Office of Science

Basic Energy Sciences

Core Research Activities

April 2010

Office of Basic Energy Sciences

Harriet Kung, Director
Wanda Smith, Administrative Specialist

BES Budget and Planning
- Bob Astheimer, Senior Technical Advisor
- Margie Davis, Financial Management
- Vacant, Program Support Specialist

BES Operations
- Rich Burrow, DOE Technical Office Coordination
- Robin Hayes, AAAS Fellow
- Katie Perine, Program Analyst / BESAC
- Ken Rivera, Laboratory Infrastructure / ES&H
- Vacant, DOE and Stakeholder Interactions

Materials Sciences and Engineering Division
Linda Horton, Director
Vacant, Program Analyst
☆ Charnice Waters, Secretary

Materials Discovery, Design, and Synthesis
Arvind Kini
Kerry Gorey, P.A.

- **Materials Chemistry** — Mary Galvin; Dick Kelley; ● Darryl Sasaki, SNL
- **Biomolecular Materials** — Mike Markowitz
- **Synthesis and Processing** — Bonnie Gersten
- **Tech. Coordination Program Management** — John Vetrano; Vacant

Condensed Matter and Materials Physics
Jim Horwitz
Marsophia Agnant, P.A.

- **Exp. Cond. Mat. Phys.** — Andy Schwartz; ●Doug Finnemore, Ames; Vacant
- **Theo. Cond. Mat. Phys.** — Vacant; △ Arun Bansil, NEU; ◆ Jim Davenport, BNL; ■ Kim Ferris, PNNL
- **Physical Behavior of Materials** — Refik Kortan
- **Mechanical Behavior and Radiation Effects** — John Vetrano

Scattering and Instrumentation Sciences
Helen Kerch
Cheryl Howard, P.A.

- **X-ray Scattering** — Lane Wilson
- **Neutron Scattering** — Thiyaga P. Thiyagarajan
- **Electron and Scanning Probe Microscopies** — Jane Zhu
- **DOE EPSCoR*** — ◆ Tim Fitzsimmons; Jane Zhu; ● Helen Farrell, INL; ●John Schlueter, ANL

* Experimental Program to Stimulate Competitive Research

Scientific User Facilities Division
Pedro Montano, Director
Linda Cerrone, Program Support Specialist
Rocio Meneses, Program Assistant

Operations
- **X-ray and Neutron Scattering Facilities** — Roger Klaffky; Peter Lee
- **NSRCs & EBMCs**** — Tof Carim; Carlos Sa de Melo; ◆ Joe Horton, ORNL
- **Accelerator and Detector R&D** — Eliane Lessner
- **Facility Coordination; Metrics; Assessment** — Van Nguyen

** Nanoscale Science Research Centers & Electron Beam Microcharacterization Centers

Construction
- **Linac Coherent Light Source** — Tom Brown
- **National Synchrotron Light Source II** — Tom Brown
- **Spallation Neutron Source Upgrades** — Tom Brown
- **Instrument MIEs***** — Stephen Tkaczyk; ◆ John Tapia, LANL
- **Advanced Light Source User Support Building** — Tom Brown

*** Major Item of Equipment projects

Chemical Sciences, Geosciences, and Biosciences Division
Eric Rohlfing, Director
Diane Marceau, Program Analyst
Michaelene Kyler-King, Program Assistant

Fundamental Interactions
Michael Casassa
Robin Felder, P.A.

- **Atomic, Molecular, and Optical Sciences** — Jeff Krause
- **Gas-Phase Chemical Physics** — Wade Sisk; △ Larry Rahn, SNL
- **Condensed-Phase and Interfacial Mol. Science** — Greg Fiechtner
- **Computational and Theoretical Chemistry** — Mark Pederson

Photo- and Bio-Chemistry
Rich Greene
Sharron Watson, P.A.

- **Solar Photochemistry** — Mark Spitler; ● Arthur Frank, NREL
- **Photosynthetic Systems** — Gail McLean
- **Physical Biosciences** — Robert Stack

Chemical Transformations
John Miller
Teresa Crockett, P.A.

- **Catalysis Science** — Paul Maupin; Raul Miranda; ◆ Jan Hrbek, BNL
- **Heavy Element Chemistry** — Lester Morss; ● Norm Edelstein, LBNL
- **Separations and Analysis** — Bill Millman; △ Larry Rahn, SNL
- **Geosciences** — Nick Woodward; ● Jennifer Blank, LBNL
- **Technology Office Coordination** — Marvin Singer; Vacant

LEGEND
- ◆ Detailee (from DOE laboratories)
- ■ Detailee, ½ time, not at HQ
- ● Detailee, ¼ time, not at HQ
- ◆ On detail to EERE/SETP, 30% (blue)
- △ IPA (Interagency Personnel Act)
- ☆ On active military duty
- P.A. Program Assistant

April 2010

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OFFICE OF BASIC ENERGY SCIENCES

Harriet Kung	**F-405**	**3-3081**
Wanda Smith	*F-405*	*3-3081*
Astheimer, Robert	F-407	3-4410
Burrow, Richard	F-425	3-3978
Davis, Margie	E-409	3-3315
Hayes, Robin	F-430A	3-9659
Rivera, Ken	F-426	3-0540
Perine, Katie	F-416	3-6529
FAX	**F-405**	**3-6594**

Bus Schedule

Departs GTN	Arrives FORS
7:00	8:30
8:45	10:00
10:15	11:15
11:30	12:30
1:15	2:30
3:00	4:15
5:00	6:15

CHEMICAL SCIENCES, GEOSCIENCES, AND BIOSCIENCES DIVISION (SC-22.1)

Rohlfing, Eric	**E-435**	**3-8165**
Division Line	*E-423*	*3-2046*
Kyler-King, Michaelene	*E-414*	*3-5802*
Marceau, Diane	*E-440*	*3-0235*
FAX	**E-423**	**3-0271**
FAX	**E-440**	**3-1003**

FUNDAMENTAL INTERACTIONS TEAM (SC-22.11)

Casassa, Michael	**E-433**	**3-0448**
Felder, Robin	*E-423*	*3-5820*
Fiechtner, Greg	E-424	3-5809
Krause, Jeff	E-438A	3-5827
Pederson, Mark	E-433	3-9956
Sisk, Wade	E-422	3-5692

CHEMICAL TRANSFORMATIONS TEAM (SC-22.12)

Miller, John C.	**E-425**	**3-5806**
Crockett, Teresa	*E-423*	*3-5804*
Maupin, Paul	E-444	3-4355
Hrbek, Jan (detailee)	E-436	3-8428
Millman, Bill	E-432	3-5805
Miranda, Raul	E-427	3-8014
Morss, Lester	E-433A	3-9311
Rahn, Larry (IPA)	E-440	3-2508
Singer, Marvin	E-428	3-9142
Woodward, Nick	E-439	3-4061

PHOTO- AND BIO- CHEMISTRY TEAM (SC-22.13)

Greene, Richard	**E-431**	**3-6190**
Watson, Sharron	*E-423*	*3-2873*
McLean, Gail	E-438	3-7807
Spitler, Mark	E-428	3-4568
Stack, Robert	E-436	3-5652

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MISCELLANEOUS

North Lobby	3-4511
SCSC Help Desk	3-5313
Conference Room Scheduling (E-055)	3-4352
SC Conference Room	Blue Room, H-209
Building Operations	3-4005
Copy Center (S-057)	3-3060
Foreign Visitors (Yvette Bowser/F-241)	3-2844
FedEx (Tommy / E-066)	3-2313
Courier (Spence Aguilar / R-003)	3-4330
Courier times: 11:30 a.m. and 3:30 p.m.	
ADTRAV Travel	(888) 205-2369
DOE Toll-Free	1-800-832-0890
DOE Closure Announcement	(301) 903-SNOW

March 31, 2010

MATERIALS SCIENCES AND ENGINEERING DIVISION) (SC-22.2)

Horton, Linda	**F-411**	**3-7506**
Jackson, Amy (Temp.)	*F-406*	*3-3427*
Miller, Patti (Temp.)	*F-417*	*3-5963*
Waters, Charnice	*F-406*	*3-3427*
FAX	**F-406**	**3-9513**

SCATTERING & INSTRUMENTATION SCIENCES TEAM (SC-22.21)

Kerch, Helen	**F-415**	**3-2346**
Howard, Cheryl	*F-408*	*3-3428*
Fitzsimmons, Tim	F-418	3-9830
Thiyagarajan, Thiyaga	F-425A	3-9706
Wilson, Lane	F-429A	3-5877
Zhu, Jane	F-424	3-3811

CONDENSED MATTER & MATERIALS PHYSICS TEAM (SC-22.22)

Horwitz, James	**F-419**	**3-4894**
Agnant, Marsophia	*F-408*	*3-3426*
Kortan, Refik	F-422	3-3308
Vetrano, John	F-416A	3-5976
Schwartz, Andrew	F-429	3-3535
Bansil, Arun (IPA)	E-435	3-2187

MATERIALS DISCOVERY, DESIGN, & SYNTHESIS TEAM (SC-22.23)

Kini, Arvind	**F-414**	**3-3565**
Gorey, Kerry	*F-406*	*3-7661*
Galvin, Mary	F-425B	3-8334
Gersten, Bonnie	F-427A	3-0002
Kelley, Richard	F-421	3-6051
Markowitz, Mike	F-430	3-6779

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SCIENTIFIC USER FACILITIES DIVISION (SC-22.3)

Montano, Pedro	**F-402**	**3-2347**
Cerrone, Linda	*E-417*	*3-0064*
Meneses, Rocio	*E-417*	*3-7792*
Brown, Tom	E-415	3-6827
Carim, Altaf	E-416	3-4895
Horton, Joe (Detailee)	F-435	3-7369
Klaffky, Roger	E-419	3-1873
Lee, Peter	F-426	3-8484
Lessner, Eliane	E-420A	3-9365
Nguyen, Van	F-409	3-3976
Sa de Melo, Carlos	F-411	3-6004
Tapia, John (Detailee)	F-435	3-7941
Tkaczyk, Stephen	E-420B	3-3288
FAX	**E-417**	**3-1690**

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Materials Chemistry

Portfolio Description

This research activity supports basic research in chemical synthesis and discovery of new materials. The major programmatic focus is on the discovery, design and synthesis of novel materials with an emphasis on the chemistry and chemical control of structure and collective properties. Major thrust areas include: nanoscale chemical synthesis and assembly; solid state chemistry for exploratory synthesis and tailored reactivities; novel polymeric materials and complex fluids; surface and interfacial chemistry including electrochemistry; and the development of new, science-driven laboratory-based analytical tools and techniques.

Unique Aspects

Research supported in this activity underpins many energy-related technological areas such as batteries and fuel cells, catalysis, energy conversion and storage, friction and lubrication, high efficiency electronic devices, hydrogen generation and storage, light-emitting materials, light-weight high-strength materials, and membranes for advanced separations. The focus on exploratory chemical formation of new materials is complementary to the emphasis on bulk synthesis, crystal growth, and thin films in the BES Synthesis and Processing Science activity. It complements the BES Biomolecular Materials Research Activity (whose emphasis is on discovery of materials and systems using concepts and principles of biology) and the Synthesis and Processing Science Research Activity (whose emphasis is on physical, rather than chemical, control of structure and properties, and on bulk synthesis, crystal growth, and thin films). The researchers supported by the program benefit from significant use of BES-supported facilities with their advanced synchrotron x-ray, neutron scattering, electron microscopy and nanoscience tools.

Relationship to Other Programs

The Materials Chemistry Research Activity is a vital component of the interface between chemistry, materials, physics and engineering. It is necessarily interdisciplinary and cultivates a number of relationships, within BES, within DOE, and within the larger federal research enterprise:

- Within BES, this research activity sponsors, jointly with other core research activities and Energy Frontier Research Centers as appropriate, individual projects, program reviews, contractor meetings, and programmatic workshops.
- Within DOE, program coordination is through the Energy Materials Coordinating Committee with representatives from the Offices of Science , National Nuclear Security Administration, Fossil Energy, Environmental Management, Nuclear Energy Science and Technology, Energy Efficiency and Renewable Energy, and Electricity Delivery and Energy Reliability.
- Within the larger federal research enterprise, program coordination is through the Federal Interagency Chemistry Representatives, which meets annually, and the Interagency Polymer Working Group. There are particularly active interactions with the National Science Foundation, through joint workshops and joint funding of appropriate and select activities (two are currently ongoing).
- Nanoscience-related projects in this activity are coordinated with the Nanoscale Science Research Center activities and reviews in the BES Scientific User Facilities Division. BES further coordinates nanoscience activities with other federal agencies through the National Science and Technology Council's Nanoscale Science, Engineering, and Technology

subcommittee, which leads the National Nanotechnology Initiative.

Significant Accomplishments

The Materials Chemistry Research Activity has a long history of accomplishments. Some can already be considered to have had significant impact on science or technology:

- The first organic magnet at any temperature (and later the first organic magnet above room temperature) – these discoveries created a new class of functional materials and a thriving new field of scientific research that in turn is expected to have a huge impact on technologies based on magnetic materials, such as spintronics;
- The first all-organic superconductor and the highest-T_c organic superconductor;
- The development of neutron reflectivity for non-destructive study of surfaces and interfaces with an unprecedented depth resolution of one-half nanometer; and
- The development of combinatorial materials chemistry, a revolutionary technique for materials discovery that has found wide application in science and industry was supported by this activity (e.g., the founding of Symyx).

Others are more recent but already show promise of significant impact:

- Demonstration of extremely large enhancements in thermoelectric efficiency in semiconductor nanowires (a factor of 100 for silicon);
- Advances in the design and fabrication of solution-processable tandem solar cells – inexpensive plastic solar cells with > 10% conversion efficiencies may now be within reach;
- The development, using block copolymers, of a self-patterning and self-organizing resist that enables fabrication of electronic components at an areal density of 10 Terabit/in^2 (more than 15 times greater than previously possible); and
- Quantitative determination and theoretical confirmation of the long-elusive nanometer-scale structure of Nafion®, the current gold-standard for fuel cell membrane material.

Mission Relevance

Materials are the tool box that enables the development of the next generation of energy technologies. The mission of this program is to build and extend that tool box by utilizing chemistry and "chemical thinking" to control the assembly, structure and function of materials and materials constructs at unprecedented levels. The resulting science and new materials have potential for long-term benefit to energy-relevant technologies, including: batteries and fuel cells, electro-catalysis, energy conversion and storage, friction and lubrication, high-efficiency electronic devices, light-emitting materials, light-weight high-strength materials, membranes for advanced separations, solar energy conversion and materials for carbon capture.

Scientific Challenges

The Materials Chemistry Research Activity seeks to explore and push back the boundary that divides those functional materials which are now possible to design and synthesize from those which are not. Doing so requires tackling a number of scientific challenges, including a cross-cut of the overarching Grand Challenges identified in Basic Energy Sciences Advisory Committee's (BESAC) *Directing Matter and Energy* report. Two especially important challenges are:

- *building an understanding (experimentally, conceptually and computationally) of materials phenomena which could enable atom-by-atom design and synthesis of innovative materials;*

- *the development and use of powerful new theory/modeling and physical/chemical characterization tools that can accelerate materials discovery*.

In addition, a number of particular energy-science challenges, identified in the BES Basic Research Needs workshops and reports, are conducive to materials chemistry approaches. These include those involving materials with tailored properties as well as those whose design and syntheses are amenable to chemical thinking: Electrical Energy Storage (including battery science, electrolyte phenomena, storage of ions in high porosity materials, and new probes of energy-storage chemistry); Catalysis for Energy, Solar Energy Utilization; Solid-State Lighting; Carbon Capture and Storage; and Superconductivity.

