermore, CrSBr is known to undergo a structural transformation when irradiated by an electron beam [3]. CrSBr consists of buckled sheets of Cr and S with Br above and below; irradiation with 200kV electrons in the [001] direction results in correlated motions of the Cr atoms, while the S/Br framework remains unaffected. This structural transformation is the basis for the on-demand material modifications we aim to achieve in this project.

Beam-solid interactions in CrSBr:

We used a focused electron beam scanned over 10x10nm regions to drive and measure structural changes in multilayer CrSBr crystals. Initial results are shown in Figure 1. Each image represents irradiation in a different direction in the CrSBr crystal, using samples prepared with focused ion beam milling to give normals [100], [010] and [110]. From these data we can track the collective movements of atoms and the development of lattice strain by measuring intensity and atomic position in time series recorded during formation of the new structure.

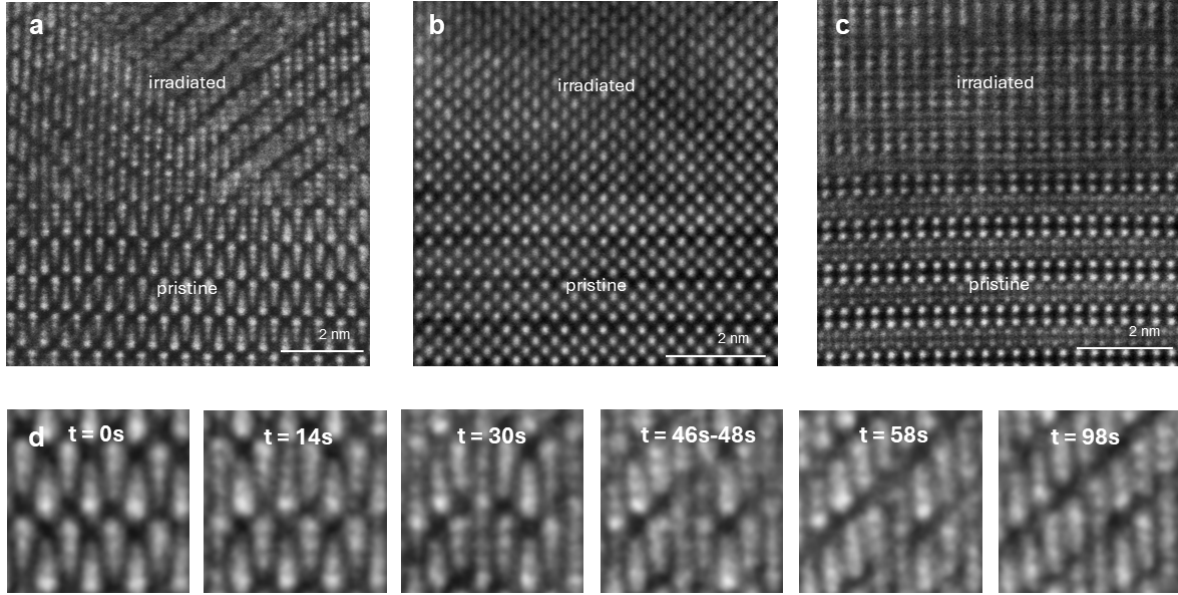


Figure 1. Cross sectional images through the layered semiconductor CrSBr. Samples were prepared by FIB cuts through exfoliated crystals. (a-c) Structural transformations induced by irradiation for 100 s with beam direction [100], [010] and [110] respectively. (d) Time series during irradiation in the [100] direction. STEM imaging was performed with a probe-corrected Thermo Fisher Scientific Themis Z G3 60-200 kV S/TEM operated at 200 kV with a convergence semi-angle of 19 mrad, probe size 0.6–1 Å, collection semi-angle 63–200 mrad, beam current 60 pA, frame size 1024×1024 pixel and dwell time 500 ns/pixel, corresponding to an electron dose $\sim 130 \text{ pm}^{-2}$ for (a-c).

A key observation from Figure 1 is that the beam-induced structural transformation depends on the orientation along which the crystal is irradiated. We found that the structural transformations generally involve large (unit cell size) motions of Cr columns and small or zero motions of the S and Br columns. In this sense, the transformations appear similar to that known from our initial experiments with irradiation in the [001] direction. Irradiation parallel to [010] and [110] results in a defect-free transformed structure (Fig. 1b, c) but symmetry-related variants are formed on irradiation parallel to [001] (Fig. 1a). Furthermore, if we initiate the transformation in one area, progressive motion of the scan area can extend one variant into the untransformed crystal. This may enable tuning of the magnetic texture of CrSBr for potential device applications.

We hypothesize that the directional dependence of the transformation arises from channeling of electron intensity along the atomic columns. An alternative explanation is that the transformation may be sensitive to differences in strain relaxation in the thin foil. We tested by irradiation of tilted

thin foils, and find that thin foil effects do not account for the results. We have started to use atom tracking software and geometric phase analysis, which is more sensitive to long range strain fields, to quantify the atomic pathways, and are collaborating with Prof. Arkady Krashennnikov at the Dresden Helmholtz Center to explore the reaction mechanisms through electron beam-solid interaction modelling.

Interactions at individual atomic columns

If CrSBr is irradiated at a single atomic column rather than over a broad area, we find that we can trigger a highly local transformation. Figure 2 shows that irradiation of an individual Cr column in a crystal 16 layers thick results in gradual motion of the Cr atoms out of this column, which progressively becomes darker. The Cr atoms are not knocked out of the crystal but move to locations in nearby columns, as shown by the increasingly brighter contrast. Our DFT modelling suggests that the displaced Cr atoms move to the van der Waals gap. Furthermore, we find that we can choose the location to which the displaced Cr atoms move. We accomplish this by scanning the beam back and forth rapidly between the initial and the target columns. This is an exciting result as it suggests that we can customize the nature of the beam-induced defects, creating a Cr vacancy in each layer of the crystal paired with a Cr interstitial at a chosen location in the gap between layers. We calculate that such vacancy-interstitial pairs should have states in the CrSBr bandgap and single photon emission properties. We have extended the experiments to create large arrays containing thousands of such defects, up to 40,000 user-defined defects across a 150nm x 100nm x 13nm volume. Reproducible atomic motion is essential: these results are based on our algorithms for precise beam placement [4], as well as machine learning strategies that allow us to evaluate the nature of the intrinsic defects in CrSBr [5].

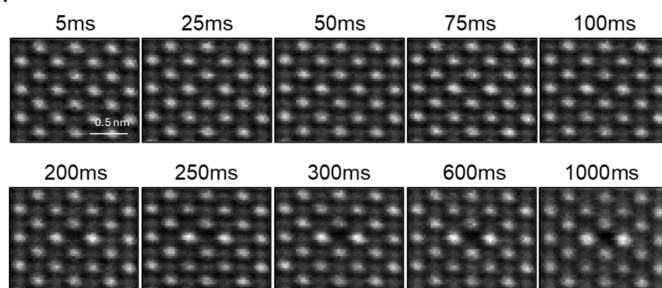


Figure 2. Averaged HAADF-STEM images from 30 experiments on a 13 nm thick CrSBr crystal in which a column of Cr atoms (central site on image) is displaced to the van der Waals gap at neighboring atomic columns (brighter S/Br locations) by rapid beam motion between the central and neighboring columns. Irradiation was performed in the Oak Ridge National Laboratory Nion UltraSTEM. Images are shown after different durations, beam energy 200 keV, frequency 0.5 kHz and current 20 pA.

Future Plans

We will continue to analyze the large-area structural transformations induced in CrSBr by electron beam irradiation. We will track intensities in each atomic column to derive kinetics for the motion of Cr, S and Br. This information is helping to develop a model for the atomic motions that cause the transformation, in particular to understand why it is the Cr atom that moves rather than the lighter S and Br, and why the effects show a directional dependence. We will also track

the development of strain in the structure using geometric phase analysis so that strain can be included in our model of the reaction pathway. We will also continue the “nucleation and growth” experiments by transforming a small region then moving the beam to an adjacent region of untransformed crystal to evaluate the influence of the nucleated structure on the continuing transformation. Changing the driving forces for atomic motion in this way will allow us to develop our model for beam-solid interactions.

For irradiation experiments on individual atomic sites, we will increase the numbers of defects created and the reliability of defect creation by improving our algorithms for precise beam placement and alignment. Unlike conventional beam scan engines, our algorithms use the detector output as a parameter, for example holding the beam on a column until the intensity has decreased to a preset value. This allows for efficient use of each electron delivered, to minimize time (reducing the effects of drift) and avoid unwanted beam effects.

In the longer term, we aim to generalize our results to different materials with interesting magnetic and electronic properties. We have started to examine irradiation effects on FeOCl, selected because it is isostructural with CrSBr and is air stable. The lighter elements will enable even more precise measurements of the heavy metal (Fe) displacement under conditions of different bond strengths and electronic structure. Other crystals that we propose to examine are CrOCl and CrSeBr. We also intend to use a newly developed ultra-high vacuum TEM (Hitachi HF5000-UHV, recently installed at MIT) to perform irradiation experiments on CrSBr in the presence of intercalated Cr. The motion of Cr within van der Waals materials is well known, and recent literature has modeled structures formed by different degrees of Cr intercalation. We hypothesize that Cr within the van der Waals gap of CrSBr will alter the pathways of beam-induced Cr motion and enable patterning of new magnetic and electronic structures.

References

1. J. Klein and F. M. Ross, *Materials beyond monolayers: The magnetic quasi-1D semiconductor CrSBr*, J. Materials Research **39**, 3045 (2024)
2. J. Klein, T. Pham, J. D. Thomsen, J. B. Curtis, T. Denneulin, M. Lorke, M. Florian, A. Steinhoff, R. A. Wiscons, J. Luxa, Z. Sofer, F. Jahnke, P. Narang and F. M. Ross, *Control of structure and spin texture in the van der Waals layered magnet CrSBr*, Nature Communications **13**, 5240 (2022)
3. E. Park, Z. Sofer, J. Klein, and F. M. Ross, *Electron Beam-Induced Phase Transformations in Different Crystal Orientations of a 2D van der Waals Magnet*, Microscopy and Microanalysis **31** (1), ozaf048.765 (2025)
4. M. Weile, S. Grytsiuk, A. Penn, D. G. Chica, X. Roy, K. Mosina, Z. Sofer, J. Schiøtz, S. Helveg, M. Rösner, F. M. Ross and J. Klein, *Defect complexes in CrSBr revealed through electron microscopy and deep learning*, Phys. Rev. X **15**, 021080 (2025)
5. K. M. Roccapiore, F. M. Ross and J. Klein, *Quantitative Electron Beam-Single Atom Interactions Enabled by Sub-20-pm Precision Targeting*. Adv. Sci. e02551 (2025)

Publications

Supported by DOE-BES under Award DE- SC0025387

1. E. Park, Z. Sofer, J. Klein, and F. M. Ross, *Electron Beam-Induced Phase Transformations in Different Crystal Orientations of a 2D van der Waals Magnet*, *Microscopy and Microanalysis* **31** (1), oza048.765 (2025), <https://doi.org/10.1093/mam/ozaf048.765>
2. M. Weile, S. Grytsiuk, A. Penn, D. G. Chica, X. Roy, K. Mosina, Z. Sofer, J. Schiøtz, S. Helveg, M. Rösner, F. M. Ross and J. Klein, *Defect complexes in CrSBr revealed through electron microscopy and deep learning*, *Phys. Rev. X* **15**, 021080 (2025), <https://doi.org/10.1103/PhysRevX.15.021080>
3. K. M. Roccapiore, F. M. Ross and J. Klein, *Quantitative Electron Beam-Single Atom Interactions Enabled by Sub-20-pm Precision Targeting*. *Adv. Sci.* e02551 (2025). <https://doi.org/10.1002/advs.202502551>

In the following publications, J. Klein and E. Park contributed their expertise to research on CrSBr and related van der Waals magnets. These papers acknowledge Award DE-SC0025387 while being less closely related to its main objectives.

4. C.-T. Chou*, E. Park*, J. Ingla-Aynes, J. Klein, K. Mosina, J. S. Moodera, Z. Sofer, F. M. Ross and L. Liu, *Large Magnetoresistance in an Electrically Tunable van der Waals Antiferromagnet*, *Physical Review Letters* **135**, 136702 (2025) [* co-first authors] <https://link.aps.org/doi/10.1103/hpmq-rnh4>
(MIT Research Highlight: <https://news.mit.edu/2025/mit-engineers-develop-magnetic-transistor-more-energy-efficient-electronics-0923>)
5. S. W. Song, J. Klein, K. Mosina, Z. Sofer, D. Sedmidubsky, J. Dong, K. Chen, F. M. Ross and R. Jaramillo, *Magnetic Secondary Phases in the Annealed van der Waals Antiferromagnet CrSBr*, *J. Phys. Chem. C* **129**, 19002-19011 (2025). <https://pubs.acs.org/doi/10.1021/acs.jpcc.5c04211>
6. M.-G. Han, J. D. Thomsen, J. P. Philbin, J. Mun, E. Park, F. Camino, L. Dekanovsky, C. Liu, Z. Sofer, P. Narang, F. M. Ross and Y. Zhu, *Electric Field Control of Magnetic Skyrmion Helicity in a Centrosymmetric 2D van der Waals Magnet*, *Nano Letters* **25**, 5174 (2025). <https://pubs.acs.org/doi/10.1021/acs.nanolett.4c06200>

Uncovering Nonequilibrium Order in Quantum Materials: Multimodal Ultrafast Electron Microscopy Platform

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Keywords: Ultrafast Electron Microscopy, Photoinduced Phase Transitions, Nonequilibrium Dynamics, Quantum Materials, Femtosecond Electron Diffraction

Research Scope

The goal of this project is to investigate emergent nonequilibrium phenomena in quantum materials by leveraging the latest ultrafast electron scattering and microscopy techniques. In the modern physical landscape, nonequilibrium states are not only common but central to the discovery of new material functionalities. At the microscopic scale, quantum mechanical interactions among constituents can give rise to complex, collective behaviors and hidden phases that have no classical counterparts. Understanding and controlling such phenomena is a frontier challenge in condensed matter physics and materials science.

This program seeks to develop a femtosecond electron microscopy platform capable of probing structural and dynamical transformations in quantum materials with combining high temporal (<50 fs) and spatial resolutions. Using advanced strategies such as high-brightness electron sources and phase-space manipulation via RF cavities and high-precision control, we aim to visualize and understand the mechanisms driving nonequilibrium phase transitions and metastable states.

The scientific focus is on layered quantum materials, particularly transition-metal dichalcogenide (TMD) thin films, which offer a rich platform due to their reduced dimensionality, strong electronic correlations, and tunable structure. Within this framework, the project investigates four interrelated areas of nonequilibrium behavior: photo-induced lattice chirality and its control, non-reciprocal phase transitions, the dynamics of quasi-crystalline orders, and the processes governing two-dimensional melting and ordering. These studies are designed to address challenges in understanding hidden phases and collective orderings by conducting multiscale experiments that correlate dynamic structural changes with emergent functionality.

By resolving the fundamental physics underlying these phenomena, the project will provide insights into how quantum materials can be actively used in future technologies, including electronics, photonics, and information systems. Ultimately, this research aims to bridge the gap between microscopic understanding and device-level application, opening pathways to design principles based on nonequilibrium quantum materials.

Recent Progress

Over the past two years, the program has made progress in both instrumentation and science, advancing our ability to probe nonequilibrium quantum materials at ultrafast timescales. The integration of optical-pump probe (OPP) techniques with ultrafast electron diffraction and microscopy (UED/UEM) has proven fruitful. This multimodal, correlative (spectral and structural) approach revealed complex dynamics previously not easily accessible through single-modality measurements. In tandem with hardware developments, we have made algorithmic

advances in machine learning and modelling that facilitate data analysis and interpretation of transient states of matter in photoinduced phase transitions (PIPTs).

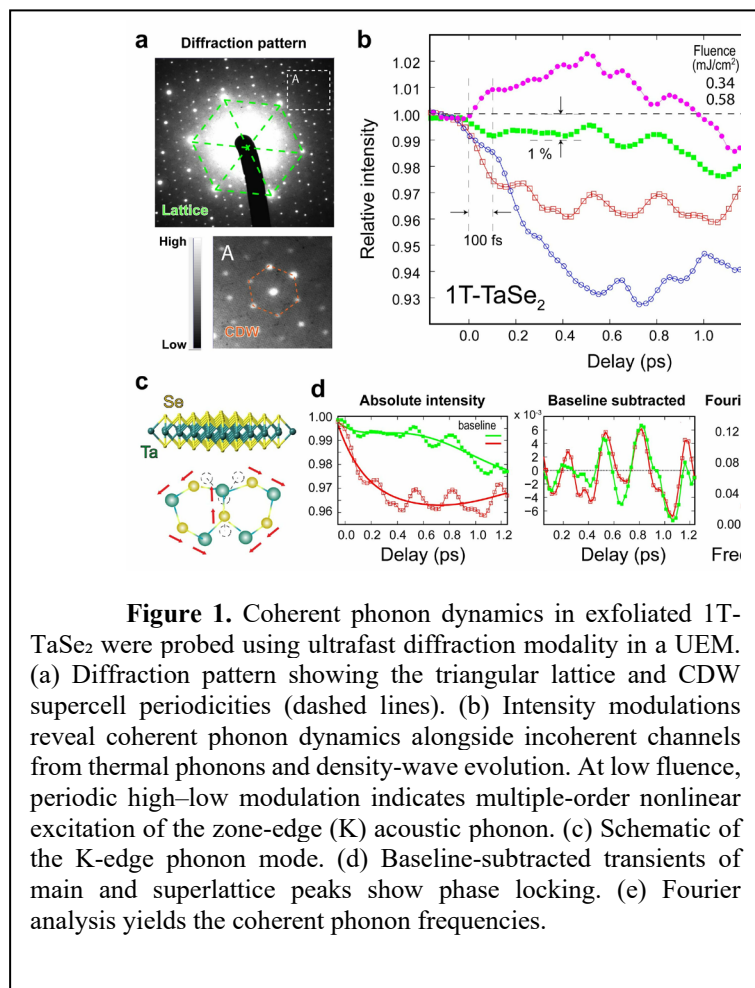


Figure 1. Coherent phonon dynamics in exfoliated 1T-TaSe₂ were probed using ultrafast diffraction modality in a UEM. (a) Diffraction pattern showing the triangular lattice and CDW supercell periodicities (dashed lines). (b) Intensity modulations reveal coherent phonon dynamics alongside incoherent channels from thermal phonons and density-wave evolution. At low fluence, periodic high–low modulation indicates multiple-order nonlinear excitation of the zone-edge (K) acoustic phonon. (c) Schematic of the K-edge phonon mode. (d) Baseline-subtracted transients of main and superlattice peaks show phase locking. (e) Fourier analysis yields the coherent phonon frequencies.

previously unattainable fidelity.

Case of VO₂. A notable result of the project is the resolution of long-standing ambiguities in the ultrafast insulator-to-metal transition (IMT) in VO₂. By deploying our dual-probe UED+OPP system, we accessed both the transient lattice distortions and the associated electronic symmetry changes with sub-100 femtosecond precision. This allowed us to capture the formation and coherent evolution of small polarons—intermediate quasiparticles that mediate the transition from the insulating monoclinic phase to the metallic rutile phase.

We identified a bi-threshold behavior in which the system first traverses a polaronic regime, then undergoes a proliferation process along the 1D zigzag V-V dimer chains to form a transient metallic state, prior embarking on the route to the conventional metallic rutile phase. This multi-step, nonthermal transition had eluded prior detection due to insufficient spatial resolution or lack of polarization sensitivity. By applying the machine learning algorithms, we are able to disentangle these overlapping dynamics and establishing an organizing principle: the presence of coherent lattice–electronic coupling as a doorway state to emergent functionality.

Instrumentation and Multimodal Capability. A technical milestone is the implementation of an imaging-based polarization-resolved OPP system. Designed to operate on microcrystals and exfoliated thin film such as VO₂ and Ta-based dichalcogenides, this system allows for in situ polarization contrast imaging along with UED/UEM experiments. Meanwhile, the UEM platform itself was upgraded to a newly designed high-brightness photoemission source and RF-based phase-space control element powered by cascade-loop phase stabilization. With these improvements, we now routinely achieve <50 fs temporal resolution and enhanced beam coherence. This spatiotemporal precision, combined with real-time polarization sensitivity from PIPTs, such as multiple order edge-mode phonons in TaSe₂ and polaron formation and domain evolution in VO₂, with

These findings answer a decades-long question about the dominant mechanism in VO₂ and serve as a model for exploring and controlling hidden phases in other strongly correlated oxides. The broader implications include informing design principles for next-generation energy-efficient phase-change devices, ultrafast quantum memories, and reconfigurable neuromorphic systems.

Decoding nonequilibrium universality. A curious understanding emerges in our findings in 1T-TaS₂, a material long studied for its rich charge-density wave (CDW) phase diagram. Using the joint UED+OPP approach, we demonstrated that the transition between commensurate and incommensurate CDW states does not occur abruptly but instead traverses a hierarchy of metastable configurations. What distinguishes this behavior is its underlying dynamical mechanism: during the early-to-intermediate stages following excitation, the system exhibits quasi-conserved behavior—maintaining wave-action and effective particle number—before thermal dissipation regains dominance. This is incompatible with traditional time-dependent Ginzburg-Landau (TDGL) models and suggests that a stochastic nonlinear Schrödinger equation (SNLSE) framework is more appropriate for modeling the evolution of these nonequilibrium states.

The experimental validation of this SNLSE-like regime represents a conceptual advance. It introduces a different type of organizing principle for ultrafast materials science: that transient isolation from the thermal bath enables the exploration of new dynamical symmetries and potentially novel phases inaccessible under equilibrium conditions. This insight prompts the possibility of steering quantum materials into functionally useful configurations by targeting specific regions of their dynamical phase space.

Emerging Evidence of Hierarchical Ordering in 1T-TaSe₂. Time-resolved UED data show that, under tailored excitation, the system transitions not directly from commensurate to incommensurate CDW phases, but rather through a cascade of metastable states characterized by distinct periodicities and spatial modulations. These observations raise the intriguing possibility that long-range quasi-periodic order—a defining feature of quasi-crystals—could emerge transiently in layered systems. Polarization-sensitive OPP is currently being adapted to resolve potential chiral textures associated with these transitions.

Algorithmic and Conceptual Advances. The progress described above would not have been possible without parallel advancements in algorithmic frameworks for data analysis. By combining machine learning—inspired dimensionality reduction with physics-guided symmetry extraction, we have developed new pipelines for identifying organizing variables in high-dimensional datasets. These methods go beyond conventional Fourier decomposition to reveal dynamical trajectories in latent phase space, enabling classification of transient states and identification of novel phase boundaries.

Furthermore, our theoretical developments in using the SNLSE as a modeling framework mark a shift in how ultrafast transitions are simulated. Unlike TDGL, the SNLSE accommodates coherent dynamics, nonthermal conservation, and spatial inhomogeneity—making it ideal for describing Devil’s staircase trajectories and quasi-crystalline emergence. Future coupling of these simulations with real-time data assimilation will enable predictive, closed-loop experiment-theory integration.

Technology Transfer and Broader Impact. In parallel with our scientific work, we have advanced the practical deployment of our technologies through two patent filings. The first covers the design of high-brightness high-throughput electron sources, which were successfully

implemented in our upgraded UEM-II system. The second patent addresses a cascade-loop GHz control system that reduces timing jitter and telegraph noise in RF beam modulation. This innovation enables time-resolved studies that span from femtoseconds to milliseconds, vital for tracking memory effects and long-lived hidden states.

These technological developments shall have implications for both fundamental science and industry. In particular, the GHz-lifetime capability of our RF-UEM architecture opens doors for applications in semiconductor metrology, lifetime mapping, and transient fault analysis in microelectronic circuits. With support from MSU Technologies, we are working to transition these developments toward broader dissemination and commercialization.

Future Plans

In the next phase, our efforts will focus on resolving the spatial and temporal hierarchies that underlie metastable and quasi-crystalline states, with particular emphasis on 1T-TaSe₂. Our recent findings show that the C-to-IC CDW transition proceeds through multiple transient states organized in a hierarchical sequence, rather than a direct quench to incommensurate order. These findings raise the possibility that excited quasi-crystalline states—with long-range aperiodic order—may emerge through controlled photoexcitation.

To probe this, we will extend the polarization-sensitive OPP methodology to detect the associated chiral textures and local symmetry modulations in the intermediate CDW states. The aim is to identify whether spatially hierarchical ordering with quasi-crystalline features can be stabilized or tuned by varying excitation fluence, pulse structure, or thermal coupling conditions. This effort eliminates reliance on photoemission-based techniques and places polarization-resolved OPP at the core of spatially selective, symmetry-resolved dynamics measurements.

On the theoretical and algorithmic front, we will develop a new modeling framework based on the SNLSE. This formalism is uniquely suited to describe the coherent, conservation-driven regime observed in our experiments, where the system temporarily decouples from the bath and exhibits nonthermal universalities. The SNLSE will be refined to include shear dynamics, interlayer coupling, and domain wall kinetics—providing a computational bridge to map measured metastable states onto a dynamic, multi-basin free-energy landscape.

We will also integrate **real-time data assimilation techniques**, using feedback between experiment and simulation to iteratively refine our understanding of mode coupling, state transitions, and symmetry evolution. This feedback loop will allow predictive design of future experiments aimed at selectively accessing desired quantum states.

Through this multi-pronged effort—merging new experimental tools, algorithmic advances, and nonlinear modeling—we seek to uncover how complex, hierarchical ordering emerges from ultrafast dynamics, and how such ordering can be harnessed in practical quantum devices. This initiative stands to not only to address open physics questions, but new strategies for engineering out-of-equilibrium functionalities in correlated materials systems.

Publications

1. X. Sun, S. Sharma, S. Sun, N. A. Sepulveda, and C.-Y. Ruan, *Probing Spatial and Temporal Hierarchies in Quantum Materials: Advances in High-Throughput Femtosecond Electron Microscopy*, M&M 2025 Annual Meeting (Microscopy & Microanalysis), 2025.
2. C.-Y. Ruan, X. Sun, S. Zhao, and S. Kunjir, *Control System for Ultrafast Electron Beam Microscope (US Patent disclosure)*, 2024.
3. C.-Y. Ruan and P. Duxbury, *Ultrafast High-Brightness Electron Beam System (US Patent disclosure)*, 2024.
4. C.-Y. Ruan, *Quantum Material Research through Femtosecond Electron Crystallography, Spectroscopy, and Microscopy*, 2024 MRS Spring Meeting, 2024.
5. X. Sun, J. Williams, S. Sharma, S. Kunjir, D. Morris, S. Zhao, and C.-Y. Ruan, *Precision-Controlled Ultrafast Electron Microscope Platforms. A Case Study: Multiple-Order Coherent Phonon Dynamics in 1T-TaSe₂ Probed at 50 Femtosecond – 10 Femtometer Scales*, *Structure Dynamics*, **11**, 024305 2024.
6. X. Sun, S. Sun, I. Gonzalezafanador, G. T. Morales, N. A. Sepulveda, and C.-Y. Ruan, *Disentanglement of Electronic and Structure Orders in Photoinduced Phase Transition of VO₂*, *CLEO*, 2023.
7. C.-Y. Ruan, *Classification of Nonequilibrium Phase Transitions in Quantum Materials Using Ultrafast Electron Microscope Platform*, 2023 MRS Spring Meeting, 2023.
8. C.-Y. Ruan, *The Many Facets of Ultrafast Electron Diffraction and Microscopy: Development and Applications*, in *Structural Dynamics with X-ray and Electron Scattering*, pp. 395-465, Royal Society Publishing, 2023.

Probing Lattice and Spin Order in van der Waals Magnetic Materials with Cryogenic and Multi-modal Electron Microscopy

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Keywords: 4D-STEM, ptychography, cryogenic electron microscopy, vdW magnets

Research Scope

Topological spin textures such as skyrmions are particle-like configurations of swirling spins that have the potential to revolutionize information and related technologies. Two-dimensional (2D) van der Waals (vdW) magnetic materials offer a unique platform for exploring novel magnetic and topological phases, owing to their highly tunable crystal symmetries and magnetic interactions across the vdW gap. Room temperature stabilization of such textures opens opportunities for spintronics applications based on atomically thin vdW crystals.

The goal of this Early Career project is to understand how crystal symmetry breaking, atomic coordination, and site occupancy influence the stabilization of room-temperature topological spin textures in these cdW magnets. Candidate systems include Fe_NXTe_2 compounds (FGTs, $N = 3-5$; $X = \text{Ge, Ga}$), Cr_xTe_y phases, and related layered chalcogenides and tellurides which have magnetic transition near or above room temperature. To achieve this, we will develop advanced techniques based on four-dimensional scanning transmission electron microscopy (4D-STEM) modalities, including cryogenic multi-slice electron ptychography (MEP) for sub-Angstrom, three-dimensional mapping of lattice distortions at relevant temperatures, and large-angle rocking beam electron diffraction (LARBED) for quantitative measurements of bonding charge densities. Using *in-situ* 4D-STEM within nanodevices, combined with controlled electrical stimuli and cryogenic temperatures, we will manipulate emergent spin textures and elucidate the mechanisms of their transformation. The findings will establish fundamental understanding of the underlying physics that governs these complex materials, thereby enabling the design and manipulation of quantum materials for future technological applications.

Recent Progress

In the past year, we have focused on overcoming two primary technical challenges essential to achieving the goals of this project: (1) enabling cryogenic electron ptychography for sub-angstrom resolution, real-space structural imaging; (2) developing automated LARBED data acquisition platform for quantitative measurement of crystal symmetry and mapping bonding charge densities in large unit-cell crystals.

a. Demonstration of Sub-0.5 Å Resolution at Cryogenic Temperatures

Many structural and magnetic phase transitions in quantum materials occur only at low temperatures. However, achieving atomic-resolution STEM at cryogenic temperatures is

notoriously difficult due to environmental instabilities—such as cryo-holder drift and vibrations, nitrogen bubbling, and contamination—that degrade phase coherence and limit attainable resolution. More importantly, the resulting STEM images are vulnerable to artifacts like probe aberrations and crystal mis-tilts. This is because the recorded image can be approximated as the convolution between the probe, stage instabilities, and the projected atomic potential. These artifacts can be easily corrected in modern microscopes but remain challenging to monitor and correct during cryogenic experiments.

Electron ptychography offers a unique opportunity to overcome this limitation by computationally separating the probe wave function from the object phase. The mixed-state [1] and multi-slice [2] ptychographic algorithms account for probe partial coherence, aberrations, and stage instabilities, enabling retrieval of the true object phase while achieving deep sub-Å lateral resolution and depth-resolved structural information. Using this approach, we implemented the cryogenic electron ptychography experiment with a liquid nitrogen holder, achieving sub-0.3 Å lateral resolution at room temperature and sub-0.5 Å resolution at 110 K.

As a proof-of-principle, we imaged CaTiO_3 thin films and revealed the three-dimensional nature of polar nanoregions (**Figure 1**). Compared with HAADF imaging which is dominated by heavy element contrast, MEP robustly resolves both heavy and light elements—including the oxygen sub-lattice—while mitigating

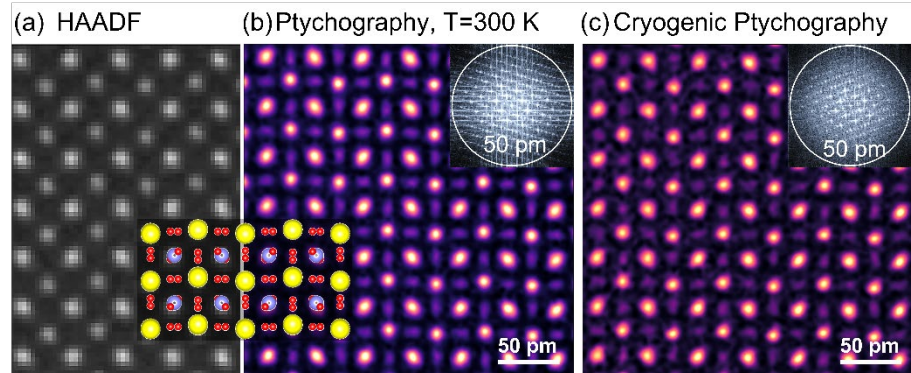


Figure 1. Demonstration of cryogenic multislice electron ptychography. Comparison of (a) conventional HAADF-STEM, (b) room-temperature ptychography, and (c) cryogenic ptychography reconstructions of a CaTiO_3 thin film. The oxygen sub-lattice is resolved with MEP while invisible in HAADF. Insets in (b) & (c) show Fourier transforms of the MEP reconstructions, demonstrating sub-0.3 Å resolution at 300 K and sub-0.5 Å resolution at 110 K.

artifacts from environmental drift and holder vibrations. This demonstration establishes the technical foundation for studying low-temperature phase transitions in quantum materials, where picometer-scale structural distortions and subtle symmetry breaking are associated with the materials' emergent functionalities.

b. Extending Real- and Reciprocal-Space Information with Automated Acquisition of Six-Dimensional Electron Scattering Data

Traditional convergent beam electron diffraction (CBED) is a powerful and well established technique in extracting rich information like symmetry and bonding charge densities, but is constrained by limitations such as overlapping diffracted discs. This limitation prevents its

application to large unit-cell crystals and beam-sensitive materials. Large-angle rocking beam electron diffraction (LARBED) addresses this by sequentially tilting the probe and stitching together the rocking curve information [3]. However, LARBED only obtains diffraction patterns at a focused spot in real space, making it unsuitable for mapping nanoscale inhomogeneities that are commonly observed in vdW magnetic materials, such as intercalated magnetic ions distribution or lattice distortion. Furthermore, because LARBED requires sequential probe tilts and diffraction pattern captures over tens of thousands of tilts, a single dataset often takes 0.5-2 hours to acquire.

To overcome these limitations, we have developed two key advances. First, by implementing hardware synchronization between probe tilting and CBED pattern acquisition on a fast direct electron detectors, we reduced LARBED acquisition times by over $50\times$ (from hours to <1 minute) [4]. Second, to extend LARBED into real-space mapping, we developed a new technique, *SCARED* (Scanning Convergent Angle Rocking Electron Diffraction). In SCARED, a 2D CBED pattern is recorded for every probe rocking point along the α and β axes and for every probe position (x, y) in real space (schematic shown in **Figure 2a**). Using Python scripting-controlled probe rocking, SCARED acquires a full 4D-STEM dataset at each probe tilt, generating a six-dimensional (6D) dataset of $(x, y, k_x, k_y, \alpha, \beta)$. For example, a single SCARED acquisition consisting of 13×13 probe rocking, 128×128 image and 192×192 pixel diffraction patterns produces a dataset >600 GB.

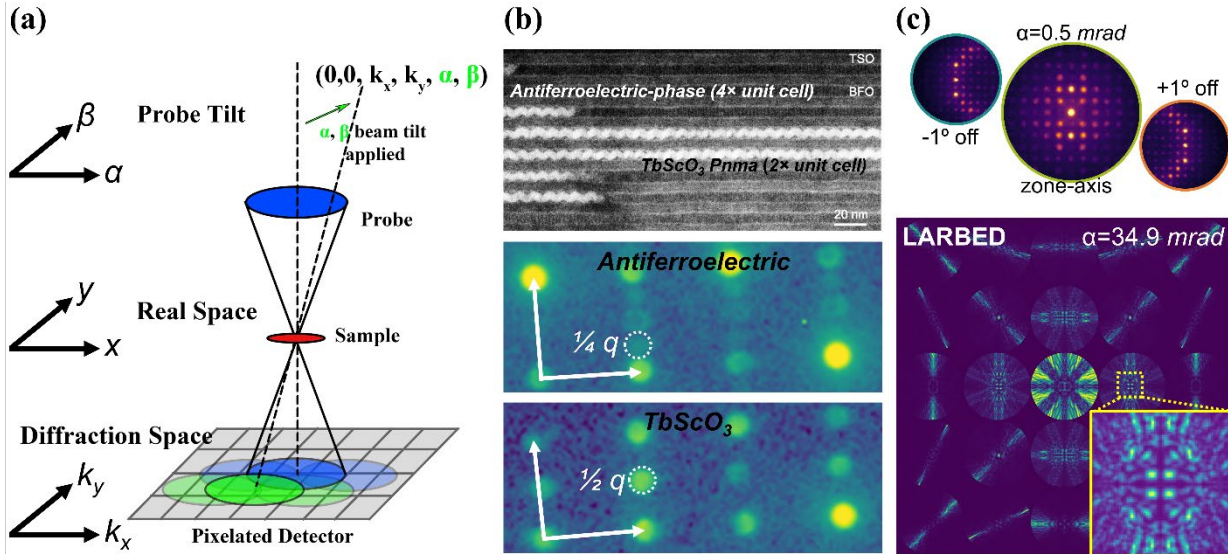


Figure 2. Demonstration of SCARED technique that expands both real- and reciprocal-space information. (a) Schematic of SCARED which captures a 4D-STEM dataset at every probe tilt, yielding 6D data. (b) Representative 4D-STEM data for a $\text{BiFeO}_3/\text{TbScO}_3$ superlattice acquired at zero probe-tilt, showing real-space distribution of the co-existing phases (top) and corresponding lattice ordering in reciprocal-space (bottom). White arrows mark the pseudocubic perovskite unit cell. (c) The 6D dataset can be further parsed as real-space-dependent LARBED data. For example, rocking curve information in TbScO_3 layer can be expanded by $\sim 70\times$, from 0.5 mrad to 34.9 mrad. Inset, Gjonnes-Moodie lines reflecting glide and screw symmetry element can be clearly observed.

As a proof-of-principle, we applied SCARED in a perovskite superlattice of (BiFeO₃)/(TbScO₃) shown in **Figure 2b**. The TbScO₃ (TSO) layers adopt the orthorhombic *Pnma* space group, where the oxygen octahedral tilting pattern doubles the pseudocubic perovskite unit cell, giving rise to half-order Bragg reflections ($\frac{1}{2} q$). On the other hand, BiFeO₃ (BFO) layers consist of two co-existing phases: a dipolar wave phase [5] and an antiferroelectric (AFE) phase. The complex oxygen octahedral tilting patterns in the AFE BFO quadruple the perovskite unit cell, giving rise to one-fourth-order Bragg reflections ($\frac{1}{4} q$).

The 6D dataset obtained from SCARED can also be parsed into real-space-resolved LARBED data. Because the real-space probe scan is recorded, probe-tilt-induced-probe-shifts can be corrected post-acquisition, enabling nanometer-resolution LARBED mapping. For example, within the 5 nm-thick TbScO₃ layer, the rocking curve information can be expanded by a factor of ~ 70 , from 0.5 mrad to 34.9 mrad (**Figure 2c**). This extended angular coverage clearly resolves Gjønnes-Moodie lines that reflect the glide or screw axes, consistent with *Pnma* space group. The implementation of SCARED lays the foundation for studying symmetry and bonding variations in large unit-cell crystals such as charge-density-wave materials or intercalated vdW magnets.