Projected Evolution

With the completion of the recent cycle of BES Basic Research Needs (and other) workshops and reports, the scientific community has articulated very clearly those areas of science and materials which are most relevant to energy. All of the reports variously identify the overarching goal of materials chemistry research as providing the knowledge needed to design and produce new materials with tailored properties from first principles. This program will make progress towards that goal by increasing activity in the following areas: (1) Development of new chemical means to direct and control the non-covalent assembly of materials, such as strategies to organize electron donors and acceptors; (2) Creation of ways to tailor the symmetry and dimensionality of crystalline lattices; (3) Utilization of chemistry to control and design interfaces between dissimilar materials. All of these activities will be conducted on materials that have potential for use in the next generation energy technologies, including research to underpin understanding of new approaches and chemistries related to carbon capture. The program will seek to increase the proportion of research in classes that demonstrate promise in providing the properties required for energy solutions. Some examples of these classes include complex inorganic oxides, metamaterials, and liquid crystals with novel electronic, magnetic, photonic and thermal properties.

Biomolecular Materials

Portfolio Description

This activity supports basic research in the discovery, design and synthesis of biomimetic and bioinspired functional materials and complex structures, and materials aspects of energy conversion processes based on principles and concepts of biology. The major program emphasis is the creation of robust, scalable, energy-relevant materials and systems with emergent behavior that work with the extraordinary effectiveness of molecules and processes of the biological world. Major thrust areas include: understanding, controlling, and building complex hierarchical structures by mimicking nature's self- and directed-assembly approaches; design and synthesis of environmentally adaptive, self-healing multi-component, e.g., inorganic, polymeric, and biological, materials and systems that demonstrate energy conversion and storage capabilities found in nature; functional systems with collective properties not achievable by simply summing the individual components; biomimetic and/or bioinspired routes for the synthesis of energy relevant materials, e.g., semiconductor and magnetic materials under mild conditions; and development of science-driven tools and techniques for the characterization of biomolecular and soft materials.

Unique Aspects

Basic research supported in this activity underpins many energy-related technological areas such as energy conversion and storage, light-weight/high-strength materials, efficient membranes for highly selective separations, and advanced catalytic systems/architectures with enzyme-like specificities and high turnover ratios. Current scientific thrusts balance discovery-class and use-inspired basic research, and require strong interactions among biology, chemistry, physics, and computational disciplines. This activity's quest for new energy-related materials by exploiting biology is complementary to the emphasis on exploratory chemical synthesis and chemical control of materials properties (BES Materials Chemistry) and the emphasis on innovative synthesis concepts and underlying physical phenomena (BES Synthesis and Processing Science). The Biomolecular Materials activity's focus on the intersection of biology and materials sciences complements the Physical Biosciences activity in the BES Chemical Sciences, Geosciences and Biosciences Division, focused on the intersection of physical sciences with biochemistry and molecular biology.

Relationship to Other Programs

The Biomolecular Materials program is a vital component of the materials sciences that interfaces materials sciences with biology. This interfacing results in very active relationships.

- Within DOE, there is coordination through the Energy Materials Coordinating Committee involving representatives of the Offices of Science, National Nuclear Security Administration, Fossil Energy, Environmental Management, Nuclear Energy Science and Technology, Energy Efficiency and Renewable Energy (EERE), and Electricity Delivery and Energy Reliability.
- Within BES, there are jointly funded programs between the DOE national laboratories and universities (about six currently), joint program reviews, joint contractor meetings (with EERE), and workshops. There is also coordination between this activity and Energy Frontier Research Centers in topically related areas.
- Nanoscience-related projects in this activity are coordinated with the Nanoscale Science

Research Center (NSRC) activities and reviews in the BES Scientific User Facilities Division. BES further coordinates nanoscience activities with other federal agencies through the National Science and Technology Council's Nanoscale Science, Engineering, and Technology subcommittee, which leads the National Nanotechnology Initiative.
- Active interactions with the National Science Foundation and National Institutes of Health through joint workshops and joint support of National Academy studies in relevant areas (two were completed recently).

Significant Accomplishments
A recent achievement is the development of a method to genetically encode unnatural amino acids with diverse physical, chemical, or biological properties in bacteria *E.Coli* and mammalian cells. This makes it possible to synthesize proteins incorporating unnatural amino acids, thereby producing "synthetic" analogs of proteins and, potentially, long-sought-after mono-disperse versions of industrial polymers such as polyesters and polyimides. Biosynthetic routes found in nature have been harnessed or mimicked to produce a wide variety of semiconductor, ferroelectric, and magnetic nanocrystals under mild, environmentally benign conditions. A novel strategy to stabilize liposomes as well as to immobilize them on surfaces has been demonstrated by use of nanoparticles, thus opening their possible use as smart materials and nanoscale chemical reactors for massively parallel synthesis. The first functional bio-nanoelectronic device that integrates membrane proteins with nanowire electronics has been created. A recent discovery is that synchrotron x-rays can act as a reversible switch for the self-assembly of disordered bundles of nanoscale filaments into a crystalline, ordered state opens up novel approaches and mechanisms to organize nanoscale filaments and wires over long distances. A broad-spectrum light-harvesting system that self-assembles into precisely shaped rods like tobacco mosaic virus and mimics the light-harvesting antenna in photosynthetic bacteria has been developed. Recently, the DNA-guided assembly of nanoparticles into three-dimensional crystalline assemblies has been demonstrated for the first time. A new benchmark for efficient hydrogen production by a hybrid photo-catalyst system comprising molecular wire-linked Photosystem I and platinum nanoparticles has been demonstrated.

Mission Relevance
Research supported in this activity underpins many energy-related technological areas such as batteries and fuel cells, catalysis, energy conversion and storage, friction and lubrication, high efficiency electronic devices, hydrogen generation and storage, light-emitting materials, light-weight high-strength materials, and membranes for advanced separations.

Scientific Challenges
The major scientific challenges that drive the Biomolecular Materials activity directly correspond to four of the five scientific grand challenges in basic energy sciences, as described in the report, *Directing Matter and Energy: Five Challenges for Science and Imagination*: (1) How do we design and perfect atom- and energy-efficient synthesis of revolutionary new forms of matter with tailored properties? (2) How do remarkable properties of matter emerge from complex correlations of the atomic and electronic constituents and how can we control these properties? (3) How can we master energy and information on the nanoscale to create new technologies with capabilities rivaling those of living systems? (4) How do we characterize and control matter--especially very far away--from equilibrium? Since biology has already figured

out ways in which matter, energy, entropy, and information are organized and/or manipulated, the challenge is to understand, adapt, and improve upon them so that it will become valuable and practical under a broader range of harsher, non-biological conditions.

Projected Evolution

This activity will continue to support curiosity-driven and multi-disciplinary approaches to model, design, and synthesize novel materials with unique functionalities. The program will continue to seek a fundamental understanding of thermodynamic, kinetic, and dynamical aspects of self-assembly processes to produce both equilibrium and far-from-equilibrium materials and systems like those found in nature. Enhanced integration of theory, computation, and experiment is sought to develop a more comprehensive understanding of the nanoscale structure and non-equilibrium behavior of bioinspired/bioderivative materials and systems leading to new design ideas and opportunities for discovery. In addition, the program will expand in the following areas: dynamically adaptive and self-repairing materials; low temperature synthesis of energy relevant materials; effective and unique strategies for interfacing biological and non-biological materials systems in search of emergent behavior; synthetic enzymes; material architectures for efficiently integrating light-harvesting, photo-redox, and catalytic functions; and biomolecular functional structures that take inspiration from biological gates, pores, channels, and motors.

Synthesis and Processing Science

Portfolio Description

This activity supports basic research for developing new techniques to synthesize materials with desired structure and properties; to understand the physical phenomena that underpin materials synthesis such as diffusion, nucleation, and phase transitions; and to develop *in situ* monitoring and diagnostic capabilities. The emphasis is on the synthesis of complex thin films and nanoscale materials with atomic layer-by-layer control; preparation techniques for pristine single crystal and bulk materials with novel physical properties; understanding the contributions of the liquid and other precursor states to the processing of bulk nanoscale materials; and low energy processing techniques for large-scale nanostructured materials. The focus of this activity on bulk synthesis and crystal and thin films growth via physical means is complementary to the BES Materials Chemistry and Biomolecular Materials research activities, which emphasize chemical and biomimetic routes to new materials synthesis and design. Equipment funding is provided for crystal growth apparatus, heat treatment furnaces, lasers, chemical vapor deposition and molecular beam epitaxial processing equipment, plasma and ion sources, and deposition instruments.

Unique Aspects

Basic research supported in this activity underpins many energy related technology areas while balancing "use-inspired basic research" and "discovery-class research." Significant interactions and collaborations exist between the investigators in this activity and other BES research activities, e.g., the X-ray and Neutron Scattering activity for the characterization of new materials by use of advanced scattering/spectroscopic tools at BES supported synchrotron and neutron facilities and the Electron and Scanning Probe Microscopies activity for high-resolution characterization of atomic scale structure at BES supported microscopy facilities. Research in materials synthesis furthers our capabilities in single crystal growth and preparation of high quality specimens used by other investigators funded by BES, often at the DOE x-ray synchrotron and neutron facilities. Many of the scientists performing work on nano-materials sponsored by this activity are also leaders of corresponding science thrust areas at the BES Nanoscale Science Research Centers (NSRCs).

Relationship to Other Programs

The Synthesis and Processing program is a critical element of the materials sciences that has emphasis in the physical sciences. This connection results in especially active interactions.

- Within BES, this research activity sponsors – jointly with other core research activities and EFRCs as appropriate – individual projects, program reviews, contractor meetings, and programmatic workshops.
- Within DOE, program coordination is through the Energy Materials Coordinating Committee, with representatives from the Offices of Science, National Nuclear Security Administration, Fossil Energy, Environmental Management, Nuclear Energy Science and Technology, Energy Efficiency and Renewable Energy, and Electricity Delivery and Energy Reliability.

- Nanoscience-related projects in this activity are coordinated with the NSRCs activities and reviews in the BES Scientific User Facilities Division. BES further coordinates nanoscience activities with other federal agencies through the National Science and Technology Council (NSTC) Nanoscale Science, Engineering, and Technology subcommittee, which leads the National Nanotechnology Initiative.
- The program also participates in the interagency coordination groups such as the NSTC MatTec Communications Group on Metals, and Interagency Coordination Committee on Ceramics Research and Development.

Significant Accomplishments

The activity supports fundamental research that has allowed for the unprecedented defect controlled thin-film growth of superconducting oxide by molecular beam epitaxy, which has enabled the discovery of superconductivity at the interface between metals and insulators. It has accomplished the synthesis of artificially structured thin-film semiconductors that has allowed the design of thin-film structures with desired opto-electronic properties and devices. Of significance is the accomplishment of novel processing of silicon nano-membrane on insulator, which has proven that even the thinnest silicon membrane can be conductive provided the proper surface is present. This activity has modeled and fabricated a tungsten photonic crystal opal structure that can be used for thermal emission. Most recently, the activity has allowed for the discovery of the polymer ferroelectric responsible for the colossal electrocolaric effect near room temperature, which can mean the next refrigeration devices can be bendable.

Mission Relevance

Synthesis and processing science is a key component in the discovery and design of a wide variety of energy relevant materials. In this regard, the activity supports DOE's mission in the synthesis of wide bandgap semiconductors for solid state lighting; light-weight metallic alloys for efficient transportation; novel materials such as metal organic frameworks for hydrogen storage; and ceramics processing, including high-temperature superconductors for near zero-loss electricity transmission. The research activity aims at providing synthesis and processing capabilities to enable the manipulation of individual spin, charge, and atomic configurations in ways to probe the atomistic basis for materials properties.

Scientific Challenges

With recent developments toward precision, *in situ*, dynamic, real-time ultra-fast and ultra-small characterization equipment and increased accessibility of computational resources, synthesis and processing has been transformed to a science with a higher level of understanding. The time is ripe to attempt to answer the many challenges presently open in this field.

- **Precision Processing**: Stochastic non-equilibrium processing that is predictable, reliable, and uniform over large scales used to control, tailor the number and distribution of defects.
- **Long- and Short-range Forces**: Better understand long- and short-range forces and their contributions to the growth of nanoscale objects and of nanoscale morphology development. Roles of electrostatics and electrodynamics, and how

these relate to the polar and acid/base approaches of the chemistry community. Roles of defects and long-range interactions on phase stability and interface motion.

- **Atomistic Deposition:** Oxide and non-oxide film deposition and growth with better control at low and high rates, better control of oxygen at high activities and *in situ* characterization improvements.
- **Synthetic Strategies**: New processing strategies to discover new classes of materials beyond the periodic table (compounds, architecture, unnatural elements).
- **Designing Interfaces**: Define the design rules for integrating soft with hard materials creating hybrid and dissimilar materials. Synthetic techniques to create tailorable hard materials and robust soft materials. Soft/hard/hybrid materials that can hierarchically organize in 3-dimensional architecture by self or through external stimuli and control the materials interfaces of heterostructures.
- **Theory**: Guide experiments beyond Edisonian approaches. Use reverse design by proposing a desired band structure and compute the thermodynamically most plausible synthetic route.

Finally, the Basic Research Needs workshop reports and the Basic Energy Sciences Advisory Committee (BESAC) Grand Challenge report *Directing Matter and Energy: Five Challenges for Science and the Imagination* provides additional discussion on these and other challenges.

Projected Evolution

Over the past few years, the activity has evolved an increasing interest in understanding nanoscale morphology through nucleation and growth kinetics and mechanisms, defect control in deposition processes, and complex chemical and structural materials growth. Over the next several years, these directions are expected to continue with strengthen research in bulk materials growth, deposition, and sintering and added emphasis in the fundamental understanding of the mechanisms for interfacing soft-hard hybrid materials and the organization of these structures. Expansion is planned in research for discovery of novel synthesis methods, especially using extreme environments of field and flux, and research to push the limits of our basic understanding in synthesis and processing related to use-inspired technologies including solid-state lighting, solar energy conversion, hydrogen storage, and electrical energy storage. This activity will continue to support hypothesis-driven fundamental science in synthesis and processing with a particular interest in high-risk, high-impact, innovative, and imaginative projects. The activity continues to support and encourages natural collaboration between theorists and experimentalists to address the opportunities described in the scientific challenges described above.

Experimental Condensed Matter Physics

Portfolio Description

This activity supports Experimental Condensed Matter Physics) emphasizing the relationship between the electronic structure and the properties of complex materials, often at the nanoscale. The focus is on systems whose behavior derives from strong correlation effects of electrons as manifested in superconducting, semi-conducting, magnetic, thermoelectric, and optical properties. Also supported is the development of new techniques and instruments for characterizing the electronic states and properties of materials under extreme conditions, such as in ultra low temperatures (millikelvin), in ultra-high magnetic fields (100 Tesla), and at ultra-fast time scales (femtosecond). Capital equipment is provided for scanning tunneling microscopes, electron detectors, superconducting magnets, and physical property measurement instruments.

Unique Aspects

The Experimental Condensed Matter Physics activity continues to support research on electronically complex materials, an area that impacts a wide range of other topics including superconductivity, magnetoresistivity, low-dimensional electron systems, and magnetism. The research on magnetism and magnetic materials focuses on hard magnet materials, such as those used for permanent magnets and in motors; on exchange biasing, which is used to stabilize the magnetic read heads of disk drives; and on spin-polarized electron transport, particularly in nanometer-scale structures. The combined projects in superconductivity comprise a concerted and comprehensive energy-related basic research program. The DOE national laboratories anchor the efforts and maintain the integration with the Office of Electricity Delivery and Energy Reliability (OE) developmental efforts. Research on the properties of materials in high magnetic fields is being conducted using the 100T multi-shot magnet at the Los Alamos National Laboratory (LANL). Two major areas of research are being pursued: magnetic field induced phase transitions and nano-quantization and quantum size effect. The ECMP activity also has unique thrusts in photoemission investigations of superconductors and other correlated electron systems. It is a source of new materials scientists through strong materials synthesis programs at Oak Ridge National Laboratory (ORNL), Ames Laboratory, Argonne National Laboratory (ANL), Brookhaven National Laboratory (BNL), SLAC National Accelerator Laboratory, LANL, and Sandia National Laboratories**.** Internationally, this activity holds a position of world leadership in the areas of magnetism, superconductivity, materials characterization, and nanoscale science. New, exciting areas launched within this activity in photonic band gap materials, two-dimensional electron systems, magnetic superconductors, and quasicrystals are now pursued worldwide. Enhanced efforts are ongoing to generate high quality single crystals of new materials at Ames, ANL, BNL, ORNL, and SLAC.