Future Plans

In the next year, a main focus will be using a newly installed cryogenic holder and ARINA pixel array detector to conduct Lorentz 4D-STEM imaging of spin textures in vdW magnetic materials. By integrating Lorentz 4D-STEM with ptychographic algorithms, we aim to resolve magnetic order at sub-nanometer resolution. Building beyond the proof-of-concept demonstration, we will fully implement SCARED by optimizing collection parameters, streamlining data parsing workflows, and applying it to study the correlation between spin textures, symmetry breaking, and bonding variations in intercalated vdW magnets.

References

1. Z. Chen, M. Odstreil, Y. Jiang, Y. Han, M.-H. Chiu, L.-J. Li, and D.A. Muller, *Mixed-state electron ptychography enables sub-angstrom resolution imaging with picometer precision at low dose*, Nature Communications **11**, 2994 (2020).
2. Z. Chen, Y. Jiang, Y.-T. Shao, M.E. Holtz, M. Odstreil, M. Guizar-Sicairos, I. Hanke, S. Ganschow, D.G. Schlom, and D.A. Muller, *Electron ptychography achieves atomic-resolution limits set by lattice vibrations*, Science **372**, 826 (2021).
3. C.T. Koch, *Aberration-compensated large-angle rocking-beam electron diffraction*, Ultramicroscopy **111**, 828 (2011).
4. R. Busch, H.-C. Ni, Y.-T. Shao, and J.-M. Zuo, *Large-angle rocking beam electron diffraction of large unit cell crystals using direct electron detector*, Microscopy and Microanalysis **31**, ozae088 (2024).
5. L. Caretta, Y.-T. Shao, J. Yu, A.B. Mei, B.F. Grosso, C. Dai, P. Behera, D. Lee, M. McCarter, E. Parsonnet, H. K.P., F. Xeu, X. Guo, E.S. Barnard, S. Ganschow, Z. Hong, A. Raja, L.W. Martin, L.-Q. Chen, M. Fiebig, K. Lai, N.A. Spaldin, D.A. Muller, D.G. Schlom, and R. Ramesh, *Non-volatile electric-field control of inversion symmetry*, Nature Materials **22**, 207 (2023).

Publications

1. B. Fein-Ashley, T.-R. Liu, K. Jagadish, M. Pamuk, and Y.-T. Shao, *Scanning convergent angle rocking electron diffraction (SCARED) for expanding real and reciprocal space information*, *Microscopy and Microanalysis* **31** (7), 158 (2025).
2. T.-R. Liu, B. Zhao, S. Singh, J. Ravichandran, and Y.-T. Shao, *Atomic-scale structural insights to optical anisotropy in quasi-one-dimensional hexagonal chalcogenides via electron ptychography*, *Microscopy and Microanalysis* **31** (7), 683 (2025).
3. Y.-T. Shao, T.-R. Liu, K. Jagadish, Z. Hong, M. Ramesh, P. Meisenheimer, H. Zhang, A. Avishai, D.G. Schlom, and R. Ramesh, *Non-destructive, depth-resolved imaging of polar domains in multiferroic heterostructures with multi-modal electron microscopy*, *Microscopy and Microanalysis* **31** (7), 586 (2025).

Sub-angstrom convergent beam electron diffraction for valence electron mapping

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Keywords: Scanning transmission electron microscopy (STEM), 4D STEM, convergent beam electron diffraction (CBED)

Research Scope

Modern aberration-corrected scanning transmission electron microscopy (STEM) techniques have made great strides in providing ever more detailed information about the atomic structure of materials. For example, four-dimensional data sets (“4D STEM”) that are obtained by recording convergent beam electron diffraction (CBED) patterns at each probe location in a scan can be used to reconstruct images for strain mapping, differential phase contrast imaging or electron ptychography. The next frontier in STEM techniques is to obtain information not only about the local atom positions but also about the local bonding environment. Towards this goal, we use a latest generation STEM to record finely spaced, precisely positioned CBED patterns (also known as ronchigrams) from within individual unit cells. Like their conventional counterparts, these “deep sub-unit cell” CBED patterns can contain a wealth information about the local atomic structure, site symmetry, and bonding, albeit with unprecedented spatial resolution and sensitivity [1,2]. To develop deep sub-unit cell CBED in STEM to simultaneously obtain atomic and electronic structure information, our recent research used a model materials system to systematically explore the technique, using comparisons with simulations.

Recent Progress

We used SrTiO_3 single crystals and strained SrTiO_3 films as platforms to demonstrate that deep sub-unit cell CBED patterns acquired in a state-of-the-art 4D STEM can be used to probe site-resolved symmetries at individual columns, including those reflecting valence electron distributions. Our experimental findings were supported by simulations using DFT-based scattering potentials.

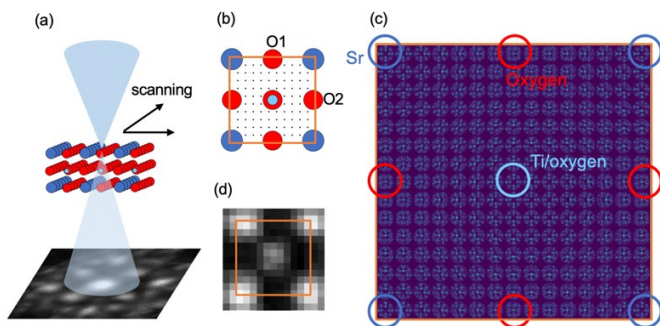


Fig. 1: (a) Acquisition of CBED patterns in 4D-STEM. (b) SrTiO_3 unit cell. The array of dots indicates the probe positions for which CBED patterns shown in (c) were calculated. (c) Calculated array of CBED patterns across a unit cell of SrTiO_3 . (d) Image of a unit cell of SrTiO_3 reconstructed from experimental 4D-STEM data. Each pixel in this image contains a CBED pattern.

Figure 1a shows a schematic of the 4D STEM setup used to record CBED patterns within a unit cell of SrTiO_3 (shown in Fig. 1b). A simulated array of CBED patterns across a unit cell is shown in Fig. 1c. Also shown is a 4D STEM image of a SrTiO_3 unit cell reconstructed from *experimental* CBED patterns (Fig. 1d). In the following, we focus on patterns recorded from the oxygen columns.

Figure 2 shows experimental CBED patterns from oxygen columns. The CBED patterns exhibit $2mm$ symmetry, which arises from asymmetry in features *in the low angle scattering region of the patterns*. The more intense of the two pairs of features is highlighted by the red circles or arrows. Patterns from O1 and O2 are rotated by 90° relative to each other, i.e., the intensity asymmetry rotates with the local site symmetry.

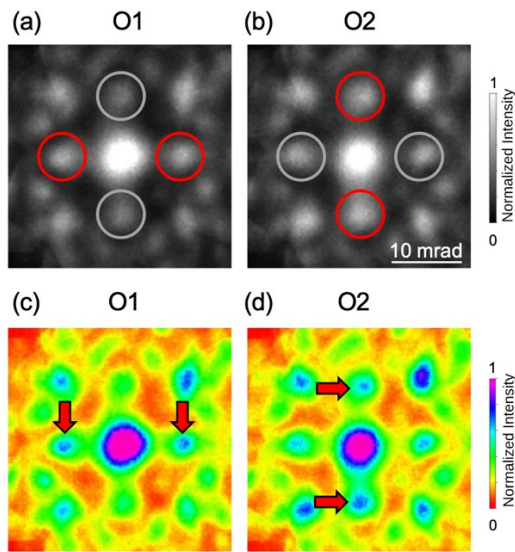


Fig. 2: CBED patterns recorded with the probe positioned on two types of oxygen columns, labeled O1 and O2 in Fig. 1(b). (a, b) Experimental CBED patterns. Two pairs of symmetry-equivalent features, having slightly different intensities, are marked with red and grey circles, respectively. The pairs in the patterns from O1 and O2 are rotated by 90° relative to each other, consistent with the site symmetries. (c, d) Same as in (a) and (b) but shown on a false-color map scale. The arrows highlight the higher-intensity pair (circled red in (a) and (b)).

We showed that the $2mm$ symmetry in the low-angle region of the patterns, in particular, the intensity differences in the features highlighted in Fig. 2, is caused primarily by an aspherical charge distribution at the oxygen sites. To this end, we calculated CBED patterns using DFT-based and independent atom model (IAM)-based electrostatic potentials, respectively. Figure 3a shows the calculated CBED pattern using the DFT-based code (abTEM [3]) for an oxygen column in a 10 nm thick sample. The fine details in the calculated pattern closely matches the experimental results, shown for comparison in Fig. 3b. Dynamical scattering will cause the patterns to reflect site symmetries, even if the valence electron distributions are (or assumed to be) spherical. To separate the effects of site symmetry from those of the valence electrons, we compared the results with the IAM-based calculation. Figure 3c two sets of intensity line profiles, taken from CBED patterns calculated using IAM (left) and the DFT-based (right) codes, respectively. The side lobes correspond to the symmetry-equivalent features discussed above. In the DFT calculations and experiments, these features have different intensities, reflecting the $2mm$ symmetry. In contrast, in the IAM-based calculations, they have almost the same intensity, i.e., the pattern is close to $4mm$

symmetric. The DFT-calculated projected scattering potential of SrTiO_3 , shown in Fig. 3d, explains the origin of the $2mm$ symmetry. In particular, it displays a subtle aspherical charge distribution near the O1 and O2 columns, with additional negative potential accumulated along the Ti-O directions. The aspherical charge distribution is not accounted for in the IAM model, which assumes a spherical charge distribution.

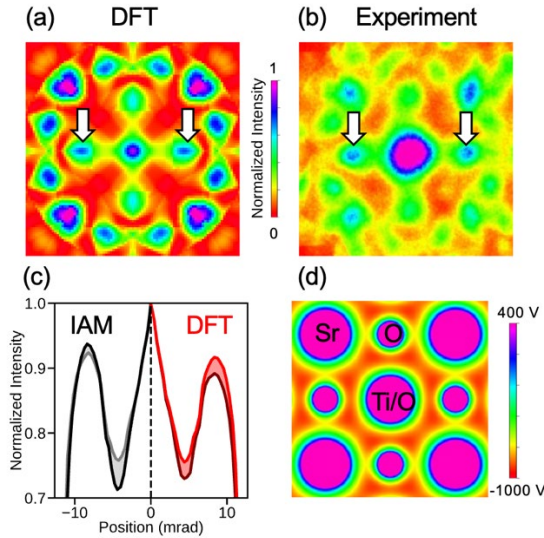


Fig. 3: (a) DFT-based calculation of a CBED pattern on an oxygen column and (b) experimental pattern. The arrows indicate regions of higher intensity, illustrating the $2mm$ symmetry of the CBED pattern. (c) Intensity line profiles across calculated CBED patterns, based on the IAM (left) and DFT-based models (right), respectively. The two line profiles in each panel are taken along directions that are rotated by 90° with respect to each other. The side lobes correspond to the features in the low angle regions (highlighted by the red and grey circles in the experimental patterns in Fig. 2). The shaded areas mark the intensity differences in the features. (d) Projected DFT-based electrostatic scattering potential of SrTiO_3 .

We also investigated whether atomic and electronic displacements, respectively, produce distinguishable changes in the patterns. To test this, we investigated a compressively strained SrTiO_3 film. At room temperature, such films have undergone a transition to long-range antiferrodistortive order, characterized by oxygen octahedral tilts. They also exhibit local polar order associated with displacements of the Ti columns within nanometer-sized domains. Both types of atomic displacements were quantified previously using STEM imaging methods in this project [4]. We showed that valence electron and atomic displacements affect different angular ranges within each pattern, which facilitates the interpretation of more complicated structures. In particular, we showed that *low-angle features* in the experimental patterns reflect the asymmetries in the scattering potential associated with the valence electron distribution, while those at higher angles reflect atomic displacements.

Future Plans

The results show that analysis of 4D STEM CBED patterns opens up new possibilities for probing atomic site-specific valence electron distributions near defects and interfaces with unprecedented spatial resolution. Future studies should also explore the information contained in patterns recorded away from the columns, as the present study focused on the oxygen columns. As a next step, we plan to go beyond model materials systems (such as the SrTiO_3 crystals studied above) to develop deep sub-unit cell CBED in STEM to simultaneously obtain atomic and electronic structure information to understand important phenomena in quantum materials. Ultimately, it is

envisioned that the analysis of the information encoded in these patterns will become an important component in reconstructing the complete internal atomic and electronic structure from 4D STEM data.

References

1. L. J. Wu, Q. P. Meng, and Y. M. Zhu, *Mapping valence electron distributions with multipole density formalism using 4D-STEM*, Ultramicroscopy **219**, 113095 (2020).
2. C. Zhang, J. Feng, L. R. DaCosta, and P. M. Voyles, *Atomic resolution convergent beam electron diffraction analysis using convolutional neural networks*, Ultramicroscopy **210**, 112921 (2020).
3. T. Susi, J. Madsen, U. Ludacka, J. J. Mortensen, T. J. Pennycook, Z. Lee, J. Kotakoski, U. Kaiser, and J. C. Meyer, *Efficient first principles simulation of electron scattering factors for transmission electron microscopy*, Ultramicroscopy **197**, 16-22 (2019).
4. G. Zhu, A. Hallett, N. G. Combs, H. Jeong, A. Genc, J. W. Harter, and S. Stemmer, *Coexistence of antiferrodistortive and polar order in a superconducting SrTiO₃ film*, Phys. Rev. Mater. **8**, L051801 (2024).

Publications

1. N. G. Combs, H. Jeong, R. Russell, L. Kautzsch, T. N. Pardue, T. E. Mates, S. D. Wilson, J. W. Harter, and S. Stemmer, *Ferroelectricity and Superconductivity in Strained Eu_xSr_{1-x}TiO₃ Films*, Phys. Rev. B **107**, 094504 (2023).
2. G. Zhu, B. Guo, and S. Stemmer, *Interface atomic structures in a cadmium arsenide/III-V semiconductor heterostructure*, Appl. Phys. Lett. **123**, 223101 (2023).
3. J. R. Chamorro, J. L. Zuo, E. N. Bassey, A. K. Watkins, G. Zhu, A. Zohar, K. E. Wyckoff, T. L. Kinnibrugh, S. H. Lapidus, S. Stemmer, R. J. Clément, S. D. Wilson, R. Seshadri, *Soft-Chemical Synthesis, Soft-Chemical Synthesis, Structure Evolution, and Insulator-to-Metal Transition in Pyrochlore-like λ -RhO₂*, Chem. Mater. **36**, 1547-1558 (2024).
4. G. Zhu, A. Hallett, N. G. Combs, H. Jeong, A. Genc, J. W. Harter, and S. Stemmer, *Coexistence of antiferrodistortive and polar order in a superconducting SrTiO₃ film*, Phys. Rev. Mater. **8**, L051801 (2024).
5. G. Zhu, E. Genc, A. Genc, and S. Stemmer, *Valence electron distributions from sub-angstrom convergent beam electron diffraction*, submitted.

Discovering Ion-Electron Interactions at Electrochemical Interfaces Using Depth-Resolved Electron Microscopy

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Keywords: Cathodoluminescence spectroscopy, Buried Solid-Solid Interface, In operando observation, Electrochemical Devices, Dynamic Defect Evolution

Research Scope

The goal of the joint project is to reveal and understand how mobile ions and electron spatial distributions combine to create interfacial dipoles and charged defects which form barriers to charge transport and phase changes, inhibiting the performance of solid-state electrochemical devices (SSEC). We will achieve these goals by utilizing depth resolved cathodoluminescence spectroscopy (DRCLS) and hyper spectral imaging (HSI) combined with unique thin film geometries to probe the buried interface in a non-invasive manner. With many mobile charge carriers active at SSEC interfaces, newly developed theory and simulations will uncover the intertwined ion-electronic behavior. If the theory is validated, the model can be used to scan many different mixed conductor/ionic conductor pairs and suggest ones with low intrinsic barriers for ion transport.

The OSU group used DRCLS to probe electronic and defect properties at a buried LiPON/V₂O₅ interface on a near nanometer scale. From this, we are learning how interfacial barriers and defects change with cycling, developing high resistance, and degrading. The movement of ions

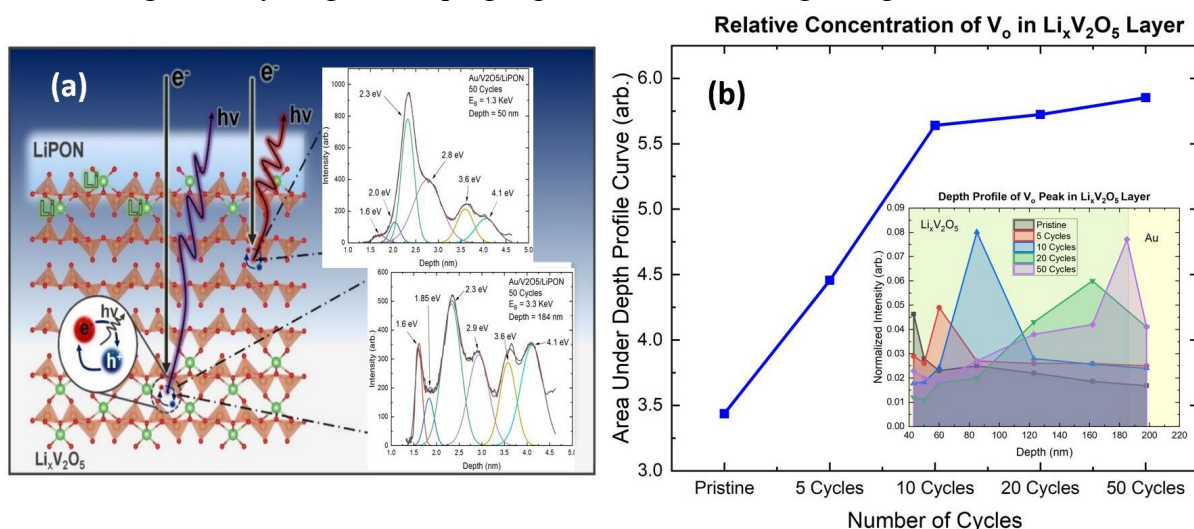


Figure 1. (a) Lattice view of DRCLS ability to detect LVO band structure at near-nanoscale resolved depth below a buried LiPON/LVO interface. Near-interface (1.3 kV) and bulk (3.3 kV) spectra exhibit characteristic LVO spectral features sensitive to lattice distortions, phase changes with Li insertion and extraction. The mid-gap state at 1.6 eV is characteristic of oxygen vacancies, which appear under the buried LiPON/LVO interface and (b) appear to move deeper into the electrode with electrochemical cycling.

and electrons across this interface is a challenge to study because this is a buried interface and because these changes can take place on a nanoscale. Nonetheless, the interface is what drives the performance of SSEC devices, especially as they move towards nanoscale devices in which the surface dwarfs the bulk.

Recent Progress

Characterization of a buried electrochemical interface via UHV DRCLS:

At OSU, a UHV field-effect scanning electron microscope (SEM) and a UHV glancing incidence electron gun were used to measure electronic structure and defects. By varying the incident beam energy (see Fig. 1a 1.3 keV vs. 3.3 keV), one can probe near the free surfaces to hundreds of nanometers below surfaces. The photons generated by electron-hole recombination have energies characteristic of the solid's band structure including defects. After cycling, a new mid-gap state at 1.6 eV was discovered to occur deeper inside the $\text{Li}_x\text{V}_2\text{O}_5$ (LVO). Fig. 1b shows how this peak grew and moved deeper with electrochemical cycling (all measurements were performed at the delithiated state).

These orbital electronic spectral features can change with excitation depth, corresponding to (1) distinct phases of $\text{Li}_x\text{V}_2\text{O}_5$ [3], (2) native point defects such as lithium interstitials and oxygen vacancies, and (3) interface specific structural and point defect features. Thus, the interpretation

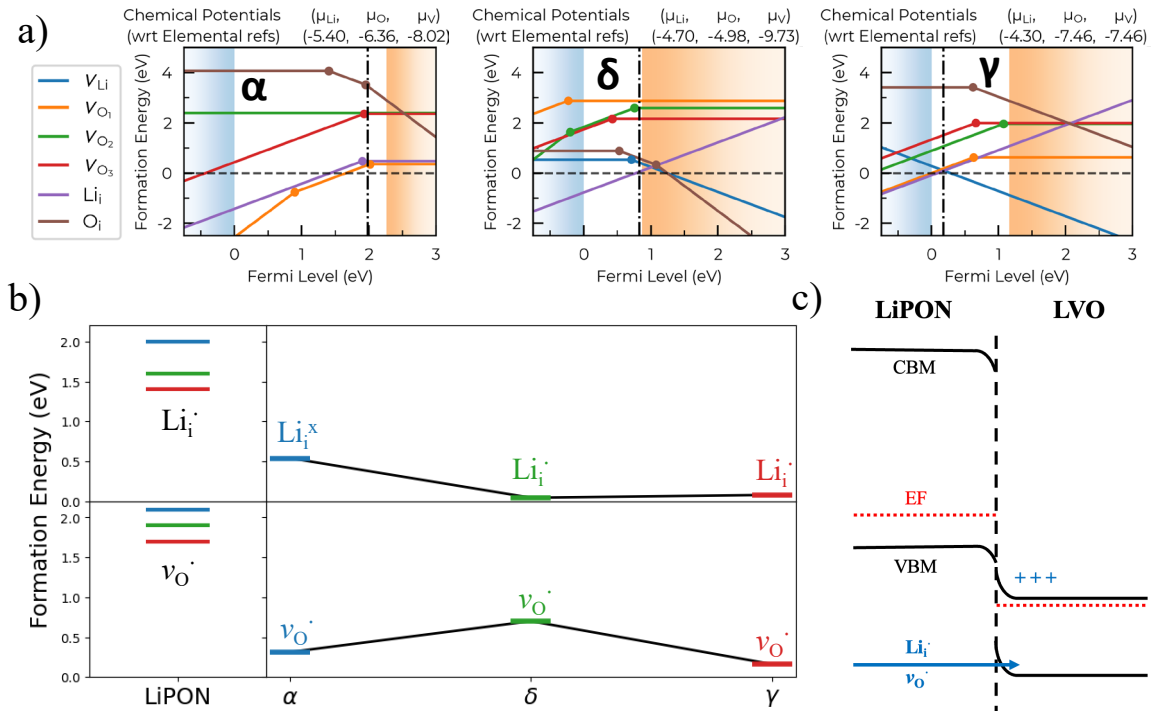


Figure 2. a) DFT computed point defect formation energies in α , δ , and γ $\text{Li}_x\text{V}_2\text{O}_5$ (LVO) phases. At the charge-neutral Fermi level, shown as a vertical dashed line, the dominating defects are Li_i and V_o (1, 2, 3 indicate different V_o sites) in α phase; Li_i , V_{Li} , and O_i in δ phase; and Li_i , V_{Li} , and V_o in γ phase. b) The formation energies of Li_i and V_o in LiPON are higher than those in LVO, thus it is energetically favorable for Li_i and V_o (both positively charged) to migrate from LiPON to LVO (colors corresponding to the Li chemical potential difference in the three LVO phases). This space charge layer driving force results in c) band-bending due to the transfer of positive defects into LVO and the creation of a localized depletion region.

of these results requires detailed modeling of electronic structures and point defects changing with lithium concentrations in LVO.

Point Defects in $\text{Li}_x\text{V}_2\text{O}_5$ and DRCLS spectral features

The Brown team first performed Density Functional Theory (DFT) calculations to evaluate the formation energies of charged point defects in α , δ , and γ phases corresponding to $x = 0, 1, 2$ in $\text{Li}_x\text{V}_2\text{O}_5$ (Fig. 2a). It was found that Li-ion interstitials (Li_i) and oxygen vacancies (V_o) are the main dominating defects in α - V_2O_5 . The formation energy for V_o is the lowest in the γ - $\text{Li}_2\text{V}_2\text{O}_5$ (0.16 eV) and the highest in δ - LiV_2O_5 (0.70 eV). This is because of the large local lattice distortion near the V_o in δ - LiV_2O_5 , in which the V-cation jumped to an interstitial position. In contrast, as Li filled all the interstitial positions in γ - $\text{Li}_2\text{V}_2\text{O}_5$, no large displacement of cations was found upon V_o formation. Fig. 2c also predicts an upward band-bending in LVO due to space charge layer formation, as positively charged Li_i and V_o transfer from LiPON to LVO. This has been observed previously by Levy et al. [4].

The spectral features shown in Fig. 1a correlate closely with the density of states (DOS) transition energies in LVO.[1] With increasing Li concentrations, the charges on V decrease from 5^+ in α - V_2O_5 to mixed 5^+ and 4^+ in δ - LiV_2O_5 , and finally all 4^+ in γ - $\text{Li}_2\text{V}_2\text{O}_5$. The “partial $3d\ t_{2g}$ ” discussed in [1] was refined in our DFT calculations as the d-orbitals on V split in a square-pyramidal oxygen-complex when coordinating with 5 oxygen ions in perfect $\text{Li}_x\text{V}_2\text{O}_5$ (different from the t_{2g} and e_g splitting in octahedral). It was found that the V_o formation in the γ - $\text{Li}_2\text{V}_2\text{O}_5$ induces V^{3+} in a square-planar oxygen-complex, showing a filled orbital. This signature was not observed in any other V^{4+} at lattice sites or interstitial sites. This might contribute to the unique 1.6 eV mid-gap state presented in DRCLS spectra in Fig. 1a, which is used to correlate with oxygen vacancies.

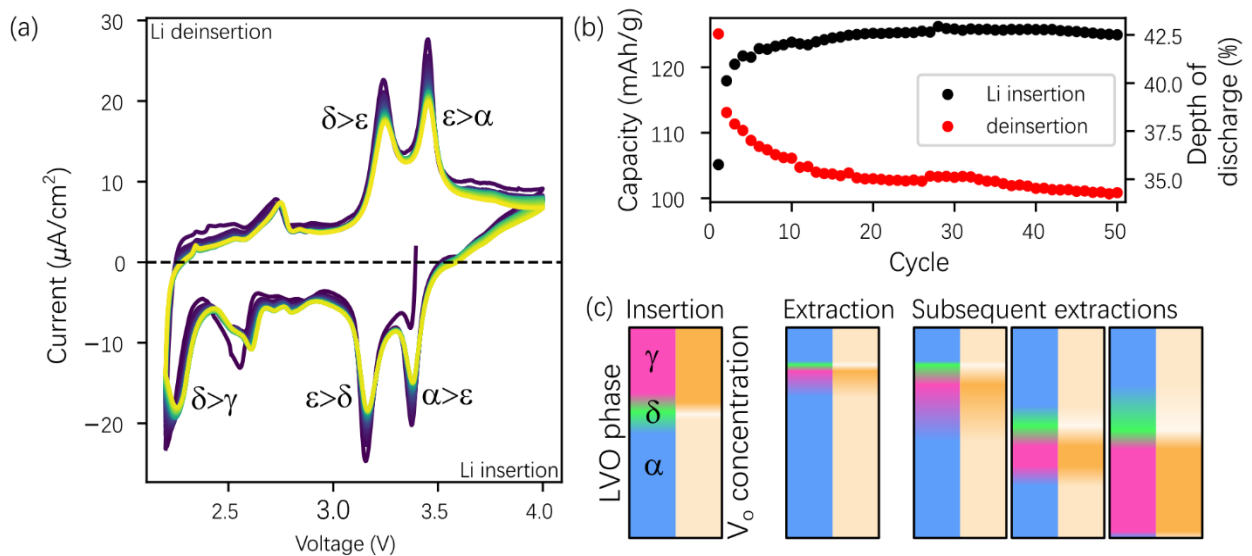


Figure 3. Electrochemical data from the LiPON/LVO devices shown in Fig. 1 (a) Cyclic voltammetry over 50 cycles. The CV data is integrated to calculate (b) the electrode specific capacity and depth of discharge (theoretical capacity 294 mAh/g), which indicates the fraction of the electrode that was being “worked.” (c) Schematic of phase and V_o variations throughout the depth of the sample and over many cycles.

Non-uniform Point Defects distribution and evolution due to cycling

Extensive cycling of Li into $\text{Li}_x\text{V}_2\text{O}_5$ is believed to produce oxygen vacancies. Cyclic voltammetry (CV, Fig. 3a) was used to insert/extract Li, and shows good reversibility of the Li reactions between 3.0-3.6 V ($\alpha > \epsilon > \delta$ phase transitions), while between 2.0-2.3 V ($\delta > \gamma$ phase transition) insertion is fast, but extraction is very sluggish or incomplete. Fig. 3b shows some Li becoming trapped on each cycle. Since the depth of lithiation on each cycle is around 41%, (70 nm) only the front half of the LVO film is initially lithiated. Upon extraction, the surface Li will be removed and some γ phase may remain deeper inside due to its sluggish kinetics, creating this non-uniform Li distribution (Fig. 3c).

After ~20 cycles, the capacity decreases become smaller, correlating with the DRCLS result (Fig. 1b) showing that the V_O signal has migrated towards the back of the electrode. Our DFT results demonstrated (i) the presence of this mid-gap state is likely due to V_O in $\gamma\text{-Li}_2\text{V}_2\text{O}_5$ and (ii) its presence depends on the state of charge and thus (3) the DRCLS results imply a non-uniform phase distribution. Fig. 1b (insert) shows that this V_O defect exists in pristine $\alpha\text{-V}_2\text{O}_5$ a few nm below the LiPON/ V_2O_5 interface, and with cycling grows in density and extends over a hundred nm deeper into the LVO. Combined with the DFT results that the γ phase can trap V_O more than δ phase, higher V_O concentration is expected deeper in the electrode at the discharged state.

Conclusions

Several factors suggest that V_O will accumulate when the cell reaches high Li (γ phase).

- 1) Based on the formation energy, it is more favorable to generate more V_O in γ phase.
- 2) Upon the LiPON/LVO interface formation, there is a driving force for both Li interstitials and oxygen vacancies to migrate to LVO phases (Fig 2b).
- 3) V_O increases the Li diffusion barrier energy, from 0.2 eV in the α phase to 0.5 eV in the, suggesting V_O slows Li diffusion and makes delithiation irreversible.

These results are significant for understanding multiple ion exchange at SSEC interfaces upon cycling for several reasons: (1) The ability to **nondestructively** measure point defects, which are spatially localized under buried electrochemical interfaces, is unprecedented; (2) The ability to measure interface electronic structure nondestructively on a near-nm scale enables the detection of localized atomic diffusion, chemical bonding, and lattice structural changes. (3) Our integrated modeling and characterization approach is powerful and necessary for deconvoluting the DRCLS spectra. (4) Our demonstrated capability to measure point defects and electronic features inside buried electrochemical interfaces enables us to monitor nondestructively the formation, spatial distribution, and evolution of defects with ionic cycling. Such evolution provides electronic and spatial information that can inform the nature of electrochemical interface degradation.

Future Plans

We plan to publish our initial LiPON/Li_xV₂O₅/V_o defect formation and diffusion results later this year. The next phase of this work is to use *in-operando* DRCLS and HSI to determine how resistance evolution is coupled to: (1) formation and diffusion of V_o and other defects in three dimensions, (2) localized electric fields coupled to nanoscale Li spatial distributions, and (3) the impact of mechanical strain/phase changes on Li indiffusion and defects with electrochemical cycling. To further exploit the unique capabilities of DRCLS for in operando measurements, the team at UMD is preparing fully solid-state devices in which the electrodes are laterally displaced so that multiple interfaces can be resolved unambiguously, and so that surface techniques such as XPS, SPS, and KPFM can also be leveraged. These devices can be biased and cycled within the UHV chamber, enabling characterization under non-equilibrium conditions and time dependent measurements.

References

1. V. Eyert and K.H. Höck, Electronic structure of V₂O₅: role of octahedral deformations, Phys. Rev.B: Condens. Matter Mater. Phys., 57, 12727 (1998).
2. D.O. Scanlon, A. Walsh, B.J. Morgan, and G.W. Watson., An ab initio Study of Reduction of V₂O₅ through the Formation of Oxygen Vacancies and Li Intercalation, J. Phys. Chem. C 112, 9903 (2008).
3. M. Walker, A. Jarry, N. Pronin, J. Ballard, G. Rubloff, and L. J. Brillson, “Nanoscale Depth and Lithiation Dependence of V₂O₅ Band Structure by Cathodoluminescence Spectroscopy,” J. Mater. Chem. A 8, 11800 (2020).
4. Levy, Z. et al. Lithium Spatial Distribution and Split-Off Electronic Bands at Nanoscale V₂O₅/LiPON Interfaces. ACS Appl. Energy Mater. 6, 4538–4548 (2023).

Publications

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Magnetic imaging of emergent phenomena in topological quantum materials

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Keywords: MFM, skyrmions, domain walls, antiferromagnets, chiral edge states

Research Scope

The objective of this project is to visualize emergent topological quantum phenomena such as surface metamagnetic transitions, topological spin texture, antiferromagnetic domain walls and topological boundary states to understand the fundamental mechanisms. Combining magnetic imaging and other complementary techniques, the PI will investigate domain walls and domain configuration in topological antiferromagnets, surface magnetism and possible surface spin-flop transitions in A-type antiferromagnets, the interplay between topology and correlated physics in kagome magnets, and magnetic domains and chiral edge states in magnetic topological insulators.

Recent Progress

Visualization of ferromagnetic domains in magnetic topological insulator-iron chalcogenide heterostructures

Topological superconductivity (TSC) has been proposed to emerge in heterostructures formed by a material with strong spin-orbit coupling (SOC) and s-wave superconductivity.¹ TSC has attracted much attention because its excitations, i.e. Majorana zero mode (MZM) can be used for fault-tolerant quantum computation. Magnetic TI/superconductor heterostructures offer an alternative platform for creating the (chiral) TSC phase and MZMs at zero magnetic field.² This scheme exploits the quantum anomalous Hall (QAH) effect to realize chiral Majorana modes propagating along the one-dimensional (1D) boundaries of the sample. In this work, our collaborator Cui-zu Chang's group at PSU used MBE to fabricate heterostructures formed by ferromagnetic TI Cr-doped $(\text{Bi,Sb})_2\text{Te}_3$ and antiferromagnetic iron chalcogenide FeTe films. Transport data clearly demonstrate that superconductivity emerges below $T_C \sim 12$ K. Ferromagnetic order was also confirmed by anomalous Hall effect above the superconducting T_C . To demonstrate ferromagnetic order persists below 12 K, the PI and his student carried out MFM imaging of the magnetic TI-FeTe heterostructure down to 2 K, well below the

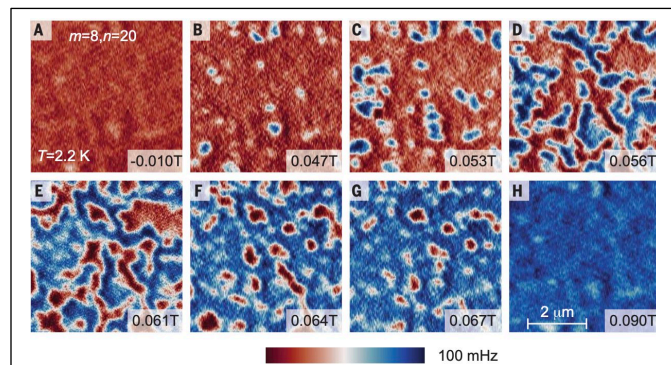


Fig.1 | Imaging magnetization reversal process the Cr-doped $(\text{Bi,Sb})_2\text{Te}_3/\text{FeTe}$ heterostructures below superconducting T_C . (A to H) MFM images of magnetic domains in a MTI/FeTe heterostructure measured at $T = 2.2$ K, and $\mu_0 H = -0.01$ T (A), 0.047 T (B), 0.053 T (C), 0.056 T (D), 0.061 T (E), 0.064 T (F), 0.064 T (G), 0.067 T and 0.090 T (H), respectively. Adapted from 1.

T_c of superconductivity.¹ The results (Fig.1) confirm the coexistence of ferromagnetic order and superconductivity in an electronic system with non-trivial topology, thus, strike all the necessary conditions for topological superconductivity which might host MZM. This work demonstrates a promising platform for realizing TSC for potential fault-tolerant quantum computing.

Besides magnetic TI-FeTe heterostructure, the PI also collaborate with Sean Oh's group at Rutgers on magnetic imaging of Fe₃GeTe₂-FeTe heterostructure, another promising platform for realize TSC.² Transport measurements confirmed the emergence of ferromagnetic order below 220 K, and superconductivity below $T_c \sim 12$ K, respectively. Using the newly commissioned He-3 MFM, the PI and his student performed MFM measurements of the heterostructures at 800 mK. The MFM results and in-situ transport confirm the coexistence of ferromagnetism and superconductivity, similar to the previous work. Temperature dependence of MFM results also demonstrate ferromagnetic domains persists to ~ 200 K, in excellent agreement with the transport results.

Hidden non-collinear spin-order induced topological surface states

Rare-earth monpnictides R(Bi,Sb) (R = Ce, Nd, Sm, etc.) are a family of materials simultaneously displaying complex magnetism, strong electronic correlation, and topological band structure.³ The recently discovered emergent arc-like surface states in these materials have been attributed to the multi-wave-vector (q) antiferromagnetic (AFM) order, yet the direct experimental evidence has been elusive.⁴ Prior power neutron diffraction studies cannot

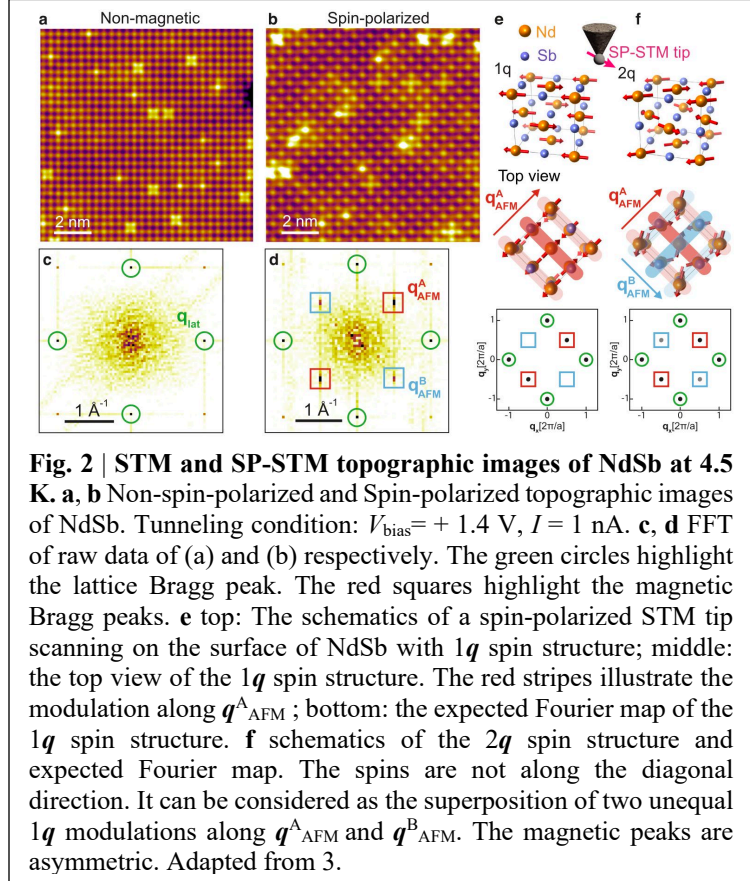


Fig. 2 | STM and SP-STM topographic images of NdSb at 4.5 K. **a, b** Non-spin-polarized and Spin-polarized topographic images of NdSb. Tunneling condition: $V_{\text{bias}} = +1.4$ V, $I = 1$ nA. **c, d** FFT of raw data of (a) and (b) respectively. The green circles highlight the lattice Bragg peak. The red squares highlight the magnetic Bragg peaks. **e** top: The schematics of a spin-polarized STM tip scanning on the surface of NdSb with $1q$ spin structure; middle: the top view of the $1q$ spin structure. The red stripes illustrate the modulation along q_{AFM}^A ; bottom: the expected Fourier map of the $1q$ spin structure. **f** schematics of the $2q$ spin structure and expected Fourier map. The spins are not along the diagonal direction. It can be considered as the superposition of two unequal $1q$ modulations along q_{AFM}^A and q_{AFM}^B . The magnetic peaks are asymmetric. Adapted from 3.