Relationship to Other Programs

The research in the program is aimed at building a fundamental understanding of the electronic behavior of materials as a foundation for future energy technologies. Improving the understanding of the physics of materials at the nanoscale will be technologically significant as these structures offer enhanced properties and could lead to dramatic improvements in technologies for energy generation, conversion, delivery, and utilization. Specifically, research efforts aimed at understanding the fundamental mechanisms in superconductivity, the elementary energy conversion steps in photovoltaics, and the energetics of hydrogen storage provide scientific underpinnings for energy technologies. This activity also supports research of fundamental interest for information technology and electronics industries in the fields of semiconductor and spintronics research. These research efforts are closely coordinated with other core research activities in BES, including the Physical Behavior of Materials on photovoltaics, Synthesis and Processing Science on single crystal growth, X-ray and Neutron Scattering on photoemission studies, and Theoretical Condensed Matter Physics on nanostructures and low-dimensional systems. They are also coordinated with DOE technology programs in the Office of Energy Efficiency and Renewable Energy and OE. This program and the National Science Foundation support the National Academy of Sciences' Condensed Matter and Materials Research Committee (formerly the Solid State Sciences Committee), which is charged with assessing the state of the field and advising federal agencies on research priorities. The program has also supported topical studies by the National Research Council, including *CMMP 2010: An Assessment of and Outlook for Condensed-Matter and Materials Physics* and *Assessment of and Outlook for New Materials Synthesis and Crystal Growth*.

Significant Accomplishments

This activity has a long history of accomplishments dating back to the 1950s and the first neutron scattering experiments at ORNL. Notable accomplishments include the discovery of ion channeling and the development of the field of ion implantation; the discovery of metallic and strained-layer superlattices; the establishment of the field of thermoacoustics and thermoacoustic refrigeration and heating; the invention of Z-contrast scanning transmission electron microscopy; the theoretical and predictive basis for photonic band gap materials; the tandem photovoltaic cell; the observation of stripes in superconductors; the invention of a Josephson junction scanning tunneling microscope; the first observation of superconductivity in a magnetically doped semiconductor ($PtSb_2$ with ~1% Yb); the observation of Bose condensation of excitons doped double layer semiconductor structures; and the characterization of BCS and two-gap superconductivity in magnesium diboride (MgB_2). In addition, the activity has supported much of the seminal work in the fields of high temperature superconductors and quasicrystals, efforts now pursued worldwide. The 100 T multishot magnet at LANL was designed and constructed under this program and currently holds the world record for long pulse, high magnetic fields in a reusable magnet.

Mission Relevance

Improving the understanding of the electronic behavior of materials on the atomistic scale is relevant to the DOE mission, as these structures offer enhanced properties and could lead to dramatic improvements in technologies for energy generation, conversion, storage, delivery, and use. Specifically, research efforts in understanding the fundamental mechanisms of superconductivity, the elementary energy conversion steps in photovoltaics, and the energetics of hydrogen storage provide the major scientific underpinnings for the respective energy technologies. This activity also supports basic research in semiconductor and spin-based electronics of interest for the next generation information technology and electronics industries.

Scientific Challenges

Among the immediate on-going scientific challenges faced by this program are the following: the solution of the mechanism for high-temperature superconductivity; the understanding of "stripes" in correlated electron systems; the understanding of novel quantum effects and of "emergent phenomena," that is, new phenomena that emerge when the complexity of a system grows with the addition of more particles; the development of a very high-magnetic field research program to exploit the 100T and 60T magnets at LANL; research in nanoscale science; low-temperature physics; and the continued development of a materials synthesis and crystal growth capability in this country. Quality materials lie at the heart of quality measurements: a thrust to develop a core competence in the synthesis of new materials and the growth of crystals is underway, and it will continue to be a priority. High-magnetic-field research coupled with low temperature physics led to the discovery of the quantum Hall effect and to the general area of novel quantum effects. The availability of very high magnetic fields over useable time scales, as is now afforded by the new magnet at LANL, offers the promise of both increasing the fundamental understanding of matter and of observing the effects of very high magnetic fields on materials properties. This will undoubtedly lead to the discovery of new and exciting physics. Similarly, low temperature physics continues to be important for the advancement of physics by providing the experimental conditions necessary to observe phenomena such as BEC, the quantum Hall effect, and superconductivity. Developing and understanding matter and materials at the nanoscale is a critical need because electronic, optical, and magnetic devices continue to shrink in size.

Projected Evolution

The Experimental Condensed Matter Physics activity will include further work at the nanoscale and at low temperatures, the development of a very high magnetic field research program, and continued development of the materials synthesis and crystal growth thrust. The portfolio can be expected to continue thrusts in electronic structure, new materials, surfaces/interfaces, and development of experimental techniques. Efforts will continue to strengthen research in unconventional superconductivity, including the high-temperature cuprate superconductors, first discovered nearly 25 years ago, and the recently discovered iron pnictide superconductors. In the last few years the program has increased support for spin physics and nanomagnetism, and new investigations of the Casimir force have been initiated. Recently the program has begun to explore whether cold atom research can provide insight into open questions about correlated electron behavior in condensed matter systems.

Theoretical Condensed Matter Physics

Portfolio Description

This activity supports Theoretical Condensed Matter Physics with emphasis on the theory, modeling, and simulation of electronic correlations. A major thrust is nanoscale science, where links between the electronic, optical, mechanical, and magnetic properties of nanostructures and their size, shape, topology, and composition are poorly understood. Other major research areas include strongly correlated electron systems, quantum transport, superconductivity, magnetism, and optics. Development of theory targeted at aiding experimental technique design and interpretation of experimental results is also emphasized. This activity supports the Computational Materials Science Network, which forms collaborating teams from diverse disciplines to address the increasing complexity of many current research issues. The activity also supports large-scale computation to perform complex calculations dictated by fundamental theory or to perform complex system simulations with joint funding from DOE's Advanced Scientific Computing Research program. Capital equipment funding will be provided for items such as computer workstations and clusters.

Unique Aspects

Research in condensed matter and materials science is intrinsically rich, not only because atoms and molecules can be assembled to produce an almost endless variety of materials, but also because we believe that there is a rational basis for complexity and emergent behavior, which derives from a few elegant laws of nature. There are three fundamental components to the program. First, theorists, working with awareness of challenges and discoveries from the experimental realm, are asked to advance the conceptual basis of our science in the form of analytic, predicable, quantifiable and verifiable theories. The second component is characterized by theoretical efforts motivated by the need to understand experimental observations. Answering why certain phenomena occur does not require new theory as often as it requires new insight. The third component involves the important role of computational tools and high performance computing. This program encourages researchers who employ computational approaches to advance science through the coupling of deep scientific insights, strong traditional theoretical talents, and creative use of computational resources. This includes working synergistically with other programs in BES where support of theoretical, computational and modeling efforts advances their programmatic focus.

Relationship to Other Programs

This activity is aggressive in maintaining interactions with other research activities within the BES, driven by the opportunity of stimulating theory through experimental discovery and bringing solid theoretical foundations and understanding to new processes of interest to experimental and facilities programs. Because this program has oversight responsibility for a portion of the supercomputer resources at the National Energy Research Supercomputer Center, there is particular interest in opportunities for implementing complex theoretical methods as predictive tools in support of experimental science and the broader community. Nanoscience-related projects are coordinated with the Nanoscale Science Research Center activities and are reviewed in the BES Scientific User Facilities Division. BES further coordinates the nanoscience activities with other federal agencies by participating in the National Science and Technology Council's Nanoscale Science, Engineering, and Technology subcommittee, which leads the

National Nanotechnology Initiative. The program also takes advantage of opportunities to collaborate with the Office of Advanced Scientific Computing Research. The BES commitment to advancing the frontiers of basic research is present in programmatic interactions with other programs in DOE such as the Office of Energy Efficiency and Renewable Energy and other Federal Agencies. Communication of ongoing research programs and goals is part of the interaction with the National Science Foundation and other agencies.

Significant Accomplishments

Consistent with an emphasis on nanoscale theory, notable advances through theory and modeling provide exciting new information and point to new possibilities for creating new tailored materials and devices. Highlights include:

- Functional nanoparticles have become the key to control and self-assembly. By judiciously modifying nanoclusters, one can guide them to assemble in a specified manner.
- Researchers have significantly enhanced our ability to simulate large scale (billion atom) clusters including electronic degrees of freedom and thus achieve *ab inito* predictive capability with wide application.
- Electronic properties of quantum dots can be predicted based on realistic materials.

Significant progress has also been made in other areas as illustrated by the following examples:

- Dynamical Mean Field Theory offers a practical way to treat the correlations which dominate the properties of many correlated electron systems.
- Progress has been made on the question of how to treat core-hole effects in x-ray absorption spectra by a collaborative research team of the Computational Materials Science network.
- A new level of accuracy and reliability of excited state properties of materials has become possible with advances in Density Functional Theory.
- Transport in nanoscale systems now has some fundamental theoretical basis and computational implementations. A breakthrough in single molecule electronics is near.
- Spintronics is evolving quickly, with the recent years seeing a shift from simplistic to realistic materials models.

Mission Relevance

This activity provides the fundamental knowledge for predicting the reliability and lifetime of energy use and conversion approaches and develops opportunities for next generation energy technology. Specific examples include inverse design of compound semiconductors for unprecedented solar photovoltaic conversion efficiency, solid-state approaches to improving capacity and kinetics of hydrogen storage, and ion transport mechanisms for fuel cell applications.

Scientific Challenges

Many fundamental aspects of condensed matter and materials science are far from being understood. Beyond high temperature superconductivity, there are continuing discoveries of complex phase behavior of correlated electronic materials, and even more remains to be discovered related to their dynamics and nonequilibrium processes. Similarly, complex materials, whether hard, soft or in the growing wealth of metamaterials, offer many opportunities for study of complex systems and emergent behavior.

Bridging length scales is a continuing major goal on which progress is ongoing. More than integrating atomic level scales with nanometer or mescoscales in materials, this also requires integrating the domain of quantum laws with classical laws of physics. Bridging time scales is similarly important with some of the most exciting advances coming now with new theoretical methods implemented in a computational environment. Basic theory has challenges. For example, density functional theory is moving to a resolution of the longstanding problems of correctly treating excited states. Treatment of non-equilibrium systems needs advances in non-equilibrium statistical mechanics. In the computational area, a variety of algorithms no longer scale to the tens of thousands of processors available now and will be faced with millions of processors in the future.

Projected Evolution

The program will continue to emphasize the development of our understanding of matter on the atomic scale and expanding to add the capability of addressing length scales both larger and smaller than the nanoscale is part of the scientific future of theory, modeling and simulation for condensed matter and materials. A rich future exists in basic science and applications surrounding highly correlated materials as well as novel superconductors. This research is motivated by the newest science of materials, as well as by the potential for impact on longstanding problems for energy technologies and for fundamental physics, including understanding of the physics of microstructure and granular material. Computationally enabled science is simultaneously growing in maturity and seeing dramatic advances. Those advances, which further the basic research and mission of BES, have a natural home in this program.

Physical Behavior of Materials

Portfolio Description

This activity supports basic research on the behavior of materials in response to external stimuli, such as temperature, electromagnetic fields, chemical environments, and the proximity effects of surfaces and interfaces. Emphasis is on the relationships between performance, such as electrical, magnetic, optical, electrochemical, and thermal performance, and the microstructure and defects in the material. Included within the activity are research to establish the relationship of crystal defects to semiconducting, superconducting, and magnetic properties; phase equilibria and kinetics of reactions in materials in hostile environments; and diffusion and transport phenomena. Basic research is also supported to develop new instrumentation, including *in situ* experimental tools, and to probe the physical behavior in real environments encountered in energy applications. Capital equipment funding is provided for items such as physical property measurement tools that include spectroscopic and analytical instruments for chemical and electrochemical analysis.

Unique Aspects

This activity is the primary supporter of research to develop a fundamental understanding and identification of detailed mechanisms responsible for the physical behavior of materials, and the incorporation of this knowledge into detailed predictive models. The understanding that has resulted from such modeling work has already led to the design of unique new classes of materials including compound semiconductors, tough structural ceramics, ferroelectrics, and magnetocaloric materials. Some specific examples include: new levels of magnetic properties from nanoscale clusters, compound semiconductors that can remove excess CO_2 from the atmosphere, highly desirable phases of ferroelectric materials that can be formed through novel processing techniques, and a breakthrough in understanding of the chemistry of friction enabling the tuning of lubrication layers.

Relationship to Other Programs

This activity closely interacts with other programs under BES, such as the Computational Materials Sciences Network. It also has contact with the Solid State Lighting/Building Technologies Program, Office of Energy Efficiency and Renewable Energy, Energy Materials Coordinating Committee and Hydrogen Coordinating Committee. Additionally, this program interacts with the National Science and Technology Committee's Materials Technology Subcommittee Interagency Working Groups on Metals, Structural Ceramics, Nondestructive Evaluation, and Nanotechnology and with the Office of Science and Technology Policy Interagency Taskforce on Hydrogen R&D.

Significant Accomplishments

This activity has had broad and significant impact in many classes of materials and phenomena. Some of the recent accomplishments include: a technique to experimentally resolve a single individual magnetic spin on an atom, using $KNbO_3$ nanowires that combines fluorescence and force microscopies; exploitation of structural bistability in liquid crystals for low energy consuming optical switches; development of predictive tools for phase stability and structure in transition-metal oxides for fuel cells; observation of superplastic deformation (280% of their original length) of single wall carbon nanotubes; realization of the smallest feature size (100 nanometer Gold) 3D metallic photonic crystal materials; observation of giant magnetoresistance in Mn-based full Heusler alloys; measuring thermoelectricity of a single individual molecule; and demonstration of 50-fold improvement in thermoelectric properties in silicon nanowires.

Mission Relevance

The research supported by this activity is necessary for improving materials reliability in chemical, electrical, and electrochemical applications and for improving the ability to generate and store energy in materials. Materials in energy-relevant environments are increasingly being exposed to extreme temperatures, strong magnetic fields, and hostile chemical conditions. A detailed understanding of how materials behavior is linked to the surroundings and treatment history is critical to the understanding of corrosion, photovoltaics, fast-ion conducting electrolytes for batteries and fuel cells, novel magnetic materials for low magnetic loss power generation, magnetocaloric materials for high-efficiency refrigeration, and new materials for high-temperature gasification.

Scientific Challenges

The challenge in this area is to develop the scientific understanding of the mechanisms that control the behavior of materials and to use that understanding to design new materials with desired behaviors. The program encompasses efforts aimed at understanding the behavior of organic and inorganic electronic materials, magnetism and advanced magnetic materials, manipulation of light/photonic lattices, corrosion/electrochemical reactions, and high-temperature materials behavior through intimately connected experimental, theory, and modeling efforts leading to a-priori design of new materials.

Projected Evolution

In the near term, four central topics define the current program: electronic and magnetic behavior of materials; corrosion and electrochemistry science; nano-scale phenomena; and multiscale modeling of materials behaviors. Major efforts in these areas will continue. Increased investment in plasmonics, metamaterials and organic electronic materials will be considered. In addition, focus in theory and modeling at universities and national laboratories, taking advantage of the vast advances in computing speed and power, will be emphasized.

The long term goals of this program to understand the macroscopic behavior of materials it is important to understand the relationship between a material's properties and its response to external stimuli. This can be achieved by determining structure over multiple length scales, with emphasis at the atomic level, and by understanding the response of the nanometer and larger features of the material to those external stimuli. Studies of the physical response of a single nanometer-scale feature needs to be related to the macroscopic behavior of the material. This can often be done with modeling, but further advances are necessary to fully couple the length scales from atomic to macroscopic. Currently, atomistic simulation methods can be used to study systems containing hundreds of thousands of atoms, but these systems are still orders of magnitude too small to describe macroscopic behavior. Continuum methods, typically using finite element methods, fail to adequately describe many important properties because they use phenomenology that has little connection to the real processes that govern physical interactions. Modeling at an intermediate length scale, the mesoscale, where many defects can be included and from which predictive models at the continuum scale can be developed is required for advances in materials science. At this intermediate length-scale it is necessary to model the collective phenomena that include well over a billions atoms. Developing and applying novel techniques to these problems will be emphasized in coordination with the investment in theory and modeling. This program also seeks to foster theory, modeling, and simulation activities that address the following key topics in organic electronic materials: charge and energy transfer; electronic structure calculation; exciton dynamics and transport; and spin dynamics.