¹ Hemian Yi, Yi-Fan Zhao, Ying-Ting Chan, Jiaqi Cai, Ruobing Mei, Xianxin Wu, Zi-Jie Yan, Ling-Jie Zhou, Ruoxi Zhang, Zihao Wang, Stephen Paolini, Run Xiao, Ke Wang, Anthony R. Richardella, John Singleton, Laurel E. Winter, Purnima P. Balakrishnan, Alexander J. Grutter, Moses H. W. Chan, Nitin Samarth, Xiaodong Xu, **Weida Wu**, Chao-Xing Liu, and Cui-Zu Chang, “Interface-Induced Superconductivity in Magnetic Topological Insulator-Iron Chalcogenide Heterostructures”, *Science*, **383**, 634–639 (2024).

² Hee Taek Yi, Xiong Yao, Deepti Jain, Ying-Ting Chan, An-Hsi Chen, Matthew Brahlek, Kim Kisslinger, Kai Du, Myung-Geun Han, Yimei Zhu, Weida Wu, Sang-Wook Cheong, and Seongshik Oh, “Universal Superconductivity in FeTe and All-Iron-Based Ferromagnetic Superconductor Heterostructures”, *Adv. Func. Mater.*, **35**, 2418259, (2025).

differentiate multi-domains of simple $1\mathbf{q}$ modulations from multi- $\mathbf{q}$ modulations. In this work, the PI and collaborators report observation of non-collinear AFM order with multiple- $\mathbf{q}$ using spin-polarized scanning tunneling microscopy (SP-STM), as shown in Fig. 2b. The $2\mathbf{q}$ spin modulation observed by SP-STM is, however, asymmetric, i.e., the intensity of one pair superlattice peaks ($\mathbf{q}^{\text{A}}_{\text{AFM}}$) is stronger than the other ($\mathbf{q}^{\text{B}}_{\text{AFM}}$). This asymmetric $2\mathbf{q}$ modulations is different from the symmetric $2\mathbf{q}$ spin modulation assumed in prior DFT studies. Thus, resolving the dichotomic reports of single- $\mathbf{q}$ and multi- $\mathbf{q}$ in NdSb and NdBi. The asymmetric $2\mathbf{q}$ modulation is uniform over hundreds of microns and is further confirmed by observing a twin domain boundary between domains with opposite asymmetry.

More interestingly, the temperature dependence SP-STM studies reveal a hidden spin-rotation transition of $1\mathbf{q}$ -to- $2\mathbf{q}$ modulations, just 2 K below the Néel temperature ($T_N \approx 15$ K). The hidden transition coincides with the onset of the surface states splitting observed by our angle-resolved photoemission spectroscopy measurements. The DFT calculations by our collaborators suggest that single modulation gives rise to a band inversion with induced topological surface states in a local momentum region while the full Brillouin zone carries trivial topological indices. DFT calculations also reveal that multiple modulation further splits the surface bands via non-collinear spin tilting. Thus, the combined studies of SP-STM, ARPES, and DFT calculations provide a physical explanation of the mysterious emergence of topological surface states below T_N and their splitting a few degrees below T_N in NdSb. The same physics is likely applicable to NdBi because of the similarity of the overall behavior of the topological surface states. The direct evidence of the non-collinear spin order in NdSb not only clarifies the mechanism of the emergent topological surface states, but also opens a new paradigm of control and manipulation of band topology with magnetism.³

Ordering of room-temperature magnetic skyrmions in a polar van der Waals magnet

Control and understanding of ensembles of skyrmions is crucial for realization of future technologies. In particular, the order-disorder transition associated with the 2D lattice of magnetic skyrmions can have significant implications for transport and other dynamic functionalities. To date, skyrmion ensembles have been primarily studied in bulk crystals, or as isolated skyrmions in thin film devices. In collaboration with colleagues at Berkeley, we investigate the condensation of the skyrmion phase at room temperature and zero field in a polar magnet. It has been shown that an ordered skyrmion crystal can be engineered through structural confinement on the μm scale, showing control over this order-disorder transition on scales relevant for device applications.⁴

Nonvolatile electric control of antiferromagnetic states on nanosecond timescales

Electrical manipulation of antiferromagnetic (AFM) states, a cornerstone of AFM spintronics, is a great challenge, requiring novel material platforms. In collaboration with colleagues at Augsburg,

³ Zengle Huang, Hemian Yi, Daniel Kaplan, Lujin Min, Hengxin Tan, Ying-ting Chan, Zhiqiang Mao, Binghai Yan, Cui-Zu Chang, **Weida Wu**, “Hidden non-collinear spin-order induced topological surface states”, Nature Comm., **15**, 2937 (2024).

⁴ Peter Meisenheimer, Hongrui Zhang, David Raftrey, Xiang Chen, Yu-Tsun Shao, Ying-Ting Chan, Reed Yalisove, Rui Chen, Jie Yao, Mary C. Scott, **Weida Wu**, David A. Muller, Peter Fischer, Robert J. Birgeneau, and Ramamoorthy Ramesh, “Ordering of room-temperature magnetic skyrmions in a polar van der Waals magnet”, Nature Comm., **14**, 3744 (2023).

we report the full control over AFM states by voltage pulses in the insulating Co_3O_4 spinel well below its Néel temperature. It has been shown that the strong linear magnetoelectric effect is fully governed by the orientation of the Néel vector. As a unique feature of Co_3O_4 , the magnetoelectric energy can easily overcome the weak magneto-crystalline anisotropy, thus, the Néel vector can be manipulated on demand, either rotated smoothly or reversed suddenly, by combined electric and magnetic fields. These results demonstrate the non-volatile switching within a few tens of nanoseconds between time-reversed AFM states in macroscopic volumes by voltage pulses. These observations render quasi-cubic antiferromagnets, like Co_3O_4 , an ideal platform for the ultrafast (pico- to nanosecond) manipulation of microscopic AFM domains and may pave the way for the realization of AFM spintronic devices.⁵

Other published work

Besides the above published work, the PI and his student contribute to other collaborative projects, including enhanced ferromagnetism in monolayer Cr_2Te_3 via topological insulator coupling,⁶ and second-harmonic signature of chiral spin structures in W/Pt/Co heterostructures with tunable magnetic anisotropy.⁷

Future Plans

Magnetic imaging of antiferromagnetic domain walls and surface magnetism

The PI and his students will continue explore the magnetic imaging of antiferromagnetic domain walls in other topological antiferromagnets using the susceptibility contrast mechanism established by the PI's group. The PI and his students will also explore the surface spin-flop/flip transitions in other A-type antiferromagnets, which would have substantial impact on spintronic devices using antiferromagnetic thin films.

Skyrmions in other chiral magnets

The PI's group will continue the effort of exploring skyrmions in chiral magnets. Besides polar magnets where inversion symmetry is broken by lattice degree of freedom, the PI will investigate chiral magnetic order that spontaneously breaks inversion symmetry.

Complex spin orders on Kagome magnets

The PI and his student have obtained very interesting preliminary results of unconventional spin density wave in a few kagome antiferromagnets that host exotic magnetic properties, such as giant anomalous Hall effect. The PI will continue exploring these interesting phenomena.

⁵ S. Ghara, M. Winkler, S. W. Schmid, L. Prodan, K. Geirhos, V. Tsurkan, Wenbo Ge, **Weida Wu**, A. Halbritter, S. Krohns, and I. Kezsmarki, “Nonvolatile electric control of antiferromagnetic states on nanosecond timescales”, Phys. Rev. Lett., **Accepted** (2025).

⁶ Yunbo Ou, Murod Mirzhalilov, Norbert M. Nemes, Jose L. Martinez, Mirko Rocci, Austin Akey, Wenbo Ge, Dhavala Suri, Yiping Wang, Haile Ambaye, Jong Keum, Mohit Randeria, Nandini Trivedi, Kenneth S. Burch, David C. Bell, **Weida Wu**, Don Heiman, Valeria Lauter, Jagadeesh S. Moodera, Hang Chi, “Enhanced Ferromagnetism in Monolayer Cr_2Te_3 via Topological Insulator Coupling”, Rep. Prog. Phys., **88**, 060501 (2025).

References

- 1 Fu, L. & Kane, C. L. *Superconducting proximity effect and Majorana fermions at the surface of a topological insulator*. Physical Review Letters **100**, 96407–96407 (2008).
- 2 Qi, X.-L., Hughes, T. L. & Zhang, S.-c. *Chiral topological superconductor from the quantum Hall state*. 1–5 (2010).
- 3 Nereson, N. & Arnold, G. *Magnetic properties of CeBi, NdBi, TbBi, and DyBi*. Journal of Applied Physics **42**, 1625–1627 (1971).
- 4 Schrunck, B. *et al.* *Emergence of Fermi arcs due to magnetic splitting in an antiferromagnet*. Nature **603**, 610–610 (2022).

Publications (supported by BES in recent 2-year)

Hemian Yi, Yi-Fan Zhao, Ying-Ting Chan, Jiaqi Cai, Ruobing Mei, Xianxin Wu, Zi-Jie Yan, Ling-Jie Zhou, Ruoxi Zhang, Zihao Wang, Stephen Paolini, Run Xiao, Ke Wang, Anthony R. Richardella, John Singleton, Laurel E. Winter, Purnima P. Balakrishnan, Alexander J. Grutter, Moses H. W. Chan, Nitin Samarth, Xiaodong Xu, **Weida Wu**, Chao-Xing Liu, and Cui-Zu Chang, “*Interface-Induced Superconductivity in Magnetic Topological Insulator-Iron Chalcogenide Heterostructures*”, Science, **383**, 634–639 (2024).

Hee Taek Yi, Xiong Yao, Deepti Jain, Ying-Ting Chan, An-Hsi Chen, Matthew Brahlek, Kim Kisslinger, Kai Du, Myung-Geun Han, Yimei Zhu, Weida Wu, Sang-Wook Cheong, and Seongshik Oh, “*Universal Superconductivity in FeTe and All-Iron-Based Ferromagnetic Superconductor Heterostructures*”, Adv. Func. Mater., **35**, 2418259, (2025).

Zengle Huang, Hemian Yi, Daniel Kaplan, Lujin Min, Hengxin Tan, Ying-ting Chan, Zhiqiang Mao, Binghai Yan, Cui-Zu Chang, **Weida Wu**, “*Hidden non-collinear spin-order induced topological surface states*”, Nature Comm., **15**, 2937 (2024).

Peter Meisenheimer, Hongrui Zhang, David Raftrey, Xiang Chen, Yu-Tsun Shao, Ying-Ting Chan, Reed Yalisove, Rui Chen, Jie Yao, Mary C. Scott, **Weida Wu**, David A. Muller, Peter Fischer, Robert J. Birgeneau, and Ramamoorthy Ramesh, “*Ordering of room-temperature magnetic skyrmions in a polar van der Waals magnet*”, Nature Comm., **14**, 3744 (2023).

S. Ghara, M. Winkler, S. W. Schmid, L. Prodan, K. Geirhos, V. Tsurkan, Wenbo Ge, **Weida Wu**, A. Halbritter, S. Krohns, and I. Kezsmarki, “*Nonvolatile electric control of antiferromagnetic states on nanosecond timescales*”, Phys. Rev. Lett., **Accepted** (2025).

Yunbo Ou, Murod Mirzhalilov, Norbert M. Nemes, Jose L. Martinez, Mirko Rocci, Austin Akey, Wenbo Ge, Dhavala Suri, Yiping Wang, Haile Ambaye, Jong Keum, Mohit Randeria, Nandini Trivedi, Kenneth S. Burch, David C. Bell, **Weida Wu**, Don Heiman, Valeria Lauter, Jagadeesh S. Moodera, Hang Chi, “*Enhanced Ferromagnetism in Monolayer Cr₂Te₃ via Topological Insulator Coupling*”, Rep. Prog. Phys., **88**, 060501 (2025).

Yang Wang, Ying-Ting Chan, Xiao Wang, Tao Wang, Xuemei M Cheng, **Weida Wu** and John Q Xiao, “*Second-harmonic signature of chiral spin structures in W/Pt/Co heterostructures with tunable magnetic anisotropy*”, J. Phys. D: Appl. Phys., **56**, 205002 (2023).

Atomic-scale characterization of strain-tunable moiré quantum materials

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Keywords: scanning tunneling microscopy, moiré quantum matter, transition metal dichalcogenides, layer pseudospin skyrmions, uniaxial strain

Research Scope

Understanding and controlling the properties of strongly correlated and topological states of matter is a long-standing goal in condensed matter physics. Moiré materials – stacks of atomically thin crystals having either a lattice mismatch or interlayer twist angle – host a rapidly growing array of emergent quantum phases. The defining feature of moiré materials is a long-wavelength beating pattern between the two atomic crystal lattices, generating a synthetic superlattice potential that can profoundly restructure the low-energy electronic bands of the composite material. In certain cases, moiré materials can host flat electronic bands endowed with substantial Berry curvature, providing new platforms for investigating the interplay of strong interactions and nontrivial topology.

A key goal of this project is to image the atomic- and superlattice-scale topographic structures of moiré materials using scanning tunneling microscopy, and to connect these structural features with careful spectroscopic measurements of their low-energy electronic states. Additionally, we aim to understand the role of strain in determining the properties of moiré quantum materials, and to achieve direct in situ control over strain using custom-built piezoelectric-based strain cells.

Recent Progress

Over the past few years, our program has made exciting progress in several complementary directions:

Continuously tunable strain

We have made several advances in our ability to apply continuously tunable uniaxial strain to van der Waals (vdW) heterostructure devices. As part of this program, we developed a new experimental technique for applying strain to vdW devices down to millikelvin temperatures. The strain device consists of three piezoelectric stacks arranged in parallel and poled such that the outer two expand while the inner one contracts (or vice versa). Titanium plates are epoxied to the ends of the piezostacks, with one of the plates having a small gap that can be widened or narrowed proportional to the bias applied to the piezos. By affixing a vdW device across this gap, uniaxial

compressive or tensile strain can be applied to the target material. As proof of principle, we showed that we could substantially tune the resistance of a magic-angle twisted bilayer graphene device with strain.

We subsequently developed a miniaturized version of the strain cell that is compatible with our STM sample plate, as shown in the photograph in Fig. 1a. We also modified our sample fabrication strategy such that devices are made on polyimide substrates rather than silicon wafers (Fig. 1b). The polyimide deforms more easily than silicon, enabling the application of much larger strains. This technique will enable us to image the microscopic properties of moiré vdW samples as they are elastically deformed. Initial STM measurements taken on a twisted graphene moiré superlattice demonstrate stable operation at cryogenic temperatures and reveal movement of features in the topography induced by biasing the piezostacks (Fig. 1c), confirming that the technique can continuously manipulate the sample structure during in situ measurements.

Atomic-scale fingerprints of topology in twisted MoTe₂

Twisted MoTe₂ was recently discovered to host the long-sought fractional quantum anomalous Hall (FQAH) effect [1-2] – an exotic topological state of matter in which strong interactions form new quasiparticles with fractionalized charge excitations. The basic properties of FQAH states, including quantization of the Hall resistance to certain rational multiples of h/e^2 in the absence of a magnetic field, closely resemble those of the well-studied fractional quantum Hall states found in two-dimensional electron systems at large magnetic fields. The formation of zero-field FQAH states in twisted MoTe₂ presents exciting new opportunities to study fundamental open questions surrounding these fascinating fractionalized quantum phases.

The flat bands hosting the FQAH states form due to the moiré superlattice generated by twisting two sheets of MoTe₂ to a small angle of a few degrees. Seminal theoretical work in 2019 predicted that these flat bands further carry non-zero Chern numbers [3], endowing the material with nontrivial topology. The bilayer system was described using Pauli spin matrices, with the layer index effectively playing the role of a two-level spin. Within this model, the layer polarization of the flat-band wavefunction varies within the moiré unit cell in such a way that it traverses the entire Bloch sphere, creating skyrmions of the layer-pseudospin in real space that are localized to certain

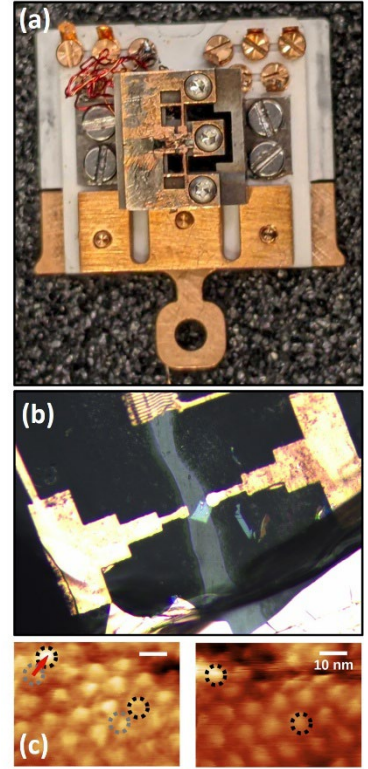


Figure 1. (a) Picture of the custom strain cell mounted on an STM sample plate. (b) Optical micrograph of a vdW device fabricated on a flexible polyimide substrate. (c) STM topography of twisted graphene during strain measurements. The two images are the same scan with 0 V (left) or 60 V (right) applied to the strain cell piezos. Circles track selected topography features.

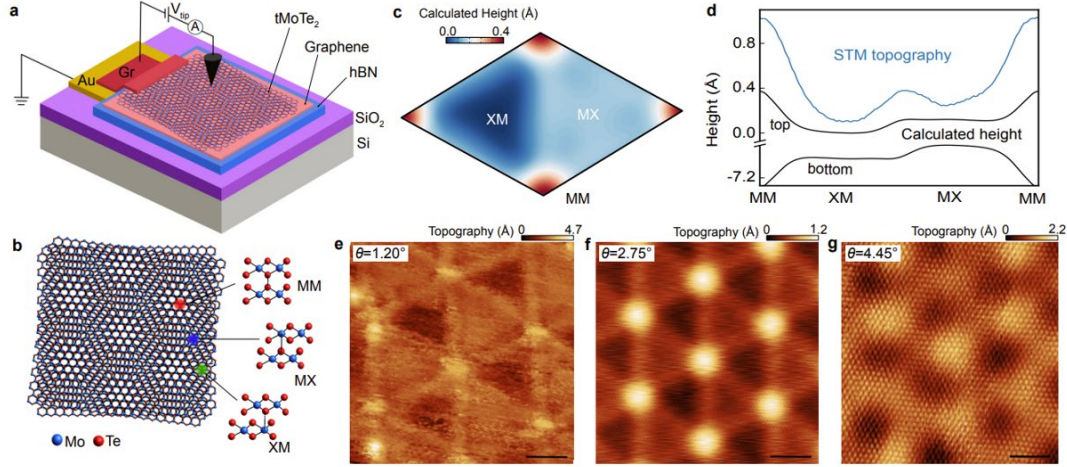


Figure 2. (a) Schematic drawing of the sample, composed of twisted MoTe₂ on a graphene substrate. (b) Schematic of the moiré lattice showing three different high-symmetry stacking sites. (c) DFT calculation of the height of the top layer of the MoTe₂. (d) Comparison of the measured STM topography (blue) with the DFT calculation (black), enabling a determination of the stacking sites. (e-g) Measured STM topographs of twisted MoTe₂ at twist angles of 1.20°, 2.75°, and 4.45°. The scale bars are 10 nm, 5 nm, and 2 nm.

high-symmetry stacking sites within the superlattice. Imaging the flat-band wavefunction with atomic resolution thus offers the possibility of discovering key new insights into the unique topological properties of twisted MoTe₂.