Mechanical Behavior and Radiation Effects

Portfolio Description

This activity supports basic research to understand defects in materials and their effects on the properties of strength, structure, deformation, and failure. Defect formation, growth, migration, and propagation are examined by coordinated experimental and modeling efforts over a wide range of spatial and temporal scales. Topics include deformation of ultra-fine scale materials, radiation-resistant material fundamentals, and intelligent microstructural design for increased strength, formability, and fracture resistance in energy relevant materials. The goals are to develop predictive models for the design of materials having superior mechanical properties and radiation resistance. Capital equipment funding is provided for microstructural analysis, nanoscale mechanical property measurement tools, and ion-beam processing instrumentation.

Unique Aspects

The ability, from a fundamental basis, to predict materials performance and reliability and to address service life extension issues is important to the Department of Energy (DOE) missions in fossil energy, fusion energy, nuclear energy, energy efficiency, renewable energy, radioactive waste storage, environmental management, and defense programs. Among the key materials performance issues for these technologies are load-bearing capability, failure and fatigue resistance, fracture toughness and impact resistance, high-temperature strength and dimensional stability, ductility and deformability, and radiation tolerance. This activity represents a major component of federally supported basic research in mechanical behavior and is the sole source of basic research in radiation damage. In the science of mechanical behavior, cutting-edge experimental and computational tools are bringing about a renaissance – researchers are now beginning to develop unified, first-principles models of deformation, fracture, and damage. The compelling need for understanding deformation mechanisms is related to the fact that virtually all structural metals used in energy systems are fabricated to desired forms and shapes by deformation processes. In radiation effects, the compelling need for valid predictive models to forecast the long-term degradation of reactor components and radioactive waste hosts is expected to become increasingly critical over the next decade. Radiation tolerance of structural metals and insulating ceramics is also of great concern for fusion energy systems.

Relationship to Other Programs

This activity interacts closely with the DOE programs in fossil energy, fusion energy, nuclear energy, , environmental management, and defense programs, especially in the areas of materials performance and reliability. Through its focus on atomic level understanding of defect-property relationships it is complementary to the emphasis on behavior of complex materials in the BES Physical Behavior of Materials and Electron and Scanning Probe Microscopies. Similarly, radiation effects projects on radiation-tolerant materials complement BES Heavy Element Chemistry research on actinide and heavy element chemistry. Principal investigators use BES scientific user facilities for x-ray and neutron scattering, electron beam microcharacterization and the Nanoscale Science Research Centers (NSRCs). Nanoscience-related projects in this activity are coordinated with the NSRC activities and reviews in the BES Scientific User Facilities Division. BES further coordinates the nanoscience activities with other federal agencies by participating in the National Science and Technology Council's Nanoscale Science, Engineering, and Technology subcommittee, which leads the National Nanotechnology Initiative.

Significant Accomplishments

New Materials for Radiation Environments – Materials capable of resisting damage from intense radiation are essential for advanced nuclear energy systems. The primary radiation-damage mechanism in materials involves the creation and accumulation of structural defects such as dislocations, point defects, and other anomalies. Multiple defects could lead to the collapse of the ordered crystalline structure of the material, adversely affecting the integrity of material components used in nuclear energy systems. Recent studies have shown that materials can be made radiation-damage resistant by creating structures that actually accommodate radiation-induced structural disorder on the atomic scale. Complex oxides are candidate materials for these structures because they exhibit strong tendencies for natural atomic disordering. As a result, the formation of radiation-induced defects causes very little structural change, allowing the crystal structure to remain mechanically intact. The materials exhibit good radiation tolerance after high-level radiation exposure. Similarly, radiation damage can be accommodated in composite materials containing a high volume fraction of nanoscale interfaces. The interfaces are found to possess a strong affinity for defects, thereby catalytically removing them from the bulk of the material. The research has provided fundamental insight into tailoring the atomic structure of materials to achieve substantial improvements in radiation damage tolerance.

Learning from Nature to Make Tough Ceramics – Nature generates strong materials, such as mother-of-pearl, with orders of magnitude more fracture resistance than any man-made materials. These strong materials are made by the formation of hybrid composites in which a hard, brittle mineral is combined with soft, organic molecules. Recently, researchers have developed a new fabrication process that mimics nature. The results are hybrid materials composed of aluminum oxide (strong, but brittle) and polymers (soft, organic materials) with toughness 300 times higher than either component alone. The processing involved controlled freezing of a suspension of aluminum oxide ceramic particles in water (which drives the particles into layered structures), sublimating the ice, and then infiltrating the remaining ceramic framework with a polymer. The layer orientation and spacing were designed to ensure that a crack that forms in the brittle mineral is shielded from stress and actually stops growing, thereby resulting in the combined high strength and facture resistance.

Mission Relevance

The ability to predict materials performance and reliability and to address service life extension issues is important to the DOE mission areas of robust energy storage systems; fossil, fusion, and nuclear energy conversion; environmental cleanup; and defense. Among the key materials performance goals for these technologies are good load-bearing capacity, failure and fatigue resistance, fracture toughness and impact resistance, high-temperature strength and dimensional stability, ductility and deformability, and radiation tolerance. Since materials from large-scale nuclear reactor components to nanoscale electronic switches undergo mechanical stress and may be subjected to ionizing radiation, this activity provides the fundamental scientific underpinning to enable the advancement of high-efficiency and safe energy generation, use, and storage as well as transportation systems.

Scientific Challenges A key challenge is the development of a fundamental understanding of the influence of large magnetic or electrical fields, chemical reactions and environmentally driven phase changes on the mechanical response of materials, and the influence of stress or strain on their physical properties. It is increasingly recognized that there is a strong linkage between physical and mechanical behavior. This is particularly apparent in processes such as magnetoplasticity, but has also been observed in metal forming, processing and sintering. Externally applied or internally generated magnetic and electric fields have been observed to influence the deformation response in a number of materials. This opens a new avenue for controlling the mechanical properties of materials.

Cooperative phenomena – What is missed when observing or modeling individual defects or processes? Often it is found that there are synergistic and system-level effects to mechanical behavior as a number of deformation processes rely on cooperative movement of defects or microstructural components. These processes include strain hardening, grain boundary sliding, and grain growth.

Bridging length and time scales – The formation and motion of defects take place over a wide range of length and time scales. In order to fully understand response of the materials, it is necessary to successfully model and measure defect motion and interactions over this range of length (from sub-nanometer to millimeter) and time scales (picoseconds to seconds to years) in a unified manner.

Projected Evolution

Research opportunities that can be realized by the application of mechanics fundamentals to the general area of self-assembly, physical behavior, and behavior under extreme environments will constitute an increasingly significant part of the development of devices that harvest energy, sense trace amounts of matter, and manipulate information. With the emerging importance of nanoscale structures with high surface-to-volume ratios, it is appropriate to take advantage of the new, unprecedented capabilities to fabricate and test tailored structures down to the nanoscale, taking advantage of more powerful parallel computational platforms and new experimental tools.

Radiation is increasingly being used as a tool and a probe to gain a greater understanding of fundamental atomistic behavior of materials. Incoming fluxes can be uniquely tuned to generate a materials response that can be detected *in situ* over moderate length and time scales. Materials also sustain damage after long times in high-radiation environments typical of current and projected nuclear energy reactors and in geological waste storage. As nuclear energy is projected to play a larger role in US energy production, these are issues that need to be addressed at a fundamental level.

New initiatives in the Energy Frontier Research Centers and the Single-Investigator and Small Group Research program include materials under extreme environments as well as advanced nuclear energy systems. Both of these topics were subjects of Basic Research Needs workshops and are expected to have a large impact on the portfolio of this CRA.

X-ray Scattering

Portfolio Description
This activity supports basic research on the fundamental interactions of photons with matter to achieve an understanding of atomic, electronic, and magnetic structures and excitations and their relationships to materials properties. The main emphasis is on x-ray scattering, spectroscopy, and imaging research, primarily at major BES-supported user facilities. Instrumentation development and experimental research in ultrafast materials science, including research aimed at generating, manipulating, and detecting ultrashort and ultrahigh-peak-power electron, x-ray, and laser pulses to study ultrafast physical phenomena in materials, is an integral part of the portfolio.

Unique Aspects
The DOE history and mission have played important roles in BES' current position as the nation's steward of major x-ray facilities. As part of its stewardship, BES maintains strong fundamental research programs at these facilities in materials and related disciplines. This includes the research that has motivated part of the largest expansion of BES construction projects in recent years - the Advanced Light Source, Advanced Photon Source, the SPEAR III upgrade, and most recently, the Linac Coherent Light Source and NSLS II. The unique properties of synchrotron and free electron laser radiation – high flux and brightness, tunability, polarizability, and high spatial and temporal coherence, along with the pulsed nature of the beam – afford a wide variety of experimental techniques whose development and early application to materials science are supported by this program.

Ultrafast materials science involves time domain investigations examining, for example, the early stages of chemical reactions, bond breakage and formation in catalytic reactions, the nucleation of defects in materials that result in the degradation of their properties, and the differences in electronic configurations and transport mechanisms that govern the flow of energy in devices engineered with attention to novel nanoscale property effects. Potential applications involve the coherent control of surface chemical reactions and structures, switching and control of magnetic spin and electrical polarization domains, and non-equilibrium optical processing during material synthesis.

Relationship to Other Programs
This activity interacts closely with the research instrumentation programs supported by other federal agencies, especially in the funding of beam lines whose cost and complexity require multi-agency support. Within the various DOE programs, x-ray techniques play a key role in the investigation of materials and processes related to energy conversion and use by providing atomic- and molecular-level information on the structure of nano-particles and catalytic surfaces under in-situ realistic chemical environments and in realistic device structures. Extending into the ultrafast regime, there is the promise of expanding understanding across the full range of chemistry and materials sciences by allowing femto-second stroboscopic investigations of the earliest stages of dynamic phenomena critical to energy conversion.

The scattering program interfaces with other programs in BES dealing with scattering theory and models; soft matter and biophysical materials interrogation through techniques such as grazing incidence small angle scattering and resonant soft x-ray scattering; geosciences research through high pressure x-ray scattering techniques; and spectroscopy applied to heavy element chemistry.

Approximately one third of the recently established BES Energy Frontier Research Centers (EFRCs) benefit from the significant involvement of synchrotron x-ray researchers and their techniques. *In situ* characterization and nanoscale tracking of active materials in realistic energy conversion environments enhances the activities of several EFRCs. Advanced synchrotron characterization supports EFRCs involved in catalysis, electrical storage, superconductivity, gas separation, high pressure extreme environments, nuclear reactor materials, and photovoltaics.

Significant Accomplishments

The program supports groups that have contributed to the development of such powerful techniques as inelastic x-ray scattering, x-ray absorption structural spectroscopy, x-ray microscopy, nanoscale focused beam diffraction, time-resolved spectroscopy, and resonant x-ray scattering providing specific chemical, magnetic, and excitation contrast.

Recent accomplishments include sensitive measurements of surface segregated atomic and electronic structure in new catalysis alloys, as well as measurements of distortions in the atomic ordering resulting from the interfacial constraints on perovskite oxide films which exhibit unique magnetic and electron transport behavior. Progress in understanding the rich magnetic and electronic structure of correlated electron materials continues in terms of mapping out phase boundaries and determining the nature of the competing quantum interactions behind transitions in physical properties. Refined *in situ* techniques have become more adept at probing small samples, surfaces, and interfaces under extreme processing environments of temperature, pressure, and reactive gases. When a material is excited by light or thermal energy to non-equilibrium states, different pathways back to equilibrium often have different time scales. Recent experiments in ultrafast science have employed multiple probes with different sensitivity to various relaxation mechanisms. Fresh results are beginning to tease out the faster dynamics of electronic structure from the slower recovery of atomic motion and lattice strain.

Mission Relevance

The increasing complexity of DOE mission-relevant materials such as superconductors, semiconductors, and magnets requires ever more sophisticated scattering techniques to extract useful knowledge and to develop new theories for the behavior of these materials. X-ray scattering probes are some of the primary tools for characterizing the atomic, electronic, and magnetic structures of materials, including in extreme environments such as high pressure.

Scientific Challenges

<u>Correlated Electron Systems</u> – The effects of strong electron-electron interactions give rise to a remarkable range of anomalous behavior in condensed matter systems, producing phenomena as varied as metal-insulator transitions, colossal magnetoresistance, and high-temperature superconductivity. Such cooperative macroscopic phenomena result from the interplay of charge, orbital, spin, and lattice degrees of freedom that can arise in correlated electron behavior. Techniques such as inelastic and resonant x-ray scattering and angle resolved photo-emission, among others, have enabled scientists to unravel the crystallographic and microscopic electronic

structure of these materials.

The ultrafast excitation and exploration of dynamic pathways to metastable states provides another knob to explore the subtle energetic phase space of correlated electron materials, (much like ultra-high pressure techniques access new states along that not fully explored dimension.) Optically pumped excited states may be far from equilibrium and short lived, but the probe measurements are ultrafast and capable of capturing the elusive physics in a unique regime of matter. Recent and foreseeable advances in high-brightness x-ray sources create an unprecedented opportunity to image the primary event at nanometer spatial dimensions and ultra-fast time scales. Understanding how ultra-fast coherent radiation can manipulate condensed matter and how matter relaxes back to its unperturbed state may ultimately lead to novel materials synthesis techniques, especially at the nanoscale.

Matter Under Extreme Conditions **–** Opportunities in high pressure research address a broad range of new scientific problems involving matter compressed to multi-megabar pressures. Extreme pressures provide a fertile ground for the formation of new materials and novel physical phenomena as compression changes the chemical bonds and affinities of otherwise familiar elements and compounds. Highly collimated and intense synchrotron beams provide the ideal source for ultrafine and sensitive x-ray diffraction microprobes necessary to measure high stresses in a very small area. Scattering experiment performed in the presence of magnetic fields can be used to study materials during magnetic, structural, and superconducting phase transitions and allow researchers to segregate magnetic field effects from those observed via doping.

In situ Studies of Complex Materials – Recent advances in both sources and instrumentation have yielded gains in intensity on sample, facilitating rapid experiments and *in situ* configurations. Smaller samples can be probed with unprecedented temporal and spatial resolution, accuracy, and sensitivity under various parametric conditions. Such information aids the development of novel processing techniques and the search for new exotic materials. In-situ studies are entering the ultrafast time domain through coupling laser excited ultra-fast electronic excitations to atomic strain driven processes. There also exists the possibility of selectively studying the dynamics of such phenomena through the photo-doped creation of metastable states that would not, necessarily, be thermally accessible.

Projected Evolution

Advances in x-ray scattering and ultrafast sciences will continue to be driven by scientific opportunities presented by improved source performance and optimized instrumentation. The x-ray scattering activity will continue to fully develop the capabilities at the DOE facilities by providing support for instrumentation, technique development and research. A continuing theme in the scattering program will be the integration and support of materials preparation (especially when coupled to *in situ* investigation of materials processing) as this is a core competency that is vital to careful structural measurements related to materials properties. New investments in ultrafast science will focus on research that develops and uses radiation sources associated with BES facilities and beam lines but also includes ultra short pulse x-ray, electron beam and THz radiation probes created by conventional tabletop laser sources.

Neutron Scattering

Portfolio Description

This activity supports basic research on the fundamental interactions of neutrons with matter to achieve an understanding of the atomic, electronic, and magnetic structures and excitations of materials and their relationship to materials properties. Major emphasis is on the application of neutron scattering, spectroscopy, and imaging for materials research, primarily at BES-supported user facilities. Development of next-generation instrumentation concepts, innovative optics, novel detectors, advanced sample environments, data analysis tools and polarized neutrons are distinct aspects of this activity. Capital equipment funding is provided for items such as detectors, monochromators, focusing mirrors, and beamline instrumentation at the facilities.

Unique Aspects

The DOE history and mission have played important roles in shaping BES' current position as the nation's steward of major neutron facilities. Historically, neutron sources descended from the nuclear reactors that were constructed in the early 1940s as part of the U.S. Atomic Energy Program. This activity has evolved from the pioneering, Nobel prize-winning efforts of Clifford G. Shull in materials science to the current program that encompasses multiple techniques and disciplines. BES is a major supporter of both the research and the instrumentation at the major US neutron scattering facilities. It maintains strong fundamental research programs in materials and related disciplines at these facilities that serve to drive advancements in the instrumentation. High impact science from this activity provided the scientific case to motivate the construction of the Spallation Neutron Source (SNS), the BES facility with the highest pulsed neutron flux and a range of optimized neutron scattering instruments.

Neutron scattering provides information on the positions, motions, and magnetic properties of materials. The neutrons used in scattering experiments with wavelengths commensurate with the inter-atomic distances have energies in the meV range that is comparable to both the lattice and magnetic excitations (phonons and magnons). This fundamental property makes neutrons an ideal probe for both the structure and dynamics in condensed matter. The high sensitivity to light elements and large difference in scattering cross-section of certain isotopes offer unique contrasts and a range of versatile tools for the investigation of ordered and disordered as well as hybrid nanostructured materials. Their high penetrating ability and low energy allow nondestructive evaluation of the structure and dynamics of materials deep within the specimens, and their magnetic moment offers as an important probe of magnetic phases in materials.

Relationship to Other Programs

This activity serves several BES supported Energy Frontier Research Centers (EFRC) with focused research in the areas of superconductivity, organic photovoltaics, materials under high pressure, structural materials under extreme conditions and interfacial structure and dynamics for energy storage and catalysis. It supports fundamental research on hydrogen storage materials through coordination with the Office of Energy Efficiency and Renewable Energy and high pressure research with the National Nuclear Security Administration. It interacts closely with the BES Scientific User Facilities Division in the development of new instrument concepts and tools for neutron scattering and coordination on complementary scientific portfolios as well as with research instrumentation programs supported by other federal agencies, especially in the funding of beam lines whose cost and complexity require multi-agency support. It coordinates with the program for Instrumentation for Materials Research – Major Instrumentation Projects at the National Science Foundation and the National Institute of Standards and Technology's Center for Neutron Research to develop instruments and capabilities that best serve the national user facility needs. Nanoscience related projects in this activity are coordinated with the BES Nanoscale Science Research Center activities. BES further coordinates the nanoscience activities with other federal agencies by participating in the National Science and Technology Council's Nanoscale Science, Engineering, and Technology subcommittee, which leads the National Nanotechnology Initiative.

Significant Accomplishments

BES supported the pioneering research of Clifford G. Shull in the development of the neutron diffraction technique at Oak Ridge National Laboratory that led to the 1994 Nobel Prize in Physics. Shull's work launched the field of neutron scattering, which has proven to be one of the most important techniques for elucidating the structure and dynamics of solids and fluids. Recent scientific accomplishments include the rich magnetic and electronic structures of correlated electron materials, such as conventional and high temperature superconductors, ferroelectrics, mutiferroics, cobaltites, colossal magnetoresistance materials and layered heterostructures. Also in the areas of high temperature thermodynamics of metallic systems; pressure-temperature stability and thermodynamics of clathrates, hydrides, boranes, crown ethers and $Xe\text{-}H_2$; superfluidity and phase boundaries in quantum solids and fluids; dynamic phase transitions in deeply super-cooled water; polymer and polymer brush behavior under nano-confinement; and metal-organic frameworks for hydrogen storage.

Neutron scattering groups supported by this activity at the DOE national laboratories (Ames, Argonne, Brookhaven, Oak Ridge, and Los Alamos) provided the leadership and expertise in the pioneering design and development of virtually all the current highly optimized time-of-flight instruments and techniques in neutron scattering and spectroscopy at the SNS. In addition, this activity supported the development of the spin-echo small-angle scattering measurement technique that extends the measurement length scales to several microns; ^3He spin filters for the production of polarized neutrons for the study of magnetism; neutron scattering confinement cell to probe polymer brushes under confinement; and neutron focusing optics for a number of applications.

Mission Relevance

The increasing complexity of DOE mission-relevant materials such as superconductors, semiconductors, magnets, batteries, photovoltaics, thermoelectrics and polymer nanocomposites requires ever more sophisticated scattering techniques to extract useful knowledge and to develop theories which can predict the behavior of these materials. X-ray and neutron scattering probes are some of the primary tools for characterizing the atomic, electronic, and magnetic structures of materials. Additionally, neutrons play a key role in hydrogen research as they provide atomic- and molecular-level information on structure, diffusion, and interatomic interactions for hydrogen. They also allow access to the morphologies that govern useful properties in catalysts, membranes, and protonic conductors. The activity is relevant to the behavior of matter in extreme environments such as high temperature and high pressure.

Scientific Challenges

Correlated Electron Systems – The effects of strong electron-electron and electron-phonon interactions give rise to a remarkable range of anomalous behavior in condensed matter systems. Quantitative understanding of the cooperative macroscopic phenomena emerging from the interplay between charge, spin, and lattice degrees of freedom in materials including high temperature superconductors, multiferroics and magnets remains a great challenge and inelastic neutron scattering and neutron diffraction will play major roles in the studies of these materials.

Matter Under Extreme Conditions – Extreme pressures provide a fertile ground for the formation of new materials and novel physical phenomena as compression perturbs significantly the chemical bonds and affinities of otherwise familiar elements and compounds. Highly optimized spectrometers with novel sample environment will enable *in situ* studies at high pressures at pressure ranges available at the synchrotron x-ray sources. Similarly, scattering experiments at high magnetic fields can be used to study materials during phase transitions, allowing researchers to segregate magnetic field effects as well as to simulate effects normally observed via doping.

In-situ Studies of Complex Materials – Highly optimized instruments at the SNS will enable the science with smaller samples with unprecedented resolution, accuracy, and sensitivity under various parametric conditions. *In-situ* studies of complex materials including those undergoing time-dependent structural or magnetic phase transformations, disordered systems such as alloys and amorphous materials, organic thin films and other condensed matter systems can be probed with a range of scattering, reflectivity, and spectroscopic techniques.

Projected Evolution

The neutron scattering activity will continue in fully developing the capabilities at the DOE facilities by providing instrumentation and research support. A continuing theme in the scattering program will be the integration and support of materials preparation as this is a core competency that is vital to careful structural measurements related to materials properties. This program will continue its stewardship role in fostering growth in the US neutron scattering community in the development of innovative time-of-flight neutron scattering instrumentation concepts and its effective utilization for high profile research.

Correlated and Complex Materials – Realization of the enormous potential in functionality of correlated electron systems requires a complete understanding of the underlying mechanisms and phenomena to ultimately control the complexities to achieve desired functionality. In addition to cuprates, the recently discovered iron pnictides family will provide as yet another platform to investigate high Tc superconductivity. Elastic and inelastic neutron scattering techniques will remain as essential tools for the investigation of complex correlated electron systems.

Research at the Intersection of Hard and Soft Condensed Matter Sciences – Polymers, biomaterials and hybrid nanocomposites are ubiquitous in the modern world. Surfaces and interfaces play strong roles in hybrid materials relevant to such applications as organic photovoltaics, thermoelectrics, fuel cells, Li-ion batteries, organic light emitting diodes, and materials for carbon sequestration and hydrogen storage. Neutron scattering will play a major role to understand the effects of interfaces on the collective behavior of these multi-component systems, enabling science in the emerging areas in soft condensed matter science.

Electron and Scanning Probe Microscopies

Portfolio Description

This activity supports basic research in condensed matter physics and materials science using electron and scanning probe microscopy and spectroscopy techniques. The research includes experiments and theory to understand the atomic, electronic, and magnetic structures and properties of materials. This activity also supports the development and improvement of electron scattering and scanning probe instrumentation and techniques, including ultrafast diffraction and imaging techniques. Capital equipment funding is provided for items such as new scanning probes and electron microscopes as well as ancillary equipment including high resolution detectors.

Unique Aspects

Materials properties at macroscopic scale originate from microscopic details, via a hierarchy of length scales. This activity is driven by the need for quantitative characterization and understanding of materials over atomic to micron length scales. High spatial resolution provides unique opportunities to characterize nanoscale structures in technologically-important materials. This activity supports comprehensive microscopy research groups which undertake the development, implementation, and exploitation of a variety of electron beam and scanning probe techniques for fundamental understanding, characterization, and analysis of materials. Research results are increasingly coupled with first-principles theory, which offers quantitative insights into the atomic origins of materials properties.

Relationship to Other Programs

This activity interfaces with other programs in BES, including the activities under X-Ray and Neutron Scattering, Condensed Matter Physics, Physical Behavior, Mechanical Behavior and Radiation Effects, Synthesis and Processing, Materials Chemistry and Biomolecular Materials, Catalysis, Energy Frontier Research Centers (EFRCs), Electron-beam Microcharacterization Centers, Nanoscale Science Research Centers, and DOE Experimental Program to Stimulate Competitive Research. The research is also relevant to the DOE Office of Energy Efficiency and Renewable Energy activities in solar energy, hydrogen and energy storage technologies. This research activity also interfaces with the National Science Foundation in materials research activities, and with other federal agencies through the National Nanotechnology Initiative.

Significant Accomplishments

This program has been a major U.S. supporter of microscopy research for developing a fundamental understanding of materials. Scientific achievements in this program include the development of the leading U.S. capabilities for materials characterization at subangstrom length scales that are coupled with advances in detectability limits and precision quantitative analytical measurement. Historical accomplishments include: the successful correction of electron microscope lens aberrations that allowed, for the first time, the direct imaging of materials at sub-Angstrom resolution and the first spectroscopic imaging of single atoms within a bulk solid; the development of dynamic transmission electron microscopy, which couples high time resolution (~nanoseconds) with high spatial resolution (~nanometers) in both images and diffraction patterns, providing a unique tool for probing and understanding materials dynamics; and the development of the Embedded Atom Method which revolutionized computational materials science by permitting large scale simulations of materials structure and evolution. Recent accomplishments include the development of a method to map complete electron wave functions, including internal quantum phase, from measured probability densities. Quantum measurement (scanning tunneling microscopy) of these “quantum drums” revealed that isospectrality provides an extra topological degree of freedom enabling robust quantum phase extraction. A new world record was set for the smallest writing, with features of letters as small as 0.3 nm. The feasibility was demonstrated for a new approach capable of achieving sub-atomic data storage. Imaging of electronic self-organization by atomic-resolution, tunneling-asymmetry scanning tunneling microscopy provided understanding of copper oxide electronic transport mechanisms for high-temperature superconductivity.

Mission Relevance

The nation’s long-term energy needs present many fundamental challenges, especially the need for new materials and characterization tools such as electron beam and scanning probes. Performance improvements for environmentally acceptable energy generation, transmission, storage, and conversion technologies depend on a detailed understanding of the structural characteristics of advanced materials. Electron and scanning probe microscopies are among the primary tools for characterization of the atomic, electronic, and magnetic structures of materials. Quantitative analysis of nanoscale structure and phenomena is crucially important for materials used in energy technologies. The processes on the surface and interior of nanostructures and the functionality of materials can be imaged and analyzed by using *in situ* microscopy techniques under various environments. The activity is relevant to materials research and energy technologies through the structural and functionality determination of nanostructured materials for energy storage and solar energy/fuels.

Scientific Challenges

Major scientific challenges are: imaging functionality at the atomic or nanometer scale; correlation of structure and function at nanometer or atomic scale; fundamental understanding of electron scattering and nanoscale ordering phenomena in matter; understanding the atomic or nanoscale origin of macroscopic properties to enable the design of high-performance materials; quantitative analysis of nanomaterials; understanding correlation between electrons and spins at nanoscale and spin structure, dynamics and transport properties; determination of interface structures between dissimilar materials and understanding the link between interface/surface/defect structures and materials properties; understanding the role played by individual atoms, point defects, and dopant in materials; understanding surface reactions at the atomic level in real space and imaging site specific reactivity; combination of electron and scanning probes to study complex properties; probing the local properties of materials at the atomic scale with *in situ* microscopy in extreme energy environments; understanding the physics at the convergence of continuum and atomic phenomena; development of time-resolved microscopy with high resolution both spatially and temporally to study the atomic level mechanisms during structural transformations; and the application of first principles theory to understand and predict the structures of real materials. To address these challenges, new state-of-the-art experimental and theoretical techniques will need to be developed. It is our long term goal to invent multiscale characterizations tools and be able to link structural evolution, dynamics, and electronic behavior with first principles understanding of materials.

Projected Evolution

This program will build upon the tremendous advancements in electron and scanning probe microscopy capabilities in the last decade and use scattering, imaging and spectroscopy methods to understand functionality and fundamental processes at the atomic or nanometer scale. Characterization of semiconducting, superconducting, magnetic, and ferroelectric materials benefits greatly from these abilities and from other research supported in this program. Concurrently, new frontiers in fundamental understanding of materials are being opened with the creation of novel characterization techniques.

Development of advanced electron and scanning probe microscopy techniques will be continued in order to meet our energy and basic science challenges. Significant improvements in resolution and sensitivity will provide an array of opportunities for groundbreaking science. These include the possibilities of understanding and controlling nanoscale inhomogeneity, new phenomena emerging at nanoscale, atomic-scale tomography, probing magnetism at the atomic scale with spin excitation spectroscopy, imaging spin density and spin waves, imaging functionality at the atomic scale, combination of multiple probes, and *in situ* analysis capabilities (under perturbing parameters such as temperature, irradiation, stress, magnetic field, and chemical environment). New methods and approaches addressing the scientific challenges will lead to the development of unique new analysis tools and breakthroughs in materials. The combined new experimental and theoretical capabilities will enable the fundamental understanding of atomic origins of materials properties. Significant advances will be made in the fundamental understanding of the mechanisms by which electrons, individual atoms, surface/interfaces and defects influence the properties and behavior of materials.

Experimental Program to Stimulate Competitive Research (EPSCoR)

Portfolio Description

This activity supports basic research spanning the broad range of science and technology programs at DOE in states that have historically received relatively less Federal research funding. The currently eligible EPSCoR states are listed at http://www.nsf.gov/od/oia/programs/epscor/eligible.jsp. The research supported by EPSCoR includes materials sciences, chemical sciences, physics, energy-relevant biological sciences, geological and environmental sciences, high energy physics, nuclear physics, fusion energy sciences, advanced computing, and the basic sciences underpinning fossil energy, nuclear energy, energy efficiency, electricity delivery, and renewable energy.

Unique Aspects

The program objective is accomplished by sponsoring two types of grants: (1) Implementation Grants and (2) State-Laboratory grants. Implementation grants address state/territory capability and infrastructure development through funding research in a focused area or research cluster with the potential to support faculty hires, a group of students or postdoctoral fellows, and the purchase of research equipment. Implementation grants are for a maximum period of six years with an initial grant period of three years. The State-Laboratory grants address building partnerships between the researchers in EPSCoR institutions, their students and postdoctoral fellows with research scientists and unique capabilities at DOE national laboratories. The State-Laboratory grants are for one period of three years.

EPSCoR has placed a high priority on promoting strong research collaboration and training of students at the DOE national laboratories where unique, world-class facilities are available. This program is science-driven and supports the most meritorious proposals based on peer review and programmatic priorities. Discussions are held with representative scientists from EPSCoR states to acquaint them with the facilities and personnel at the DOE national laboratories.

Relationship to Other Programs

The activity interfaces with all other research activities within BES. In addition, it is responsive to programmatic needs of other program offices within DOE. Most of the research clusters that have graduated from the DOE EPSCoR program after six years of funding have found alternate funding for continuing the research activity. This demonstrates that the research clusters funded by EPSCoR are becoming competitive. In addition, EPSCoR grants are supporting graduate students, undergraduates, and postdoctoral associates, and encouraging them to be trained in frontier research areas by making use of world-class research facilities at the DOE National Laboratories. The work supported by the EPSCoR program impacts all DOE mission areas including research in materials sciences, chemical sciences, biological and environmental sciences, high energy and nuclear physics, fusion energy sciences, advanced computer sciences, fossil energy sciences, and energy efficiency and renewable energy sciences.