We reported the first STM study of twisted MoTe₂, enabled by our development of new sample-fabrication techniques for creating ultra-clean, surface-exposed samples of air-sensitive materials (Figs. 2a-b). We first imaged the topographic structure of the moiré superlattice at a variety of twist angles. By comparing to machine-learning-assisted DFT calculations, we were able to identify different high-symmetry stacking sites within the moiré unit cell (MX: metal-on-chalcogen, XM: chalcogen-on-metal, MM: metal-on-metal) by tracking their in-plane and out-of-plane atomic-scale lattice relaxations (Figs. 2c-g).

We then acquired maps of the local density of states as a function of energy (Figs. 3a-b). For bands forming from the K point of the monolayer Brillouin zone, we found that the local density of states (LDOS) in the top MoTe₂ layer is aggregated almost entirely onto the MX site within the moiré unit cell, in excellent agreement with our DFT calculations (Fig. 3c). This finding indicates that the north (south) pole of the layer-pseudospin skyrmion lattice resides at MX (XM), consistent with the flat band having a Chern number of +1 (Figs. 3d-e). In contrast, analogous measurements performed on states arising from the Γ point reveal an equal weight of LDOS at MX and XM in the top layer, consistent with the absence of layer-pseudospin skyrmions and a Chern number of 0 (Figs. 3f-g). Our work provides the first experimental understanding of the real-space origin of band topology from the microscopic structure of the moiré TMD lattice, and reveals a prescription for controlling the topological and correlated properties of the material by straining the lattice to manipulate its microscopic structure.

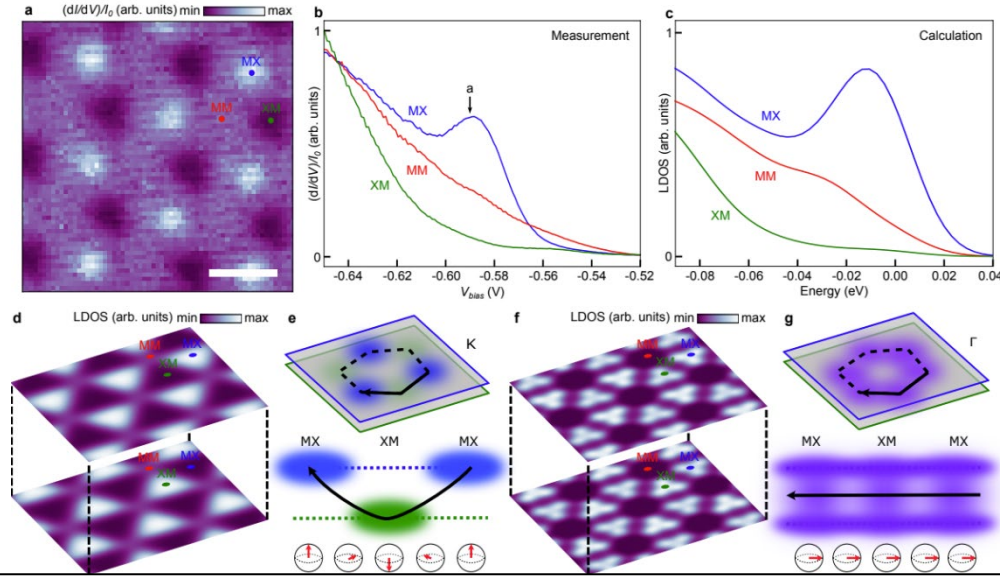


Figure 3. (a) Measurement of the local density of states (dI/dV) in the highest moiré valence band. Scale bar is 5 nm. (b) Individual traces at different high-symmetry stacking sites versus energy. (c) Comparison to DFT calculations. (d) DFT calculations of the LDOS on the top and bottom layers. (e) Layer-pseudospin model for the topological K-point band. (f) Comparable DFT calculation for the moiré band originating from the Γ point of the Brillouin zone. (g) Layer-pseudospin model for the trivial Γ -point band.

Future Plans

Going forward, we will advance our study of the physics of moiré lattices of twisted MoTe_2 and other TMDs using several new experimental strategies. We have recently developed techniques to establish ohmic electrical contacts to twisted MoTe_2 , enabling groundbreaking STM studies of the correlated states that form upon hole-doping. Accessing the full set of emergent quantum states in twisted MoTe_2 further requires independent control over charge doping and displacement field, however this is generally incompatible with conventional STM measurements. We have thus fabricated devices with more complex dual-gated geometries employing a monolayer graphene “sensor layer” to study potential charge-ordered states in the material, including generalized Wigner crystals [4] and possible crystalline topological states. Lastly, we will integrate our samples into our newly developed piezo-based strain cell to study how the layer-pseudospin skyrmion lattice and resulting correlated states evolve as a function of uniaxial strain.

References

1. H. Park et al., *Observation of fractionally quantized anomalous Hall effect*, Nature **622**, 74 (2023).
2. F. Xu et al., *Observation of integer and fractional quantum anomalous Hall effects in twisted bilayer MoTe_2* , Phys. Rev. X **13**, 031037 (2023).
3. F. Wu et al., *Topological insulators in twisted transition metal dichalcogenide homobilayers*, PRL **122**, 086402 (2019).
4. H. Li et al., *Imaging two-dimensional generalized Wigner crystals*, Nature **597**, 650 (2021).

Publications

1. Z. Liu, X. Ma, J. Cenker, J. Cai, Z. Fei, P. Malinowski, J. Mutch, Y. Zhao, K. Hwangbo, Z. Lin, A. Manna, J. Yang, D. Cobden, X. Xu, M. Yankowitz and J.-H. Chu, *Continuously tunable uniaxial strain control of van der Waals heterostructure devices*, Journal of Applied Physics **135**, 204306 (2024).
2. D. Waters, R. Su, E. Thompson, A. Okounkova, E. Arreguin-Martinez, M. He, K. Hinds, K. Watanabe, T. Taniguchi, X. Xu, Y.-H. Zhang, J. Folk and M. Yankowitz, *Topological flat bands in a family of multilayer graphene moiré lattices*, Nature Communications **15**, 10552 (2024).
3. R. Su, D. Waters, B. Zhou, K. Watanabe, T. Taniguchi, Y.-H. Zhang, M. Yankowitz and J. Folk, *Moiré-driven topological electronic crystals in twisted graphene*, Nature **637**, 1084 (2025).
4. E. Thompson, K. T. Chu, F. Mesple, X.-W. Zhang, C. Hu, Y. Zhao, H. Park, J. Cai, E. Anderson, K. Watanabe, T. Taniguchi, J. Yang, J.-H. Chu, X. Xu, T. Cao, D. Xiao and M. Yankowitz, *Microscopic signatures of topology in twisted MoTe_2* , Nature Physics DOI:10.1038/s41567-025-02877-x (2025).

Visualizing Correlated and Topological Quantum Phases in Two-Dimensional Materials

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Research scope:

Studies of correlated and topological quantum states of matter are at the forefront of research in condensed matter physics. With the advent of and rapid advance of utilizing two-dimensional (2D) materials as a platform to create novel nanostructures, the study of 2D materials has entered an exciting new chapter. The ability to engineer electronic correlations and topology using crystalline monolayer materials and their stacks has become a powerful approach to creating new quantum phases in materials. The discovery of superconductivity and plethora of correlated and topological phases in bilayers of graphene that are stacked and twisted at a magic-angle twisted bilayer graphene (MATBG) has catalyzed this emerging area of research in condensed matter physics. The possibility that these chemically pristine materials can elucidate insight to long-standing puzzles, such as understanding superconductivity in correlated electron systems, is tantalizing. At the same time, the opportunity to create fundamentally new phenomena, such as strongly correlated topological phases without a magnetic field that host exotic quasiparticles, is motivating intense exploration of 2D materials and their stacks.

In the last two years, we have shown that the power of scanning probe microscopy/spectroscopy techniques (along with our concentrated efforts to create ultra-clean devices) can be fully utilized to understand the novel quantum phases forming in 2D materials and their stacks. As detailed here, our work has been unique in both advancing the understanding of correlated phases in magic-angle twisted bilayer graphene

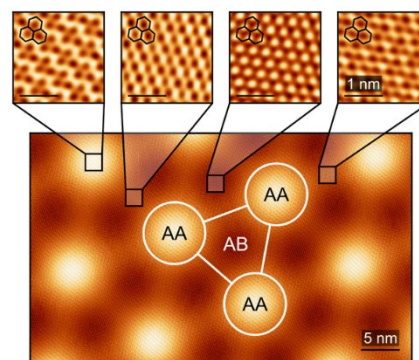


Figure 1. This STM image shows signature of intervalley coherence on the top graphene layer in MATBG. The phases of these wavefunctions strongly modulate spatially, giving rise to apparent variations as imaged in the panels (left). These modulations are indicative of an incommensurate Kekulé state (IKS).

(MATBG) in initiating fundamental new ways to examine elusive states such as the Wigner crystal, detection of the Hofstadter fractal spectrum, and developing new approaches to study fractional quantum Hall (FQH) phases hosting Abelian and non-Abelian anyons. With four papers published in the journal Nature, publications overall, the program has been a success. We are also establishing capabilities for millikelvin atomic force microscopy (AFM), developing charge sensing microscopy and spectroscopy techniques using monolayer graphene as a sensor, and implementing scanning noise spectroscopy to explore the novel quantum phenomena in our crystalline devices.

Recent Progress:

A. Visualizing quantum textures of the many-body wavefunction in magic-angle graphene (Nature 2023) [1]

Broken symmetry states are often detected using bulk scattering techniques, which cannot be applied to 2D devices. In the field of 2D materials, many studies focus on the transport properties of these systems, and little direct information about broken symmetry states can be obtained from such measurements. Therefore, developing the means to detect broken symmetries more directly and correlating them with different properties of the system, i.e. opening of a gap is critical. In the last cycle, we focused on understanding the correlated insulating states of MATBG, from which the superconducting state emerges when the system is doped. Early on in our studies, when entering the insulating phase, such as that near filling $\nu=-2$ of two electrons in a moiré unit cell, we detected on the atomic scale a tripling of the unit cell for local density of state near the Fermi energy (Fig. 1). As we had observed similar behavior in monolayer graphene's zeroth Landau level at half filling, we realized that an intervalley coherent state could be the reason for the formation of half-filled insulating states. One can consider such states as a generalization of quantum Hall ferromagnetic phases, even if the flat band of MATBG is not generated by a magnetic field like that of LLs. However, the problem became far more complex than simply intervalley coherent states, as the pattern of tripling of the unit cell varied from location to location on the sample (Fig. 1). The outcome of analysis of high-resolution data and comparison to predictions for various states, allowed us to show that in almost all MATBG devices in which there is some degree of strain, an incommensurate Kekulé state (IKS) with spiral order is the ground state. This state breaks symmetries on both the atomic and moiré scales, and without the STM data it would have been impossible to identify it. This solved the five-year puzzle of understanding the

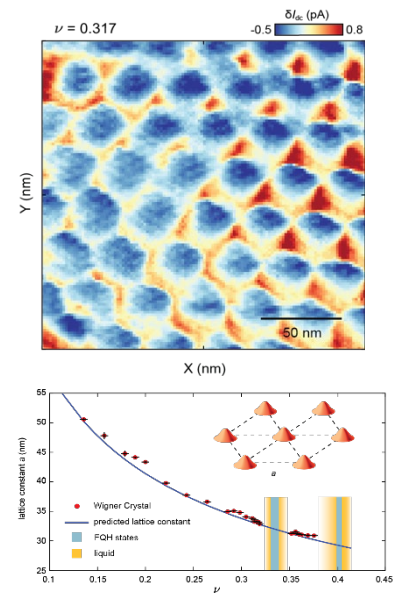


Figure 2. Top panel shows direct visualization of the Wigner crystal in $N=0$ Landau level of BLG. The size of each site can be understood as that associated with the zero-point motion of localized electrons in the crystal. The bottom panel shows the crystal lattice constant as function of filling (electron density) of the LL. The solid curve is the predicted Wigner crystal lattice constant as function of filling. The Wigner crystal melts approaching

nature of correlated insulator in MATBG, which was originally mis-identified at a Mott insulator, and not a broken symmetry state as we demonstrated.

B. Direct observation of magnetic field-induced Wigner crystal (Nature 2024) [2]

Wigner predicted that when the Coulomb interactions between electrons become much stronger than their kinetic energy, electrons crystallize into a closely packed lattice. A variety of 2D systems in both zero and high fields have shown evidence for electron crystallization using a wide range of experimental techniques. Most techniques provide indirect evidence for a Wigner crystal formation, making it difficult to distinguish crystallization from localization by disorder, and are unable to provide information on the Wigner crystal's lattice structure and symmetry. We used high-resolution STM measurements to directly image a magnetic field-induced electron Wigner crystal in Bernal-stacked bilayer graphene (BLG) and examined its structural properties as a function of electron density, magnetic field, and temperature. At high fields and the lowest temperature, we observed a triangular lattice electron Wigner crystal in the lowest Landau level (Fig. 2). The Wigner crystal possesses the expected lattice constant and is robust between $\nu \sim 0.13$ and $\nu \sim 0.38$ except near fillings where it competes with fractional quantum Hall (FQH) states (Fig. 2). Increasing the density or temperature results in the melting of the Wigner crystal into a liquid phase that is isotropic but has a modulated structure characterized by the Wigner crystal's Bragg wavevector. Analysis of individual lattice sites reveals signatures that may be related to the quantum zero-point motion of electrons in the Wigner crystal lattice.

C. First experimental demonstration of self-similar behavior in Hofstadter energy spectrum, Nature 2025) [3]

The Hofstadter's butterfly, the predicted energy spectrum for non-interacting electrons confined to a 2D lattice in a magnetic field, is one of the most remarkable fractal structures in nature. At rational ratios of magnetic flux quanta per lattice unit cell, this spectrum shows self-similar distributions of energy levels that reflect its recursive construction. Prior to our work, direct spectroscopy of the fractal energy spectrum predicted by Hofstadter nearly 50 years ago has remained out of reach. We used high-resolution STM imaging and spectroscopy to probe the flat electronic bands in twisted bilayer graphene near the predicted second magic angle, an ideal setting for spectroscopic studies of Hofstadter's spectrum. Our study shows the fractionalization of flat moiré bands into discrete Hofstadter sub-bands and discerns experimental signatures of self-similarity of this spectrum (Fig. 3). Moreover, investigating the Hofstadter spectrum as a

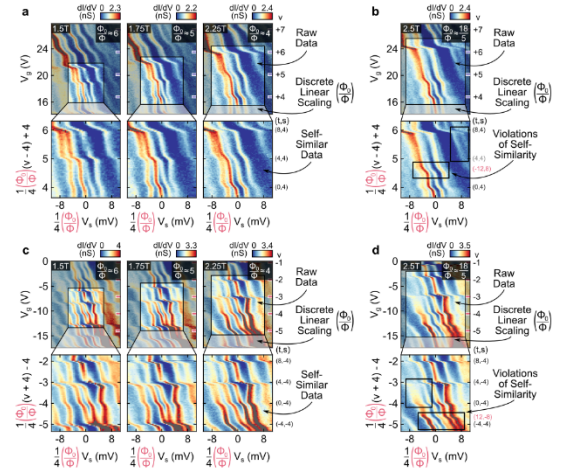


Figure 3. $dI/dV(V_s, V_g)$ obtained at the center of an AA site in Device A1 near $\nu = +4$ at $B = 1.5T$ ($\Phi/\Phi_0 \approx 1/6$; left), $1.75T$ ($\Phi/\Phi_0 \approx 1/5$; middle), and $2.25T$ ($\Phi/\Phi_0 \approx 1/4$; right). Top row of panels shows raw $dI/dV(V_s, V_g)$ (horizontal axes range from -13.5mV to 13.5mV). The bottom row shows data scaled in energy and density by a discrete linear scaling factor of $\frac{1}{4}(\Phi_0/\Phi)$ where Φ_0/Φ is an integer. The full density expression $\frac{1}{4}(\Phi_0/\Phi)(\nu - \nu_{ref}) + \nu_{ref}$, where $\nu_{ref} = +4$, both

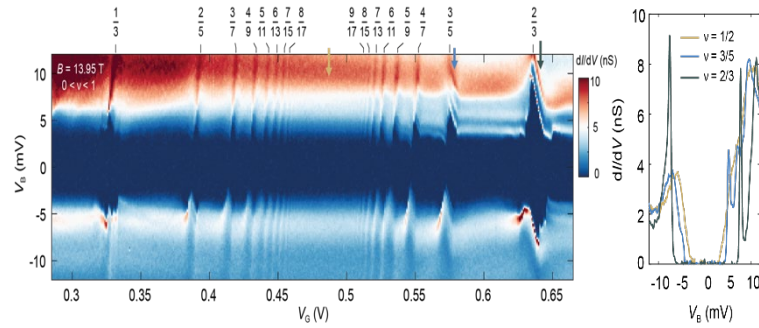


Figure 4. Left panel shows STM spectroscopy of an odd denominator sequence of FQH states for $N=0$ Landau level in BLG. These data show the low energy Coulomb gap is modified by a spectroscopic signature of the FQH state. The right panel shows that such spectra in the FQH states exhibit very sharp features, which are indicative of

function of energy, magnetic field, and carrier density enables active control over the complex interplay of many electronic effects beyond Hofstadter's simplified model. This allowed us to disentangle these effects using spectroscopic information that is inaccessible to transport and thermodynamic probes typically used to study Hofstadter systems. Our measurements uncover a spectrum that evolves dynamically with electron density, displaying phenomena beyond that of Hofstadter's original model due to the combined effects of strong correlations, Coulomb interactions, and the quantum degeneracy of electrons in twisted bilayer graphene.

D. High-resolution tunneling spectroscopy of FQH states (Nature Physics 2025) [4]

Fractional quantum Hall (FQH) states and their low-energy excitations with anyonic statistics have been of interest for many decades but there is renewed interest in such states because of their potential application for creating topologically protected qubits. Much of what is known about these states and their excitations has been obtained through macroscopically averaged experiments or studies of their edge states. We made a fundamental advance in the study of FQH states by showing how STM spectroscopy can probe this novel state and uncovered new ways of characterizing FQH states, find new ones, and provide a new approach to study the excitation spectrum of these states. We performed high-resolution scanning tunneling microscopy and spectroscopy of FQH states in ultra-clean Bernal-stacked bilayer graphene (BLG) devices (**Fig. 4**). These measurements can be analyzed to extract quasiparticle and thermodynamic gap energies for FQH states that can be compared to theoretical calculations. A particularly intriguing feature resolved in our experiments are sharp excitations in tunneling experiments that have been predicted for electron fractionalizing into bound states of anyons (**Fig. 4**). Our experiments detected the sequence of Jain states while filling the $N=0$ LL and an even-denominator FQH state and its daughter states at half filling of the $N=1$ LL in BLG. The appearance of the daughter states suggests that the even-denominator states we found are non-Abelian, Moore-Read states, which in our samples show a remarkably large energy gap of 20K. This energy gap is by one or two orders of magnitude larger than other platforms for hosting non-Abelian anyons, making BLG a promising platform for the manipulation of these novel quasiparticles and for the creation of a topological quantum bit. Unlike transport studies, our STM experiments characterize the bulk properties of FQH states in the absence of disorder, which also reveal previous undiscovered FQH states in such ultra-clean samples.