Significant Accomplishments

The EPSCoR program funds basic research in support of all programmatic needs of DOE. Select accomplishments are presented, grouped according to the relevant DOE program office.

Basic Energy Sciences

- A group at the University of Oklahoma is in the race to measure the electric dipole moment of the electron. Approximately 20 groups world-wide are seeking to measure this important fundamental property that will allow the world to assign a size to the electron. Current experimental limits already show that the ratio of size of an electron to the size of a proton is less than the ratio of the size of an ant to the distance between the Earth and Sun. Specifically, the size of the electron differentiates between many competing models of how particles interact. These models include the venerable Standard Model of Physics and the newer Super Symmetric Theories. Using a lead fluoride molecule researchers at the University of Oklahoma are helping to differentiate these models (N. Shafer-Ray, U. Oklahoma).

- Thermal energy exists in many forms ranging from solar energy to waste heat from existing power sources. For example, over 70% of the input power into an automobile engine is lost, a large majority of the loss in the form of waste heat. One way to harness thermal energy is through the use of thermoelectric materials and devices that enable us to transform this thermal energy into usable high quality electrical energy. Research in current thermoelectric materials is attempting to significantly increasing their efficiency. Over the past decade, significant advances have been achieved in low dimensional structures such as superlattices and quantum dots. New investigations by researchers in South Carolina using novel nanostructures and nanocomposites including exotic "cage structure" materials consist of matrices of bulk and nanomaterials are offering to nearly double the performance of low-dimensional materials. Such improved performance and continued development of high efficiency thermoelectric nanocomposites may provide environmentally safe and reliable power sources to sustain the nation's future (T. M. Tritt, Clemson University).

Biological and Environmental Research

- Most doses of radiation exposures associated with human activity are predicted low dose in nature. These may arise from medical diagnostics, hazardous waste abatement, power systems operation, and even terrorist acts such as dirty bombs. While the precise risk of exposure continues to be debated, recent findings indicate that a measurable risk exists even at very low doses. By measuring gene activity before and after exposure, researchers in Tennessee are working to identify biological pathways that are activated or repressed in response to the radiation insult. Work at the University of Tennessee on *in situ* gene expression is enhancing our understanding of low dose radiation's effects at all levels of biological organization, from genes to cells to tissues and finally to complex organisms such as humans. Understanding the risks to human health associated with low dose radiation is critical if we are to protect the nation's workforce while making the most effective use of national resources (M. A. Langston, U. Tennessee).

Fossil Energy

- Coal has a wide variety of trace elements such as arsenic, selenium and antimony that can have undesirable environmental consequences. In order to mitigate this potential hazard, it is important to develop a fundamental understanding of how these trace elements are partitioned in the combustion products between the gas phase and particulate matter. To correctly predict how this partitioning occurs, the generation of currently unavailable thermodynamic and kinetic data is required. Researchers in North Dakota are performing novel experiments to generate this data for these hazardous trace elements as well as for major elements, such as calcium, iron, and aluminum, over melts that replicate the solid surfaces of ash particles. Computational calculations have also been performed to compare the thermodynamic stabilities of compounds of these trace elements. Ab initio calculations suggest that oxygen-rich compounds of the trace elements are preferred to the simple oxide forms predicted by classical thermodynamic calculations. Such results are helping researchers envision the reduction of the environmental impact of burning coal (W. Seames, U. North Dakota).

Mission Relevance
The core activity interfaces with all other core activities within the Office of Science and DOE. It is also responsive and supports the DOE mission in the areas of energy and national security and in mitigating their associated environmental impacts.

Scientific Challenges
The DOE EPSCoR activity will continue to support basic research spanning the broad range of science and technology programs within DOE.

Projected Evolution
A recent trend has been to increase the potential award sizes of both the Implementation Grants and the State-Laboratory Grants. Future Funding Opportunity Announcements (FOAs) will incorporate Congressional language increasing the funding limit on implementation grants from $1,000,000 per year in the most recent Implementation Grant FOA to $2,500,000 per year. Another modification to the program will be removing the limitation of one implementation award per EPSCoR state. Maximum funding for State-Laboratory grants has been increased from $150,000 per year to $200,000 per year in the most recent FOA. These changes will allow for more rapid capability development at EPSCoR institutions and enable increased contact time and improved collaborations between the EPSCoR research scientists and DOE National Laboratories. An additional change is that FOAs beginning with FY 2009 do not require state matching funds.

X-ray and Neutron Scattering Facilities

Portfolio Description

This activity supports the operation of four synchrotron radiation light sources and three neutron scattering facilities. These are: the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL); the Advanced Photon Source (APS) at Argonne National Laboratory (ANL); the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL); the Stanford Synchrotron Radiation Laboratory (SSRL) at the Stanford Linear Accelerator Center (SLAC); the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL); the Manuel Lujan Jr. Neutron Scattering Center (Lujan Center) at Los Alamos National Laboratory (LANL); and the Spallation Neutron Source (SNS) at ORNL, which is the most powerful short-pulse spallation neutron source in existence. The construction of the free-electron laser facility, Linac Coherent Light Source (LCLS) at SLAC will be completed in June 2010, providing laser-like radiation in the short x-ray region of the spectrum with 10 orders of magnitude greater peak power and brightness than that available from any existing synchrotron radiation x-ray light source. Under construction is the NSLS-II which will replace NSLS to enable the study of material properties and functions at the nanoscale level and to provide the world's finest x-ray imaging capabilities.

Unique Aspects

The synchrotron radiation light sources and the neutron scattering facilities are the most advanced facilities of their kind in the world. Together, they serve more than 10,000 users annually from academia, Department of Energy (DOE) national laboratories, and industry, a number that has more than tripled in the past decade and that can more than double again in the next decade as current facilities and those under construction are fully instrumented. These light sources and neutron scattering sources represent the largest collection of such facilities operated by a single organization in the world. Conception, design, construction, and operation of these facilities, which in current costs are in the hundreds of millions to in excess of a billion dollars, are among the core competencies of the BES program.

Relationship to Other Programs

This activity has very strong interactions with all BES programmatic research that use synchrotron and neutron sources. This includes research in atomic physics, condensed matter and materials physics, chemical dynamics, catalysis, geosciences, high-pressure science, environmental sciences, engineering, biosciences, and much more. Interaction also exists with other parts of the Office of Science, notably the Office of Biological and Environmental Research, and DOE, notably the National Nuclear Security Administration, the Office of Energy Efficiency and Renewable Energy, and the Office of Environmental Management. There are frequent contacts with other federal agencies in order to better coordinate efforts in optimizing beamlines and instruments. This activity participates in a number of Office of Science and Technology Policy (OSTP) and National Science and Technology Council (NSTC) interagency activities, e.g., OSTP Interagency Working Groups on macromolecular crystallography at the synchrotron light sources and on neutron sources and instrumentation. This activity is establishing more frequent contacts with international user facilities such as ESRF, SPring-8, ILL, ISIS, and others. The objectives are to share experiences and to make optimal use of present facilities.

Significant Accomplishments

The synchrotron radiation light sources. During the past two decades, BES has been the nation's major supporter of synchrotron x-ray light sources. BES support pioneered new storage ring lattices for improved beam stability and brightness; developed wiggler and undulator insertion devices that provide 10-12 orders of magnitude greater brightness than the best conventional x-ray sources; and discovered or developed such powerful experimental techniques as magnetic x-ray scattering, microbeam diffraction, x-ray microscopy, photoelectron spectroscopy and holography, x-ray nanoprobe, full-field and diffraction imaging, Rapid Acquisition Pair Distribution Function (RA-PDF), inelastic x-ray scattering using nuclear resonances, extended x-ray absorption fine structure (EXAFS), and near-edge absorption fine structure (NEXAFS). The newly constructed fourth generation light source, LCLS, the world's first "hard" x-ray free-electron laser, has achieved its full performance specification and its first experimental station has successfully been commissioned. The unique capabilities of this facility have attracted 107 proposals involving 672 scientists from 22 countries for the Fall 2010 run. The BES light sources are used by over 9,000 researchers annually from academia, government laboratories, and industry for state-of-the art studies in materials science, physical and chemical science, geoscience, environmental science, bioscience, medical science, and pharmaceutical science. Recent research at the light source facilities supported by BES, other agencies, industry, and private sponsors includes: infrared transmission measurements of dual-gated bilayer graphene revealed that electric field control of its bandgap may allow it to become a remarkably flexible component of nanoscale electronic devices; structural determinations of one of many human antibodies, H5-F10, which is able to neutralize different types of flu viruses including H5N1 'bird flu' and 1918 H1N1 'Spanish flu', points the way towards developing immunotherapy for curing viral diseases; determination of atomic to nanometer scale structural information to make the essential link between the synthesis and optimization of industrial process gas sensors will increase the combustion efficiency of combustion burners in furnaces and process heaters saving valuable energy; high-energy x-ray scattering data providing information on length scales from atoms to porous networks under various pressures within the oil shale may lead to the development of strategies enabling the economic and environmentally acceptable recovery of this fossil fuel resource; and particularly significant was the award of the 2009 Nobel Prize in Chemistry for studies on ribosome which works as a protein factory for all life organisms. This work was performed at the four BES supported synchrotron radiation facilities.

The neutron scattering sources **.** Since the late 1940s, BES, and its predecessors, has been the major supporter of neutron science in the United States—from the earliest work of Clifford Shull and E. O. Wollan at ORNL's Graphite Reactor in the 1940s to the Nobel Prize in Physics shared by Clifford Shull and Bertram Brockhouse in 1994 for their work on neutron scattering. Based on its experience in nuclear reactors and particle accelerators over the years, DOE developed research reactors and spallation sources as high-flux neutron sources for spectroscopy, scattering, and imaging and helped pioneer virtually all the instruments and techniques used at these facilities. Researchers at ANL, BNL, and ORNL led these pioneering advances. Most of the important techniques used today have been developed at ANL, BNL, and ORNL. Neutron scattering provides important information on the positions, motions, and magnetic properties of solids. Neutrons possess unique properties such as sensitivity to light elements, which has made the technique invaluable to polymer, biological, and pharmaceutical sciences. Neutrons also have magnetic moments and are thus uniquely sensitive probes of magnetic interactions. Neutron scattering studies have led to higher strength magnets for more efficient electric generators and motors and to better magnetic materials for magnetic recording tapes and computer hard drives. Finally, the high penetrating power of neutrons allows nondestructive property measurements deep within a specimen and has been used to study defects in automotive gears and brake discs and in airplane wings, engines, and turbine blades.

Recent research at the neutron scattering sources supported by BES includes: evidence that the same mechanisms responsible for superconductivity could be present for copper-based high temperature superconductors and the recently discovered iron-based superconductors; the study of enzymatic digestion of cell wall cellulose biopolymer whose breakdown into fermentable sugars is critical to producing biofuels for transportation; the study of the mobility of ions in room temperature ionic liquids which are promising ionic charge-carrying media for advanced batteries and supercapacitors; and the study of the atomic structure bond lengths and angles of new geopolymer-based concrete which emits 80 to 90 percent less carbon dioxide than standard concrete during the curing process. Curing reactions in traditional concrete are estimated to account for 5 to 9 percent of anthropogenic carbon dioxide emissions. In addition, at HFIR there was an ongoing program for the production of important medical and industrial isotopes and for studying the effects of neutron irradiation on nuclear materials for fission and fusion reactors.

Mission Relevance

These facilities were born from the most fundamental of needs, i.e., the need to characterize materials at the atomic and molecular level. In order to understand, predict, and ultimately control materials properties, it is necessary to determine the atomic constituents of materials, the positions of the atoms in materials, and how the materials behave under the influence of external perturbations such as temperature, pressure, magnetic or electric field, chemical attack, and excitation by photons, electrons, and other particles. A large number of experimental and theoretical tools are used to achieve these ends. In the last two decades, the experimental demands have motivated the development of centralized facilities, like the ones in existence for synchrotron radiation and neutron scattering. Such highly sophisticated and expensive tools are by nature centralized and staffed with specialists that provide to the user community expertise in order to optimize the scientific use of the facility. The development, construction, and operation of these facilities are one of the most important missions and core competencies of BES. The scientific accomplishments of these facilities, as determined by triennial peer review, are reflected in the large number of publications appearing annually in the most important scientific journals.

Scientific Challenges

<u>The synchrotron radiation light sources.</u> First, the x-ray beam stability has always been a top priority and challenge for synchrotron facilities. The ability to produce nanoscale size x-ray beam has amplified this challenge. Second, the facilities must be operated optimally, which means optimizing instrument-hours of operation, not just accelerator hours of operation, and making the instruments widely available to the general user community. Third, optimal utilization of the LCLS coherent short-wavelength x-ray source will require successful fabrication, installation, and commissioning of advanced instruments.

<u>The neutron scattering sources.</u> New instrumentation at HFIR and SNS must be successfully integrated into robust user programs producing world-class scientific results.

Projected Evolution

X-ray and neutron scattering will continue to play a central role in the growth of BES programmatic science. The facilities will need continuous growth and advanced in terms of beamline upgrades, new neutron scattering instruments, and increase in availability of user time. The set of instruments associated with these facilities provides unique scientific and technical capabilities, rarely available in other parts of the world. These facilities need to be kept in an optimal operational condition in order to maintain and increase the tremendous scientific achievements they have facilitated.

The SNS at ORNL will be for years to come the most important neutron spallation source in the world. It is important to foster full use and judicious increases in the capabilities of SNS in order to optimize its utilization by the scientific community.

Finally, the LCLS will have properties vastly exceeding those of current x-ray sources in three key areas: peak brightness, coherence, and ultrashort pulses. The peak brightness of the LCLS is 10 orders of magnitude greater than current synchrotrons; the light is coherent or “laser like” enabling many new types of experiments; and the pulses are short (70 femtoseconds in standard operation with planned improvements that will further reduce the pulse length), enabling studies of fast chemical and physical processes. These characteristics open new realms of scientific applications in the chemical, material, and biological sciences including fundamental studies of the interaction of intense x-ray pulses with simple atomic systems, structural studies on single nanoscale particles and biomolecules, ultrafast dynamics in chemistry and solid-state physics, studies of nanoscale structure and dynamics in condensed matter, and use of the LCLS to study matter under extreme conditions.

Nanoscale Science Research Centers

Portfolio Description

The Nanoscale Science Research Centers (NSRCs) are DOE's premier user centers for interdisciplinary research at the nanoscale, serving as the basis for a national program that encompasses new science, new tools, and new computing capabilities. Each center has particular expertise and capabilities in selected theme areas, such as synthesis and characterization of nanomaterials; catalysis; theory, modeling and simulation; electronic materials; nanoscale photonics; soft and biological materials; imaging and spectroscopy; and nanoscale integration. The centers are housed in recently-constructed and custom designed laboratory buildings near one or more other major BES facilities for x-ray, neutron, or electron scattering, which complement and leverage the capabilities of the NSRCs. These laboratories contain clean rooms, nanofabrication resources, one-of-a-kind signature instruments, and other instruments not generally available except at major user facilities. These facilities are routinely made available to the research community during normal working hours. In FY 2011 funds are provided to continue operations for all five NSRCs.

Unique Aspects

Nanotechnology is the understanding and control of matter at dimensions of roughly 1 to 100 nanometers, where unique phenomena enable novel applications. With a nanometer corresponding to one billionth of a meter, nanoscale phenomena occur at the level of small numbers of atoms, molecules, and supramolecular structures. The NSRCs make sophisticated research tools for nanoscience and nanotechnology available to the broad scientific community, and facilitate access to other collocated major facilities including synchrotron radiation light sources, neutron scattering centers, and electron beam microcharacterization facilities. The NSRCs are the DOE signature activity in nanoscale research and constitute the nation's largest scientific infrastructure investment under the National Nanotechnology Initiative (NNI).