Other notable research efforts supported by DOE:

- Development of a new high resolution charge sensing technique (PNAS 2025) [5].
- Signatures of strong electron-phonon coupling in MATBG (Nature 2025) [6]

Future plans:

Our ongoing program builds upon the success of the last cycle in both creating ultra-clean, two-dimensional (2D) crystalline devices in which novel correlated, and topological phases have been realized by utilizing both well-established, high-resolution scanning tunneling microscopy (STM) as well new microscopy techniques we developed to study them. We are exploring five related but distinct research areas. The first area will be focused on electronic crystallization in a broad range of settings, from advancing our first direct observation of the Wigner crystal of electrons to those of holes and other more exotic crystals, such Skyrme crystals, and investigate the potential crystallization of fractionally charged quasiparticles. The second direction will utilize the advances we have made in sensing FQH states with our microscopy techniques to study the newly discovered fractional quantum anomalous Hall (FQAH) phase in twisted MoTe₂ bilayers. The last year, we had integrated the nanofabrication of split gates in our devices with our microscopy experiments, which we will exploit in the third direction to study edge phenomena in various topological phases including those found in MATBG, FQH and FQAH phases. The fourth area will focus on application of our newly developed charge sensing techniques, developed under this program to sense individual, fractionally charged quasiparticles in FQH and FQAH phases. A final research area will revisit a previous approach for band structure engineering, using newly developed methods for fabrication of periodic structures in gated 2D devices and our measurement approach that can probe such systems locally. In addition to these research directions, we are implementing a new experimental technique for local noise spectroscopy measurements of the novel quantum phases forming in our 2D materials.

Publications acknowledge DOE-BES support (2023-2025): Primary Supported publication in are noted with a *

1. * K. P. Nuckolls, R. L. Lee, M. Oh, D. Wong, T. Soejima, J. Pyo Hong, D. Călugăru, J. Herzog-Arbeitman, B. A. Bernevig, K. Watanabe, T. Taniguchi, N. Regnault, M. P. Zaletel, and A. Yazdani, "Quantum textures of the many-body wavefunctions in magic-angle graphene," *Nature* **620**, 525-532 (2023). DOI: <https://doi.org/10.1038/s41586-023-06226-x>
2. * Y.-C. Tsui, M. He, Y. Hu, E. Lake, T. Wang, K. Watanabe, T. Taniguchi, M. P. Zaletel, and A. Yazdani, "Direct observation of a magnetic field-induced Wigner crystal," *Nature* **628**, 287-292 (2024). DOI: <https://doi.org/10.1038/s41586-024-07212-7>
3. * K. P. Nuckolls, M. G. Scheer, D. Wong, M. Oh, R. L. Lee, J. Herzog-Arbeitman, K. Watanabe, T. Taniguchi, B. Lian, and A. Yazdani, "Spectroscopy of the Fractal Hofstadter Energy Spectrum," *Nature* (2025). <https://doi.org/10.1038/s41586-024-08550-2>

4. * Y. Hu, Y.-C.n Tsui, M. He, U. Kamber, T. Wang, A. S. Mohammadi, K. Watanabe, T. Taniguchi, Z. Papic, M. P. Zaletel, and A. Yazdani, “High-resolution tunneling spectroscopy of fractional quantum Hall states,” *Nat. Phys.* (2025) <https://doi.org/10.1038/s41567-025-02830-y>.
5. * C.-L. Chiu, T. Wang, R. Fan, K. Watanabe, T. Taniguchi, X. Liu, M. P. Zaletel, and A. Yazdani, “High spatial resolution charge sensing of quantum Hall states,” *Proc. Natl. Acad. Sci. U.S.A.* **122** (8) e2424781122 (2025). <https://doi.org/10.1073/pnas.2424781122>
6. * C. Chen, K. P. Nuckolls, S. Ding, W. Miao, D. Wong, M. Oh, R. L. Lee, S. He, C. Peng, D. Pei, Y. Li, C. Hao, H. Yan, H. Xiao, H. Gao, Q. Li, S. Zhang, J. Liu, L. He, K. Watanabe, T. Taniguchi, C. Jozwiak, A. Bostwick, E. Rotenberg, C. Li, X. Han, D. Pan, Z. Liu, X. Dai, C. Liu, B. A. Bernevig, Y. Wang, A. Yazdani, and Y. Chen, “Strong electron-phonon coupling in magic-angle twisted bilayer graphene,” *Nature* **636**, 342-347 (2024). <https://doi.org/10.1038/s41586-024-08227-w>
7. * S. Pu, A. C. Balram, Y. Hu, Y.-C. Tsui, M. He, N. Regnault, M. Zaletel, A. Yazdani, and Z. Papić, “Fingerprints of composite fermion Lambda levels in scanning tunneling microscopy,” *Phys. Rev. B* **110**, L081107 (2024) <https://journals.aps.org/prb/abstract/10.1103/PhysRevB.110.L081107>
8. C.-X. Liu, Y. Chen, A. Yazdani, and B. A. Bernevig, “Electron- K -phonon interaction in twisted bilayer graphene,” *Phys. Rev. B* **110**, 045133 (2024) <https://journals.aps.org/prb/abstract/10.1103/PhysRevB.110.045133>
9. K. P. Nuckolls and Ali Yazdani, “A microscopic perspective on moiré materials,” *Nature Reviews Materials* **9**, 460-480 (2024); <https://doi.org/10.1038/s41578-024-00682-1>
10. D. Wong, K. P. Nuckolls, M. Oh, R. L. Lee, K. Watanabe, T. Taniguchi, and A. Yazdani, “Insulators at Fractional Fillings in Twisted Bilayer Graphene Partially Aligned to Hexagonal Boron Nitride,” *Low Temperature Physics* **49**, 655-661 (2023). DOI: <https://doi.org/10.1063/10.0019422>
11. G. Farahi, C.-L. Chiu, X. Liu, Z. Papic, K. Watanabe, T. Taniguchi, M. P. Zaletel, and A. Yazdani, “Broken symmetries and excitation spectra of interacting electrons in partially filled Landau levels,” *Nature Physics* **19**, 1482-1488 (2023). DOI: <https://doi.org/10.1038/s41567-023-02126-z>

Probing the electric double layer through 3D atomic force microscopy and multiscale simulations

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Keywords: solid-liquid interfaces, electric double layers, atomic force microscopy, molecular dynamics, deep learning-based simulations

Research Scope

This project aims to enable electrochemical 3D atomic force microscopy (EC-3D AFM) to probe the complex atomic scale structure of the electrode-electrolyte interfaces or the electric double layers (EDLs) by tackling two major challenges: first, existing efforts to apply 3D AFM to electrode electrolyte interfaces did not achieve subnanometer lateral resolution because of inadequate force resolution; second, it is difficult to interpret these subnanometer features even if they were readily available. PI Ye is working with co-PI Ashlie Martini and collaborator David Prendergast to develop EC-3D-AFM capable of mapping the 3D arrangement of solvent molecules and ions. Ye's expertise in AFM and surface electrochemistry is complemented by Martini's expertise in simulations of tip-surface interactions and Prendergast's in *ab initio* molecular dynamics (MD) simulations of EDLs. Atomistic modeling of tip-sample interactions at the EDLs is carried out to understand the contrast mechanisms and interpret imaging results.

Recent Progress

Development of superresolution EC AFM.

After the successful installation of Asylum Research Cypher AFM in summer 2024, we tested the capability in atomic resolution imaging of solid-liquid interfaces. Atomic resolution can be routinely achieved on mica, showcasing the performance of that the customized AFM has high spatial resolution (Figure 1A). This AFM also allowed *in situ* high resolution imaging of

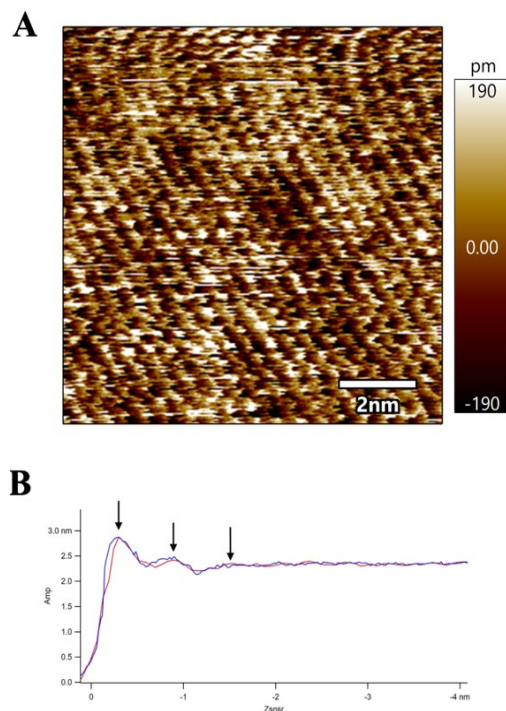


Figure 3 (A) AFM image of mica in water using the custom-built AFM. Atomic lattice was successfully resolved. (B) Amplitude vs distance curves of an oligoethyleneglycol self-assembled monolayer on gold. Arrows mark three distinct hydration layers on the monolayer.

biomaterials (Figure 2), which led to a manuscript submitted for review.

As a step toward mapping electrode-electrolyte interfaces, we have used the custom AFM to acquire force curves on hydrophilic surfaces. Hydrophilic surfaces are known to have ordered hydration layers near the surface.¹ Oligoethyleneglycol self-assembled monolayers on gold, which are known to bind water strongly, are a good model system. Indeed, we observed three peaks that are indicative of three distinct hydration layers (Figure 1B). The success shows that the AFM possesses the noise performance that is needed to probe the potential-dependent structures of water molecules near solid surfaces.

Although Cypher ES AFM features the highest resolution and lowest noise among commercial liquid AFMs in part due to its small mechanical loop, the small size makes it difficult to integrate electrochemistry. We have developed a new electrochemical cell to enable *in situ* EC AFM (Figures 3). We constructed a new ultrasmall, double junction Ag/AgCl electrode with a cross section of 1 mm (Figure 3A). This new design allows the small liquid cell of the AFM to be integrated with a stable reference electrode instead of a quasi-reference electrode that is used in commercial configurations (Figure 3B, C). Moreover, the double junction reduces the leakage of chloride contamination into the liquid cell, a common concern for Ag/AgCl reference electrodes. We have successfully used this new EC liquid cell to perform potentiodynamic imaging of a gold surface (Figure 3D). As a high potential is applied, the gold surface became roughened due to electrochemical oxidation, showing that electrochemistry has been successfully integrated.

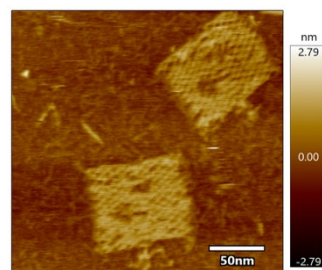


Figure 4 AFM image of DNA origami acquired using the customized Cypher AFM.

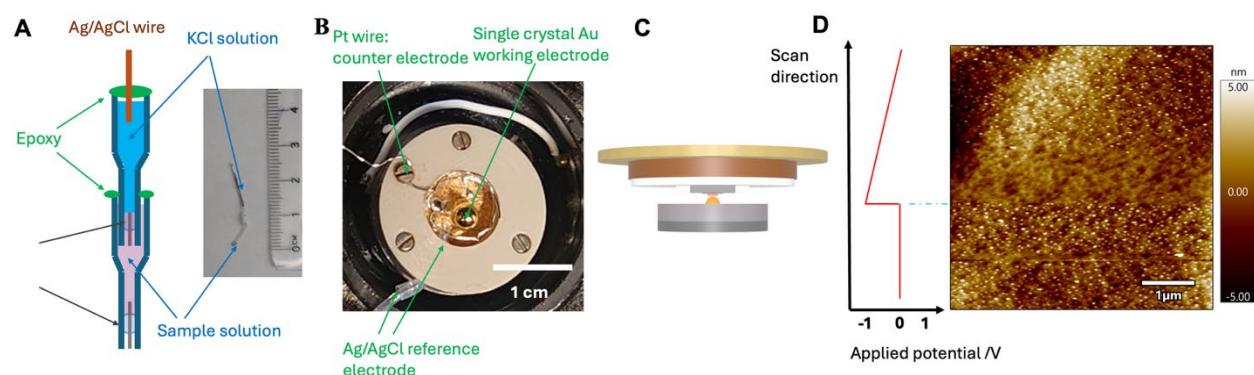


Figure 5 (A) Novel ultrasmall double junction Ag/AgCl reference electrode. (B) Top view photo of electrochemical cell integrated into the Cypher AFM. (C) A 3D rendered side view of the scanning head of the EC AFM. (D) In situ imaging of Au(111) under 0.1 M H₂SO₄ as the potential is changed. While the bottom image was collected at 0 V, the potential was stepped to -1V then ramped back to 0V.

Predict and interpret subnanometer contrast in 3D imaging. Since ionic force field parameters are typically developed to describe bulk solvation of salts, it is unclear if they can accurately describe the electrode-electrolyte interface. To address this limitation, we systematically investigated how ion force field parameters affect the adsorption free energy profiles of Na⁺, Cl⁻, and F⁻ at the water–

Au(111) interface. Using enhanced sampling techniques, we first quantified the sensitivity of interfacial ion adsorption to four different widely used classical Lennard-Jones (LJ) parameter sets: Jorgensen,^{2,3} Dang,⁴ and Sengupta (Figure 4). We also analyzed the effect of the 12-6 LJ parameters on adsorption behavior and propose a simple scheme to predict changes in parameters.

Beyond classical force fields, we assessed the capability of state-of-the-art Machine Learning Interatomic Potentials (MLIPs), specifically the Universal Models for Atoms (UMA), to describe ion adsorption at the gold/water interface. We benchmarked the free energy profiles predicted by MLIPs against both classical MD results and experimental trends, evaluating their transferability and accuracy for complex interfacial systems. Finally, we integrated the free energy profiles obtained from molecular simulations into a physics-informed continuum model of the electric double layer. This multiscale approach allowed us to investigate how differences in atomistic parameterization propagate to macroscopic experimental observables such as differential capacitance and the structure of the electric double layer.

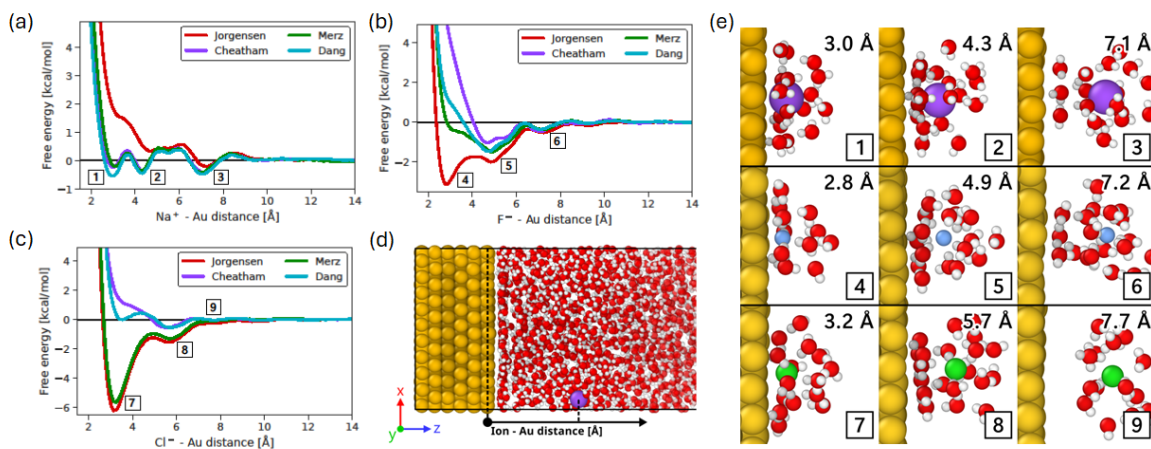


Figure 4 Comparison of the free energy profile of Na⁺ (a), F⁻ (b), Cl⁻ (c) in TIP3P water as a function of their distance from a Au(111) surface. (d) Schematic of a classical MD system with a single Na⁺ ion, water and the gold slab. (e) Snapshots from the classical MD trajectory for Na⁺ (purple, top, Cheatham), F⁻ (blue, center, Jorgensen), and Cl⁻ (green, bottom, Merz). The other elements are Au (yellow), O (red), and H (white). The distance from the Au(111) surface for each snapshot is given in the top-right corner. Water molecules further from the surface are not shown for visualization purposes. The numbering corresponds to the minima labeled in (a), (b), and (c).

By combining molecular dynamics simulations, free-energy sampling, and continuum modeling of aqueous NaF and NaCl at the Au(111) electrode, we demonstrated how standard mixing rules for LJ parameters can lead to dramatically different outcomes in terms of ion concentration profiles, potentials of zero charge, and differential capacitance curves. This is despite different LJ parameters taken from previous studies leading to similar bulk electrolyte thermodynamics. To retain the computational efficiency of these classical models, we used the UMA-S(OMat) MLIP as a surrogate *ab initio* benchmark and proposed new LJ parameters for the ion-Au interactions, for each specific starting set of ion LJ parameters, that approximate the adsorption free-energy profiles generated using the more accurate MLIP. These ion-Au interaction parameters can be viewed as approximately intrinsic, being relatively insensitive to the starting ion interaction

parameters. This finding indicates that LJ mixing rules may not be advisable for studies of interfaces. However, as demonstrated for NaF solutions, LJ potentials with corrected interfacial interactions may still provide useful predictions of electrochemical observables, provided that all local minima in the ion adsorption free energy profile can be reproduced. Systematic differences in differential capacitance behavior at large positive potentials were observed for NaCl solutions, primarily due to lack of specific adsorption of Cl⁻ in the classical LJ models. Future studies may consider correcting for these shortcomings by also updating other force field parameters (ion-water or water-electrode) or by introducing different analytic functional forms for the ion-electrode interaction. Nevertheless, this work establishes a robust protocol for future work on integrating molecular insights into continuum models of the electric double layer through atomistic free-energy sampling. A manuscript reporting these findings is accepted for publication at Journal of Chemical Physics.

Future Plans

With the successful completion of EC liquid cell, we plan to use this AFM to image some of the model surfaces under electrochemical control. One of the systems of interest is the potential-dependent structure of iodine adlayer on Au(111) surface. Force distance curves of the gold electrode under different applied potentials. These results will reveal the water structure near the electrode surface under different potentials, which will be compared to simulation results. With the machine learning forcefield training nearing completion, we have initiated the development of a simulation protocol to investigate the sub-nanometer contrast in Atomic Force Microscopy (AFM). We will first create and test a representative system to replicate the AFM process. We have already employed classical and reactive forcefields to train the models, with plans to transition to the newly developed machine learning forcefield for final simulations. Once the optimal model is finalized, the second stage will involve analyzing the effects of tip atom distribution through systematic perturbation of the tip structure. The primary goal here is to develop a machine learning model capable of predicting anomalies observed in experimental 3D AFM images. By systematically varying the tip configuration, we aim to identify key structural factors influencing the AFM contrast at the sub-nanometer scale.