NSRCs provide unique scientific and engineering capabilities not available in any of the parallel programs sponsored by other entities. For example, other federal agencies sponsor research in nanoscience at universities, but such programs are generally limited in scope and size, are focused on specific research issues or topical areas, and primarily involve researchers of the host institution and a limited number of partners. The NSRCs are larger-scale facilities with a broad range of capabilities and are broadly accessible without usage fees for non-proprietary work, with instrument time and staff support allocated on the basis of peer-review of proposals. The purposes of the NSRCs are as follows:

- Advance the fundamental understanding and control of materials at the nanoscale regime.
- Provide an environment to support research of a scope, complexity, and disciplinary breadth not possible under traditional individual investigator or small group efforts.
- Provide the foundation for the development of nanotechnologies important to DOE.
- Provide state-of-the-art equipment to in-house laboratory, university, and industry researchers and leverage the capabilities of national user facilities for materials characterization employing electrons, photons, and neutrons.
- Provide a formal mechanism for both short- and long-term collaborations and partnerships

among DOE laboratory, academic, and industrial researchers.
- Provide training for graduate students and postdoctoral associates in interdisciplinary nanoscale science, engineering, and technology research.

Relationship to Other Programs
The fundamental science being carried out at the NSRCs is closely related to BES programmatic research on the nanometer scale at both universities and national laboratories. Researchers supported by BES, by other parts of the Office of Science, by other parts of DOE, and by other federal agencies as well as industry participate in the overall NSRC user community. While not a requirement, a major benefit is the opportunity for users to collaborate with the NSRC scientists. In addition, the NSRCs are collocated with, and serve as access points to, existing major BES user facilities for x-ray, neutron, and electron scattering. The DOE nanoscience activities as a whole are coordinated with other agencies through the Nanoscale Science, Engineering, and Technology (NSET) Subcommittee of the National Science and Technology Council (NSTC); this Subcommittee is responsible for the federal NNI program and is currently co-chaired by representatives from BES and the Office of Science and Technology Policy (OSTP).

Significant Accomplishments
Physical construction of six new buildings has been completed for the five NSRCs, the initial complement of technical equipment has been successfully installed and commissioned, and all five facilities entered full user operations between FY 2006 and FY 2008. All five had robust pre-operations "jump-start" user programs in which existing capabilities of the host laboratories were made available to outside users as a prelude to operations of the NSRCs themselves. Hundreds of user proposals were accommodated during this period, leading to substantial advances in a number of areas; a few examples include the development and application of methods for the controlled synthesis of hollow or filled nanospheres; new insights on charge transport within two-dimensional and quasi-one-dimensional nanocrystal arrays; and the development of modular microlaboratories that facilitate sophisticated, reproducible measurement of the behavior and properties of nanomaterials. In the operations phase of the NSRCs, user activity has picked up accordingly, with nearly 800 unique users in FY 2007 for the four centers that had operations funding that year. Currently, the facilities have increased substantially their user base and new and exciting discoveries have emerged. Research highlights include the DNA-mediated crystallization of nanoparticle arrays into three-dimensional ordered structures; the production of hollow protein nanotubes by self-assembly of surface-modified hexameric ring structures; the deposition of metallic nanoparticles on a preapplied film of carbon nanotubes on plastic to create flexible hydrogen sensors; potential on-off switch for nano-electronics using mechanically controlled conductance of a single-molecule junction; improved hybrid solar cells via *in situ* ultra-violet polymerization.

Mission Relevance
A part of the mission of the Office of Science is to "deliver the premier tools of science to our Nation's research enterprise." The NSRCs join the suite of major DOE user facilities that fulfill this objective. A seminal DOE-BES workshop and subsequent report on *Basic Research Needs to Assure a Secure Energy Future* cited nanoscience as a critical cross-cutting theme, and this has been reiterated in numerous follow-up reports on Basic Research Needs for specific focused

aspects of energy research, such as the hydrogen economy, solar energy utilization, and solid-state lighting. In addition, BES and the NSTC co-sponsored a major workshop and report on *Nanoscience Research for Energy Needs* that identified key research targets and foundational themes for energy-related nanoscience. As stated in the Executive Summary of that report, "At the root of the opportunities provided by nanoscience to enhance our energy security is the fact that all of the elementary steps of energy conversion (e.g., charge transfer, molecular rearrangement, chemical reactions, etc.) take place on the nanoscale."

Scientific Challenges

Strategic investments in scientific areas of opportunity are necessary to help our nation develop a balanced research and development infrastructure, advance critical research areas, and nurture the scientific and technical workforce of the 21st century. Nanotechnology R&D is a top federal priority with broad potential implications for the nation's competitiveness. DOE's participation in this effort includes the development and operation of the NSRCs, whose goals include: (1) to attain a fundamental scientific understanding of nanoscale phenomena, particularly collective phenomena; (2) to achieve the ability to design and synthesize materials at the atomic level to produce materials with desired properties and functions; (3) to take full advantage of other existing major user facilities, and (4) to develop experimental characterization techniques and theory/modeling/simulation tools necessary to drive the nanoscale revolution.

There are a large number of specific scientific challenges, many of which benefit from the collocation of disparate disciplines in order to fabricate, assemble, and otherwise manipulate nanosized components. One of the most challenging scientific problems is interfacing hard and soft matter, i.e., the world of electronic and structural materials with the world of biomaterials. These centers employ advanced experimental and theoretical tools to tailor and control the functionality (e.g., detection ability and sensitivity), compatibility, performance, and integration of materials at such interfaces.

Projected Program Evolution

The NSRCs have completed the transition to standard user operations within the new facilities and with their initial suite of specialized technical equipment. This process brought major new resources on-line for users, including nanoprobe beamlines at synchrotron radiation sources, extensive cleanroom facilities, nanoscale electron beam writers, and extensive nanomaterials synthesis and assembly capabilities. User programs are adapting to respond to the needs of the community, with targeted acquisitions of new capital equipment and allocation of staff and accompanying resources to those areas that are most in demand. While a substantial user base is established already, the NSRCs are still being assimilated into the national scientific infrastructure; there will continue to be an increase in submitted proposals with a corresponding increase in users and/or corresponding decrease in the proposal approval rate, until a steady state is reached. The NSRCs are expected to perform as world-leading institutions, excelling both in scientific impact and productivity and in working with users. These are the fundamental criteria for evaluation of the NSRC facilities; each has undergone an initial (baseline) operations review and subsequent reviews will follow triennially.

Electron-beam Microcharacterization Centers

Portfolio Description

This activity supports three electron-beam microcharacterization centers, which operate as user facilities, work to develop next-generation electron-beam instrumentation, and conduct corresponding research. These centers are the Electron Microscopy Center for Materials Research at Argonne National Laboratory (ANL), the National Center for Electron Microscopy at Lawrence Berkeley National Laboratory (LBNL), and the Shared Research Equipment program at Oak Ridge National Laboratory (ORNL). Operating funds are provided to enable expert scientific interaction and technical support and to administer a robust user program at these facilities, which are made available to all researchers with access determined via peer review of brief proposals. Capital equipment funding is provided for instruments such as scanning, transmission, and scanning transmission electron microscopes; atom probes and related field ion instruments; related surface characterization apparatus and scanning probe microscopes; and/or ancillary tools such as spectrometers, detectors, and advanced sample preparation equipment.

Unique Aspects

Electron probes are ideal for investigating local structure and chemistry in materials because of their strong interactions with atomic nuclei and bound electrons, allowing signal collection from small numbers of atoms–or, in certain cases, just one. Furthermore, the use of these charged particles allows electromagnetic control and lensing of electron beams resulting in spatial resolution that can approach single atomic separations or better (i.e., approaching or exceeding 0.1 nm; the world-leading Transmission Electron Aberration-corrected Microscope (TEAM) instrument at NCEM is capable of 0.05 nm direct spatial resolution). The BES electron-beam characterization user facilities provide unparalleled access to specialized equipment and expert staff and develop next-generation instrumentation and characterization techniques. They make these capabilities available to the scientific community on the basis of submitted proposals and at no cost to non-proprietary users, and are the only facilities of this type focused on electron-beam characterization that are available in the nation.

Relationship to Others

These activities couple with many others in BES programs and enable a broad range of research across numerous fields, including physics, chemistry, and materials science, within national laboratory programs as well as for academic and other scientists. The most direct relationship is with the BES Electron and Scanning Probe Microscopies research program; operation of the Electron Beam Microcharacterization Centers was part of this program, then referred to as Structure and Composition of Materials, prior to FY 2007. There are also strong interactions with other BES user facilities, particularly with the collocated Nanoscale Science Research Centers. The electron beam centers support use by researchers funded by BES, by other parts of the Office of Science, by other parts of the Department of Energy, and by numerous other federal agencies as well as industry.

Significant Accomplishments

Major historical accomplishments for the electron-beam characterization centers have spanned instrumental improvements in resolution and other performance measures, development of unique capabilities, and outstanding scientific results. This includes the development and operation of the Atomic Resolution Microscope (in the early 1980s) and One-Ångstrom Microscope (in the late 1990s) at NCEM, followed by the multi-laboratory project to create the TEAM instrument (completed in 2009); all constituted world-leading instruments in demonstrated lateral spatial resolution. Extensive in-situ work and new technique development, including real-time observation of radiation damage in materials and the demonstration of scanning confocal electron microscopy, has been carried out using unique facilities at EMC. The SHaRE program has emphasized chemical identification and spectroscopy, with notable achievements in pinpointing the elemental segregation phenomena leading to brittleness or toughening behavior at ceramic interfaces and in developing and using novel methods and tools such as atom location by channeling-enhanced microanalysis (ALCHEMI) and the laser-assisted local electrode atom probe (Laser LEAP). Recent advances across this suite of facilities have included detection of picometer-scale strain relaxation in magnetic nanoparticles leading to core-shell segregation and catalytic surface activity, and development of new approaches to characterize magnetic spins and other properties at higher spatial resolution than was previously possible.

Mission Relevance

Electron scattering allows the capture of meaningful signals from very small amounts of material, including single atoms under some circumstances. Electron beam characterization therefore provides unsurpassed spatial resolution and the ability to simultaneously get structural, chemical, and other types of information from sub-nanometer regions, allowing study of the fundamental mechanisms of catalysis, energy conversion, corrosion, charge transfer, magnetic behavior, and many other processes. All of these are fundamental to understanding and improving materials for energy applications and the associated physical characteristics and changes that govern performance.

Scientific Challenges

A wide variety of major scientific challenges that could be uniquely or most effectively addressed by electron scattering methods have been delineated in workshops on future science needs and opportunities for the field, including broad BES-sponsored workshops and facility-driven meetings focused on the TEAM project, in-situ approaches, soft matter and soft/hard interface characterization, and other topics. These challenges include:

- Investigating synthesis and assembly of nanomaterials
- Clarifying size effects on thermodynamic properties of nanostructures
- Direct comparison of theory and experiment at the nanoscale through the determination of the three-dimensional atomic-scale structure of nanostructures
- Determining the nanoscale origins of macroscopic properties, such as strength and conductivity, for high-performance materials ranging from those used in structural applications to those used in microelectronics
- Understanding the roles of individual atoms, point defects, and dopants in materials, such as in GaN for solid-state lighting or the role of oxygen in high-temperature superconductivity

- Characterization of interfaces in materials at arbitrary orientations, between ordered and disordered materials, and at hard/soft interfaces and phase boundaries
- Mapping of electromagnetic (EM) fields in and around nanoscale matter, including the atomic-scale origins of magnetism at the nanoscale
- Probing structures in their native environments, including atomic-scale investigation of functioning catalysts, corrosion processes, oxidation, biomaterials, and organic-inorganic interfaces
- Explaining the behavior of matter far from equilibrium, such as dynamic/transient behavior and environments involving high radiation, pressure, or temperature
- Development of tools to probe soft and biological matter without damaging/destroying samples

Projected Program Evolution

Full user operations are expected to continue at all three of these facilities, which are routinely available to users during normal working hours. The Transmission Electron Aberration Corrected Microscope (TEAM) instrument at the National Center for Electron Microscopy at LBNL will, in addition, be available to the research community for extended hours. This instrument was developed as a DOE Major Item of Equipment project and completed in FY 2009. It leads the world in spatial resolution and embodies the first chromatic aberration corrector in an instrument of this kind, and thus its availability opens new frontiers in imaging of materials on the nanoscale for the broad scientific community. Further program evolution will be driven by the scientific challenges described above and will require corresponding instrumental and technique improvements including work on in-situ environments; advanced electron, photon, and x-ray detectors; better temporal resolution; improved and specialized electron sources; electron optical configurations designed for interrogating materials under multiple excitation processes; and community software tools including virtualized instruments and improvements in remote operation.

Accelerator and Detector Research

Portfolio Description

This activity supports basic research in accelerator physics and x-ray and neutron detectors. Accelerator research is the corner stone for the development of new technologies that will improve performance of light sources and neutron spallation facilities. The research explores new areas of science and technologies that will facilitate the construction of next generation accelerator-based user facilities. The program is investing aggressively in research leading to a new and more efficient generation of photon and neutron detectors, an overlooked but crucial component in the optimal utilization of the provided beam. Research includes studies on creating, manipulating, transporting, and diagnosing ultra-high brightness beam behavior from its origin at a photocathode to propagation through undulators. Studies on achieving sub-femtosecond (hundreds of attoseconds) free electron laser (FEL) pulses are also undertaken. Demonstration experiments are being pursued in advanced FEL seeding techniques, such as echo-enhanced harmonic generation and other optical manipulations, to reduce the cost and complexity of seeding harmonic generation FELs. Theoretical and experimental studies on collective electron effects, such as micro-bunch instabilities from coherent synchrotron and edge radiation, and development of beam bunching techniques, such as magnetic compression or velocity bunching, are supported. Research on fast instruments to determine the structure of femtosecond electron bunches, and detectors capable of acquiring x-ray and neutron scattering data at very high collection rates are also promoted.

Unique Aspects

Technological advances demanded by novel and improved sources of energy require new material and chemical processes possible only through a fundamental understanding and characterization of the structure and dynamics of matter at the molecular and atomic levels. The necessary tools enabling control and observation of the temporal evolution of electrons, atoms and chemical reactions demand machines capable of producing high-brightness, high duty-factor, and short beam pulses. This research activity seeks to develop concepts to enable the new machines. The accelerator and detector research carried out by the program aims to improve the output and capabilities of synchrotron radiation light sources and the neutron scattering experiments at facilities that are the most advanced of their kind in the world. Together, they serve more than 11,000 users annually from academia, Department of Energy (DOE) national laboratories, and industry. The number of users has more than tripled in the past decade and may more than double again in the next decade as current facilities and those under construction are fully instrumented. These light sources and neutron scattering sources represent the largest collection of such facilities operated by a single organization in the world.

Relationship to Other Programs

The Accelerator and Detector R&D program strongly interacts with BES programmatic research that uses synchrotron and neutron sources. This includes research in atomic physics, condensed matter and materials physics, chemical dynamics, catalysis, geosciences, high-pressure science, environmental sciences, engineering, biosciences, and much more. There is an ongoing collaboration with the Advanced Scientific Computing Research (ASCR) to support code development relevant to beam dynamics. The activity also interacts with other DOE offices, especially in the funding of capabilities whose cost and complexity require shared support. The Brookhaven National Laboratory Advanced Test Facility (ATF) is jointly funded by the High Energy Physics Program and BES. There is also collaboration with the National Science

Foundation (NSF) on machine physicsresearch, and a coordinated effort between DOE and NSF to facilitate the development of x-ray detectors. There are ongoing industrial interactions through DOE Small Business Innovation Research and Small Business Technology Transfer (SBIR/STTR) Program awards for the development of advanced accelerator technology and x-ray detectors.