References

1. Fukuma, T.; Garcia, R., Atomic- and Molecular-Resolution Mapping of Solid-Liquid Interfaces by 3d Atomic Force Microscopy. *ACS Nano* **2018**, *12*, 11785–11797.
2. Jensen, K. P.; Jorgensen, W. L., Halide, Ammonium, and Alkali Metal Ion Parameters for Modeling Aqueous Solutions. *J Chem Theory Comput* **2006**, *2*, 1499–1509.
3. Joung, I. S.; Cheatham, T. E., Determination of Alkali and Halide Monovalent Ion Parameters for Use in Explicitly Solvated Biomolecular Simulations. *J Phys Chem B* **2008**, *112*, 9020–9041.
4. Smith, D. E.; Dang, L. X., Computer-Simulations of NaCl Association in Polarizable Water. *J Chem Phys* **1994**, *100*, 3757–3766.

Publications

1. Petrek, Z. J.; DeMello, A.; Dudkin, R.; Lwin, B.; Giagou, T.; Chong, H.; Ye, T., (2025), Surface Crowding Effects on Protein Target Capture on Aptamer Functionalized Gold Nanoparticles. *Langmuir*, 41(39), 26730-26737.
2. Roncoroni, F. F., Abrar; Li, Yichen; Ye, Tao; Martini, Ashlie; Prendergast, David, (2026) Deriving Effective Electrode-Ion Interactions from Free-Energy Profiles at Electrochemical Interfaces. *J. Chem Phys.*, Accepted
3. Li, Y., Shao, R., Sterling, S., Goodlad, M., Ke, Y., Arya, G. & Ye, T., Engineering Surface Interactions for High-Precision Placement of DNA Origami onto Nanoscale Lithographic Patterns. *Under Revision*.

Spin-resolved imaging of quantum materials

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Keywords: spin-polarized scanning tunneling microscopy (SP-STM), quantum materials, magnetic domains, altermagnets, electron-spin resonance scanning tunneling microscopy

Research Scope

Understanding the interplay of electronic, magnetic and structural information in solids is of fundamental importance and it is often facilitated by local detection probes. Within this realm, uncovering spin-related information in quantum materials with atomic-resolution still presents a special challenge. This project aims to use spin-polarized scanning tunneling microscopy (SP-STM) to study pressing quantum materials problems. The overarching goal is to visualize inhomogeneous magnetic, electronic and impurity information in select unconventional superconductors and magnets. Another objective is to improve sensitivity of spin-polarized tips by exploring using magnetic atom terminated superconducting tips. We are also implementing electron spin resonance in combination with SP-STM, for fresh exploration of spin properties of individual defects and the interaction between a collection of defects in materials. The overall experimental approach will continue to establish the foundation to study electron spin and charge information at the atomic length scales in quantum solids in which different degrees of freedom intertwine to create new states of matter.

Recent Progress

1. Imaging magnetic field tunable density waves in a layered altermagnet

In recent years, several groups reported theoretical predictions of collinear antiferromagnets demonstrating various time-reversal symmetry breaking phenomena and spin-polarized behaviors, subsequently named altermagnets. Altermagnetism exists in the space between antiferromagnetism and ferromagnetism – it is characterized by a net zero magnetization, yet the Kramers degeneracy is lifted by a nonrelativistic, momentum-dependent spin-splitting of the electronic bands. Due to intrinsic time-reversal symmetry breaking predicted to emerge in these systems, altermagnets have been theorized to exhibit numerous exotic phenomena. Atomic-scale spectroscopic insights into altermagnets are highly-desirable, but remain elusive.

We studied a newly discovered layered triangular lattice altermagnet, Co-intercalated NbSe₂¹. Differential conductance dI/dV spectra at low temperature reveal a surprising partial gap opening centered at the Fermi level, which is not captured by density functional theory calculations of the system in the pure altermagnetic state. Spatial mapping using spectroscopic-imaging STM and SP-STM further reveals emergent tri-directional charge and spin density modulations with a $2a_0$ wave length (Figure 1b-c). Interestingly, we discover that out-of-plane magnetic field can serve as a knob to tune the amplitudes of the modulations as well as alter the overall electronic density-of-

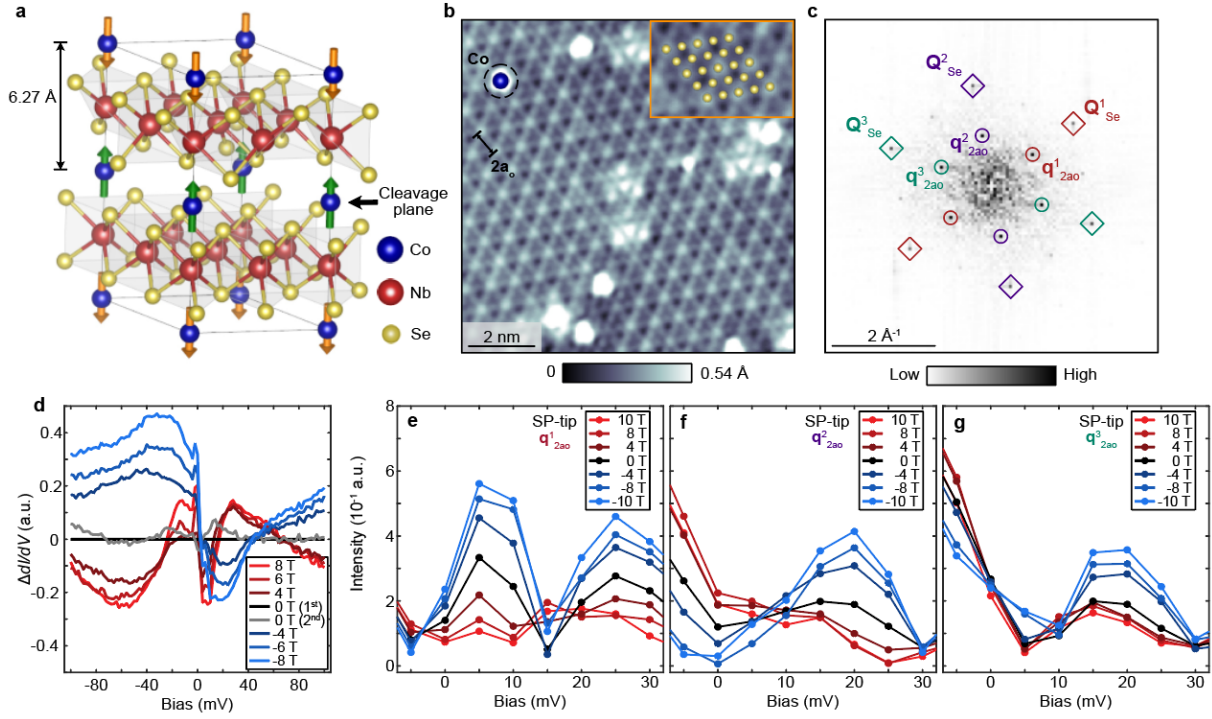


Figure 6. SP-STM imaging of $\text{Co}_{0.25}\text{NbSe}_2$. (a) Crystal structure. (b) STM topograph of Se-terminated surface and (c) its Fourier transform. (d) Change in dI/dV spectra with magnetic field. (e-g) The intensity of $2a_0$ peaks (circled in (c)) as a function of magnetic field. Negative fields denote reversal of field applied along the c -

states in a manner that is strongly dependent on the field direction and strength (Figure 1d-g). This can be attributed to the tilting of spins by the external magnetic field, which can have profound implications on the electronic properties of the altermagnet. Our work uncovers tunable modulations accompanied by concomitant changes in the electronic band structure, and sets the foundation for studies of magnetic field tunable phenomena in altermagnets.

2. The impact of single atom impurities and domain formation in an altermagnet

We investigated inhomogeneity and the effects of single atom defects in the same altermagnet, Co-intercalated NbSe_2 . Our SP-STM experiments revealed two types of nanoscale regions on the sample, which can be visualized in SP-STM spin-resolved $M(r)$ maps as red/blue regions of higher/lower apparent height (Figure 2b). Interestingly, both types of regions are magnetic and appear to break time-reversal symmetry, as evidenced by dI/dV spectra being distinctly different when measured with tip's spin polarization being up vs down. Domains appear to

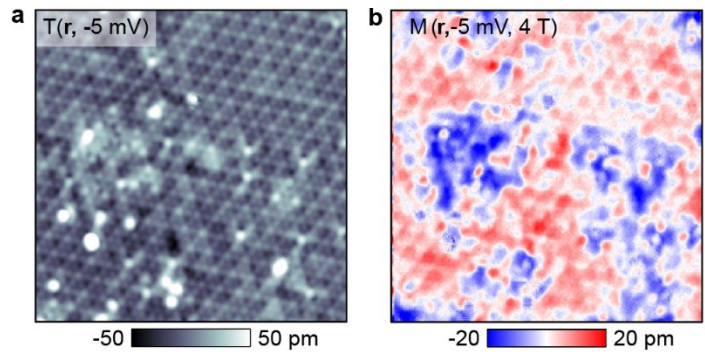


Figure 7. SP-STM of magnetic inhomogeneity in $\text{Co}_{0.25}\text{NbSe}_2$. (a) STM topograph, and (b) Spin-resolved $M(r)$ map over the area in (a). $M(r)$ map is obtained by subtracting topographs acquired with spin-up and spin-down

nucleate near atomic-scale impurities. These experiments provide a thus far unique atomic-scale insight into the inhomogeneity in altermagnets.

3. High temperature melting and decoupling of charge density waves in UTe_2

We studied the temperature and magnetic-field evolution of charge density waves in the rare spin-triplet superconductor candidate UTe_2 using spectroscopic imaging STM ². We revealed that charge modulations composed of three different wave vectors gradually weaken in a spatially inhomogeneous manner (Figure 3a,b), while persisting to a surprisingly high temperatures of 10–12 K ², much higher than the superconducting transition temperature of 1.6 K. Our observations matched closely to the temperature scale potentially related to short-range magnetic correlations, providing a possible connection between density waves observed by surface probes and intrinsic bulk features. Importantly, we found that charge density wave modulations became suppressed with magnetic field both below and above superconducting T_c in a comparable manner (Figure 3b,c). Our work may point towards an intimate connection between hidden magnetic correlations and the origin of the unusual charge density waves in UTe_2 .

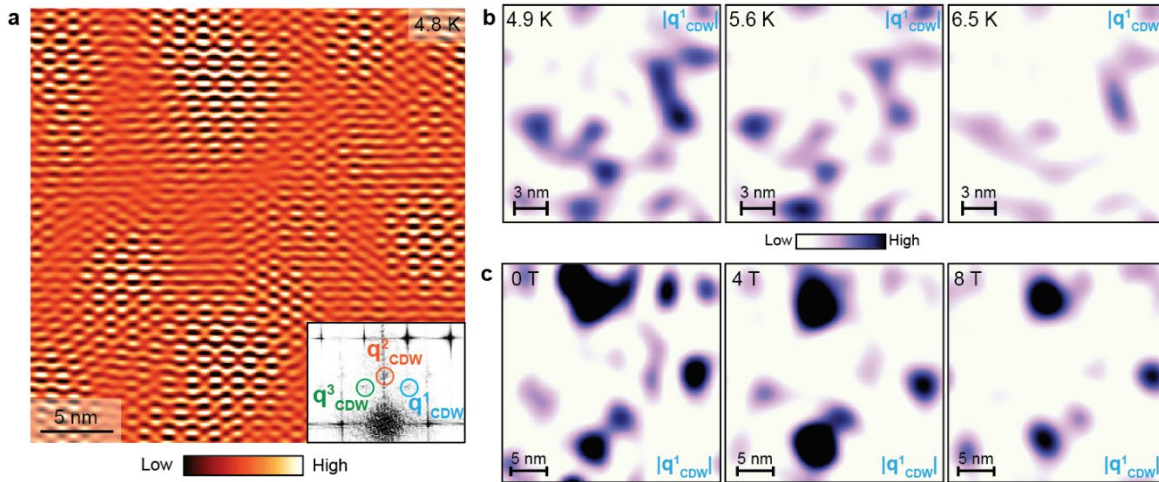


Figure 8. CDW suppression via temperature and magnetic field increase in UTe_2 . (a) Filtered integrated dI/dV map over the (0-11) surface. (b) Spatial amplitude maps of q^1_{CDW} over area (I) as a function of temperature. (c) Spatial amplitude maps of q^1_{CDW} over area (II) as a function of magnetic field. Both (b,c) show gradual shrinking of puddles, which revert to original shape when the field is removed or when the temperature is

4. Imaging orbital magnetic moments in a kagome metal

Emergent theory of topological materials suggests that certain materials can have enormous orbital magnetic moments even in the absence of spin magnetism. Such orbital magnetism can be driven by non-zero Berry curvature associated with particular portions of electronic bands. For example, in Dirac systems, a small Dirac mass gap can be generated by spin-orbit coupling, which in turn produces non-zero Berry curvature concentrated around the momentum of the Dirac crossing. We explored this concept in kagome metal TbV_6Sn_6 . To uncover the topological orbital moments, we

used spectroscopic-imaging scanning tunneling microscopy to image the Dirac band as a function of magnetic field (Figure 4a). In combination with first-principles electronic structure calculations and ARPES, we discovered colossal orbital Zeeman effect of topological origin in TbV_6Sn_6 ³. The magnitude of the effect is enormous – to achieve the same effect from conventional Zeeman spin splitting, one would need to apply fields at the order of 500 T. The observed orbital Zeeman splitting of the Dirac band is fueled by the large spin-Berry curvature induced orbital magnetic moments coupling to external magnetic field (Figure 4d). Our work also revealed the first direct insight into the momentum-dependence of orbital magnetic moments (Figure 4b,c).

5. Towards ESR-STM

We started the redesign of the STM head of our STM-2 instrument, to add radio frequency (RF) antennas for the purpose of being able to perform ESR-STM experiments. We have worked closely with Unisoku Ltd. to design the microscope suitable for retrofitting the existing system. The new microscope head will have three sources for the RF signal: one through the tip, one through the coax-wire for medium RF frequencies and one through the lens antenna for high RF frequencies.

Future Plans

We will investigate the source of disorder driving inhomogeneity in altermagnet Co-intercalated NbSe_2 by collaborating with theoretical modeling groups. We will investigate if and how SP-STM can be used to demonstrate that a material is an altermagnet. We will also aim to apply SP-STM to UTe_2 to look for time-reversal symmetry breaking domains. Lastly, we will continue with ESR-STM upgrade with hopes of performing test measurements during the next reporting period.

References

1. Candelora, C. *et al.* *Discovery of magnetic-field-tunable density waves in a layered altermagnet*. ArXiv 2503.03716 (2025).
2. LaFleur, A. *et al.* *Inhomogeneous high temperature melting and decoupling of charge density waves in spin-triplet superconductor UTe_2* . Nat Commun **15**, 4456 (2024).
3. Li, H. *et al.* *Spin Berry curvature-enhanced orbital Zeeman effect in a kagome metal*. Nat Phys **20**, 1103 (2024).

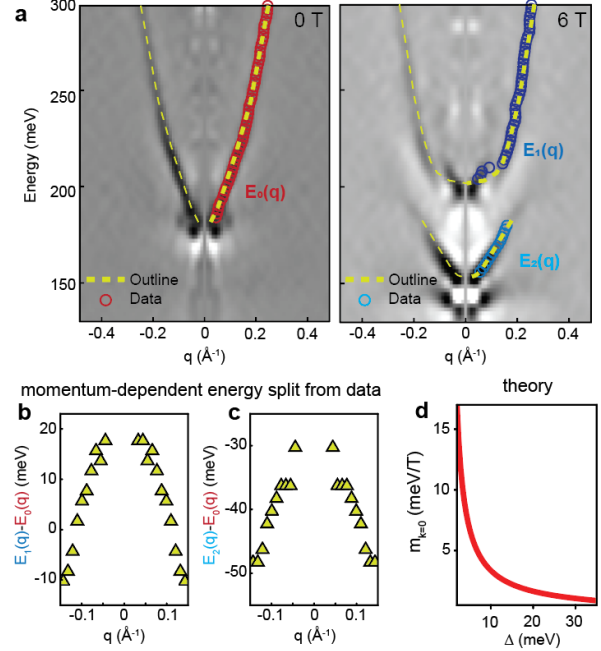


Figure 9. Orbital Zeeman band splitting in TbV_6Sn_6 . (a) A radially averaged Fourier transform line cut starting at the center of the Fourier transform at 0 and 6 T, showing large splitting of the Dirac band. (b,c) The difference between energies of equivalent momentum-space states at different fields. (d) Theoretically calculated evolution of the orbital moment at the Dirac point as a function of Dirac gap Δ .

Publications

1. Christopher Candelora, Muxian Xu, Siyu Cheng, Alessandro De Vita, Davide Romanin, Chiara Bigi, My Bang Petersen, Alexander LaFleur, Matteo Calandra, Jill Miwa, Younghun Hwang, Ziqiang Wang, Federico Mazzola and Ilija Zeljkovic, *Discovery of magnetic-field-tunable density waves in a layered altermagnet*, arxiv: 2503.03716 (2025)
2. Alessandro De Vita, Chiara Bigi, Davide Romanin, Matthew D Watson, Vincent Polewczyk, Marta Zonno, François Bertran, My Bang Petersen, Federico Motti, Giovanni Vinai, Manuel Tuniz, Federico Cilento, Mario Cuoco, Brian M Andersen, Andreas Kreisel, Luciano Jacopo D'Onofrio, Oliver J Clark, Mark T Edmonds, Christopher Candelora, Muxian Xu, Siyu Cheng, Alexander LaFleur, Tommaso Antonelli, Giorgio Sangiovanni, Lorenzo Del Re, Ivana Vobornik, Jun Fujii, Fabio Miletto Granozio, Alessia Sambri, Emiliano Di Gennaro, Jeppe B Jacobsen, Henrik Jacobsen, Ralph Ernstorfer, Ilija Zeljkovic, Younghun Hwang, Matteo Calandra, Jill A Miwa and Federico Mazzola, *Optical switching in a layered altermagnet*, arxiv: 2502.20010 (2025)
3. Hong Li, Siyu Cheng, Ganesh Pokharel, Philipp Eck, Chiara Bigi, Federico Mazzola, Giorgio Sangiovanni, Stephen D. Wilson, Domenico Di Sante, Ziqiang Wang and Ilija Zeljkovic, *Spin Berry curvature-enhanced orbital Zeeman effect in a kagome metal*, Nature Physics **20**, 1103 (2024)
4. Alexander LaFleur, Hong Li, Corey E. Frank, Muxian Xu, Siyu Cheng, Ziqiang Wang, Nicholas P. Butch and Ilija Zeljkovic, *Inhomogeneous high temperature melting and decoupling of charge density waves in spin-triplet superconductor UTe_2* , Nature Communications **15**, 4456 (2024)
5. Christopher Candelora, Hong Li, Muxian Xu, Brenden R Ortiz, Andrea Capa Salinas, Siyu Cheng, Alexander LaFleur, Ziqiang Wang, Stephen D Wilson, Ilija Zeljkovic, *Quantifying magnetic field driven lattice distortions in kagome metals at the femtometer scale using scanning tunneling microscopy*, Phys. Rev. B **109**, 155121 (2024)
6. Domenico Di Sante, Chiara Bigi, Philipp Eck, Stefan Enzner, Armando Consiglio, Ganesh Pokharel, Pietro Carrara, Pasquale Orgiani, Vincent Polewczyk, Jun Fujii, Phil D. C. King, Ivana Vobornik, Giorgio Rossi, Ilija Zeljkovic, Stephen D. Wilson, Ronny Thomale, Giorgio Sangiovanni, Giancarlo Panaccione and Federico Mazzola, *Flat band separation and robust spin Berry curvature in bilayer kagome metals*, Nature Physics **19**, 1135 (2023)
7. Shrinkhala Sharma, Hong Li, Zheng Ren, Wilber Alfaro Castro and Ilija Zeljkovic, *Nanoscale visualization of the thermally-driven evolution of antiferromagnetic domains in $FeTe$ thin films*, Phys. Rev. Materials **7**, 074401 (2023)

*Author
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