Significant Accomplishments

This activity has been a major supporter of theoretical and experimental studies that led to the realization of the brightest light source available, the Linear Coherent Light Source (LCLS). Theoretical and simulation studies supported by the activity have addressed many of the fundamental physics questions concerning Self-Amplified Spontaneous Emission (SASE) FELs and high-brightness beam leading to remarkably successful experiments and the demonstration that high peak beam brightness is possible with a very low average current, as realized at LCLS. Bunch compression and coherent radiation studies at ATF using a chicane have led to the first observation of multi-Tera Hertz (THz) coherent edge radiation. Measurements of phase space distortions from acceleration fields have been carried out and are a basis for FEL bunch length diagnostics. A holographic THz Fourier transform spectrometer test bed at the Jefferson Laboratory FEL facility was completed, the first required step for developing a single shot device to completely characterize bunch shapes. Tests have shown very satisfactory results on the development of an advanced ^{3}He neutron detector prototype that is capable of measuring pulse height distributions with the highest energy resolution in this mode. The latter is an example of research relevant to neutron scattering facilities, in particular to the Spallation Neutron Source (SNS). Gigabyte per second data rates will be achievable that will provide neutron imaging with position resolution less than 1 mm, very high throughput, and the capability to cover large areas as required by many neutron source instruments. A proof-of-principle demonstration of Echo-Enabled Harmonic Generation is being carried at the SLAC National Accelerator Laboratory, whereby high harmonics of the original beam are generated by beam manipulations that produce high up frequency conversion and relatively small energy modulation. The resulting beam can generate a fully coherent and short wavelength FEL radiation, and the scheme has the potential to enhance greatly the performance of FEL machines while reducing their cost. The program sponsors the development of high-gradient Super Conducting RF accelerating structures that capable of handling high average beam current required by high-average brightness beams featuring harmonic damping of higher order modes to avoid beam breakup and degradation of beam quality, and optimized performance with respect to RF, cryogenics, and cryostat engineering to minimize costs. A program is underway that explores the application of 3-D techniques to the difficult problem of integrating X-ray sensors of high-resistivity silicon and readout Application Specific Integrated Circuits of low-resistivity silicon. If successful, these sensors will be capable of handling synchrotron radiation at energies up to 100 keV and high energy resolution. As part of our goal to encourage the development of photocathode guns capable of generating low-emittance beams at high repetition rates a normal conducting Very High Frequency (VHF) electron gun is being built under the specifications of repetition rates up to 1 MHz, small beam size, variable bunch length for controlling space charge effects, and capable of high charge per bunch. The program also sponsors five Young Career award recipients associated with four DOE laboratories and one university, and three Presidential Early Career Award Scientists and Engineers (PECASE) recipients.

Mission Relevance

The Accelerator and Detector R&D program supports the most fundamental of research needs, i.e., the need to characterize and control materials at the atomic and molecular level. In order to understand, predict, and ultimately control materials properties, it is necessary to determine the atomic constituents of materials, the positions of the atoms in materials, and how the materials behave under the influence of external perturbations such as temperature, pressure, chemical attack, and excitation by photons, electrons, and other particles. The activity seeks to develop new concepts in accelerator science to be used in the design of accelerator facilities for synchrotron radiation and spallation neutron sources that will provide the means necessary to achieve a fundamental understanding of the behavior of materials. Also supported is the development of detectors capable of acquiring data several orders of magnitude faster than the state-of-the-art detectors in order to exploit fully the fluxes delivered by the new facilities.

Scientific Challenges

- Development of new accelerator concepts crucial to the design and upgrade of synchrotron light sources and neutron scattering facilities.
- Start-to-end simulations of the SASE electron source, transport, and SASE FEL will give details of the physics mechanisms and provide benchmark models for x-ray FELs.
- Experimental studies must be conducted on the creation and transport of ultra-high brightness electron beams to drive SASE photons.
- New detectors must be developed that are capable of using the high data rates associated with high brightness sources thus increasing beamline efficiencies and user throughput.
- Detectors must also be developed that are capable of acquisition of all required x-ray data from a single femtosecond LCLS pulse.
- Development of injector capable of delivering high peak current, low transverse emittance, and high-repetition rate required by next generation light sources.
- Comprehensive study of cathode materials of good quantum efficiency and low intrinsic emittance.
- Special emphasis in R&D leading to more energy efficient machines and devices that go beyond the most common methods of particle acceleration that are in general not optimized for electric power utilization.

Projected Evolution

X-ray and neutron scattering will continue to play a central role in the growth of BES programmatic science. SNS will be for years to come the most powerful neutron spallation source in the world. It is important to be prepared for full use and judicious increases in the capabilities of the SNS as recommended by all advisory committees to DOE. The peak brightness of the LCLS is 10 orders of magnitude greater than current synchrotrons; the light is coherent or “laser like” enabling many new types of experiments; and the pulses are short (70 femtoseconds in standard operation, with planned improvements that will further reduce the pulse length) enabling studies of fast chemical and physical processes. These facilities will need continuous growth in terms of accelerator upgrades, and x-ray and neutron detectors capable of fully exploiting their high fluxes and brightness.

Two major components will be required for the advancement of material science: the production of photon beams with increased average flux and brightness and the detection tools capable of responding to the high photon beam intensity. The first component will require higher repetition rate photocathode guns and RF systems, and photon beams of enhanced temporal coherence, such as produced by improved seeding techniques or X-ray oscillators, in the case of free-electron lasers, or high brightness injectors with enhanced beam manipulation capabilities, in the case of energy recovery linacs. Detectors will require higher computational capabilities per pixel, improved readout rates, radiation hardness, and better energy and temporal resolutions. Additionally, R&D will be required to produce ultrafast beam instrumentation capable of measuring accurately femto and attosecond bunch lengths, and photon optics bandwidth. R&D will also be needed to explore cross-cutting technologies for laser generating EUV/XUV radiation, laser-plasma accelerators offering compact electron sources and extremely high accelerating fields, and laser-driven vacuum structures capable of ultrafast time scales and Terawatt peak power. Higher neutron flux capabilities at the Spallation Neutron Source will demand high intensity H^{-} currents, possibly provided by the development of high power and high frequency lasers, and detectors designed for advanced neutron imaging with very high throughput. The community has indicated the need for shared test facilities of comprehensive general purpose where different approaches and architectures can be demonstrated at lower cost and more efficiency than specific test beds at every institution. Finally, R&D emphasizing energy efficient machines and strong collaborations among the national laboratories and laboratories and universities will allow a cost-effective, coordinated, and interdisciplinary approach to research and development in accelerators and detectors.

Atomic, Molecular, and Optical Sciences

Portfolio Description

This activity supports theory and experiments to understand structural and dynamical properties of atoms, molecules, and nanostructures. The research emphasizes the fundamental interactions of these systems with photons and electrons to characterize and control their behavior. These efforts aim to develop accurate quantum mechanical descriptions of properties and dynamical processes of atoms, molecules, and nanoscale matter. The study of energy transfer within isolated molecules provides the foundation for understanding chemical reactivity, i.e., the process of energy transfer to ultimately make and break chemical bonds. Topics include the development and application of novel, ultrafast optical probes of matter, particularly x-ray sources; the interactions of atoms and molecules with intense electromagnetic fields; and studies of collisions and many-body cooperative interactions of atomic and molecular systems, including ultracold atomic and molecular gases. Capital equipment funding is provided for items such as lasers and optical equipment, unique ion sources or traps, position-sensitive and solid-state detectors, control and data processing electronics, and computational resources.

Unique Aspects

The knowledge and techniques developed by investigators in the AMOS program are critical components of the fundamental science effort of the Department of Energy (DOE), and research conducted at BES user facilities. The results of this research have applicability in a wide array of science and technology. The AMOS activity provides new ways to control and probe interactions in the gas and condensed phases, enhances our ability to understand materials, and enables full exploitation of the BES x-ray sources and Nanoscale Science Research Centers (NSRCs). This enabling aspect will continue to be emphasized, particularly with respect to research involving the generation and application of ultrafast, intense x-ray pulses at Lawrence Berkeley National Laboratory (LBNL) at the Advanced Light Source (ALS) and the Ultrafast X-ray Science Laboratory (UXSL); at Argonne National Laboratory (ANL) at the Advanced Photon Source (APS); and at SLAC National Accelerator Laboratory (SLAC) at the Linac Coherent Light Source (LCLS) and the PULSE Institute for Ultrafast Energy Science (PULSE). AMOS is a major supporter of synchrotron-based AMO science in the United States, and continues its role as the principal U.S. supporter of research into the properties and interactions of atomic and molecular ions relevant to fusion plasmas.

Relationship to Other Programs

The AMOS program supports experiments concerning x-ray characterization and AMO science at the LCLS at SLAC, in coordination with the BES Scientific User Facilities Division. The program funds research at the PULSE Institute for Ultrafast Energy Science at SLAC, which is co-supported by the BES Materials Sciences and Engineering Division. Numerous complementary relationships exist between AMOS program elements and other core research activities across the BES Chemical Sciences, Geosciences, and Biosciences Division. Fundamental insight and data obtained in the AMOS activity are relevant to Office of Fusion Energy Sciences (FES) programs to provide atomic and molecular data for fusion modeling and basic plasma physics. This synergy is notable at the Multicharged Ion Research Facility (MIRF) at Oak Ridge National Laboratory (ORNL), which is co-funded by BES and FES. A close working relationship exists with the National Science Foundation (NSF) Atomic Molecular and Optical Physics Program. These two programs co-funded the National Academy of Sciences/National Research Center Physics Decadal Survey, *AMO 2010: An Assessment of and*

Outlook for Atomic, Molecular, and Optical Science, and co-fund the National Academy of Sciences Committee on Atomic, Molecular, and Optical Sciences (CAMOS). In FY 2008, the AMOS Program provided partial support for the Gordon conference on Multiphoton Processes and the American Conference on Theoretical Chemistry (ACTC). In 2009, the Program provided partial support for the Attosecond Physics meeting at Kansas State University, and the Materials Research Society (MRS) Symposium on Ultrafast Materials Sciences.

Significant Accomplishments

The AMOS activity has been a major U.S. supporter of experimental and theoretical studies of the fundamental properties of atoms, ions, and small molecules and of collision interactions between atoms, ions, molecules, and surfaces. This has produced a vast knowledge base, with a broad impact on science and technology. It has led to the development of powerful new methods for momentum imaging of collision fragments that have seen wide application in atomic, molecular, and chemical physics. This knowledge is being used to control the quantum behavior of atoms and molecules and has propelled further development and scientific applications of ultrafast x-ray sources using table-top lasers and 3rd generation synchrotrons (ALS and APS). Enhanced high-harmonic generation and fundamental interactions of intense controlled laser fields with atoms and small molecules leading to ionization and fragmentation have been explored in great detail. Recent efforts involving high-field interactions, ultrafast processes, and ultrashort x-ray pulses are creating the science base required for research at 4th generation light sources such as the LCLS. X-ray pulses with durations of femtoseconds can produce stop-action pictures of the motion of atoms during molecular transformations. New sources, with pulses of attosecond duration enable imaging of the real-time motion of electrons during the course of chemical reactions. Recent progress has been reported in the generation of ultrashort x-ray pulses from table-top, laser-based sources that provide complementary capabilities to x-ray free electron lasers. In one example, high harmonic generation in gases has been used to shift laser light from the infrared or visible to extreme-ultraviolet or soft x-ray wavelengths. Optical manipulation of the harmonics has been used to produce isolated XUV (extreme ultraviolet) pulses as short as 100 attoseconds in duration. Theorists suggested a method to use intense, ultrafast laser pulses to make a gas transparent to x-rays for the duration of the laser pulse. This prediction has been verified in experiments at the ultrafast slicing source at the ALS. This method may find application as an ultrafast switch to slice a femtosecond pulse from a much longer x-ray pulse. Recognition of international scientific leadership by AMOS-sponsored investigators include MacArthur, Rabi, Goeppert-Mayer, Davisson-Germer awards, American Physical Society Fellowships, and National Academy memberships.

Mission Relevance

The knowledge and techniques produced by this activity form a science base that underpins several aspects of the DOE mission. New methods for using photons, electrons, and ions to probe matter lead to more effective use of BES synchrotron, nanoscience, and microcharacterization facilities. Similarly, the study of formation and evolution of energized states in atoms, molecules, and nanostructures provides a fundamental basis for understanding elementary processes in solar energy conversion and radiation-induced chemistry.

Scientific Challenges

In recent years, AMO science has transformed from a field in which the fundamental interactions of atoms, molecules, photons, and electrons are probed to one in which they are controlled. Systems studied are increasingly complex, and exhibit highly correlated, non-perturbative interactions. AMOS scientists can shape the quantum mechanical wave functions of atoms and small molecules using controllable laser fields, trap and cool atoms and molecules to temperatures near absolute zero, create nanoscale structures that manifest novel light-matter interactions and properties, and coherently drive electrons to generate ultrafast x-ray pulses. Theoretical advances are enabling modeling and simulation of increasingly complex systems to provide interpretation of existing data, and predictions for new experiments. These capabilities create opportunities to investigate chemical processes under conditions that are far from equilibrium, where complex phenomena are predominant and controllable, and on ultrafast timescales commensurate with the motions of atoms and electrons. Research in AMO science is fundamental to meeting the grand challenges for basic energy sciences, as identified in the report from the Basic Energy Sciences Advisory Committee: *Directing Matter and Energy: Five Challenges for Science and the Imagination.*

Projected Evolution

The AMOS activity will continue to support science that advances DOE and BES mission priorities. Closely related experimental and theoretical efforts will be encouraged. AMOS will continue to have a prominent role at BES facilities in understanding the interaction of intense, ultrashort x-ray pulses with matter and in the control and investigation of ultrafast light-matter interactions. Key targets for greater investment include: ultrafast electron diffraction; attosecond physics with phase-controlled pulses; electron-driven processes; quantum control of molecular processes; nonlinear optics relevant to generating ultrafast, short wavelength pulses; and nanoscale physics.

The program will emphasize ultrafast, ultra-intense, short-wavelength science. The development and application of novel x-ray light sources using synchrotrons or table-top lasers will continue. Topics of interest include the use of high-harmonic generation or its variants as soft x-ray sources, development and characterization of femtosecond and attosecond pulses of x-rays at existing synchrotrons as well as new accelerator-based and table-top sources. Applications of these light sources include ultrafast imaging of chemical reactions, diffraction from aligned molecules, and atomic and molecular inner-shell photoionization. Coherent control of nonlinear optical processes and tailoring quantum mechanical wave functions with lasers will continue, particularly in chemical systems. Fundamental studies of atomic and molecular ions and their interactions with atoms, molecules, and surfaces will further develop the knowledge base vital to understanding fusion plasmas. Experimental and theoretical AMOS tools will be used in the study of low-energy electron-molecule interactions in the gas and condensed phases, and collisions of ultracold molecules.

Chemical Physics Research

Portfolio Description

This activity supports experimental and theoretical investigations in the gas phase, condensed phase, and at interfaces aimed at elucidating the molecular-scale chemical and physical properties and interactions that govern chemical reactivity, solute/solvent structure, and transport. New opportunities to attain predictive understanding of chemical reactivity are also supported, including structural and dynamical studies that emphasize a complete understanding of reactive chemistry at full quantum detail. These activities include the development and implementation of predictive computational modeling and simulation approaches, incorporating advanced theory and experimental validation, for scientific discovery across multiple scales. The impact on DOE missions is far reaching, including energy utilization, catalytic and separation processes, energy storage, and environmental chemical and transport processes.

The Chemical Physics portfolio comprises three program areas: (1) Gas Phase Chemical Physics (GPCP), (2) Condensed Phase and Interfacial Molecular Science (CPIMS), and (3) Computational and Theoretical Chemistry (CTC):

- Gas Phase Chemical Physics (GPCP) research emphasizes studies of the dynamics and rates of chemical reactions at energies characteristic of combustion, and the chemical and physical properties of key combustion intermediates. The overall aim is the development of a fundamental understanding of chemical reactivity enabling validated theories, models and computational tools for predicting rates, products, and dynamics of chemical processes involved in energy utilization by combustion devices. Important to this aim is also the development of experimental tools for discovery of fundamental dynamics and processes affecting chemical reactivity. Combustion models using this input are developed that incorporate complex chemistry with the turbulent flow and energy transport characteristics of real combustion processes.
- Condensed Phase and Interfacial Molecular Science (CPIMS) research emphasizes molecular understanding of chemical, physical, and electron-driven processes in aqueous media and at interfaces. Studies of reaction dynamics at well-characterized metal and metal-oxide surfaces and clusters lead to the development of theories on the molecular origins of surface-mediated catalysis and heterogeneous chemistry. Studies of model condensed-phase systems target first-principles understandings of molecular reactivity and dynamical processes in solution and at interfaces. The approach confronts the transition from molecular-scale chemistry to collective phenomena in complex systems, such as the effects of solvation on chemical structure and reactivity.
- Research in Computational and Theoretical Chemistry (CTC) emphasizes integration and development of new and existing theoretical and computational approaches for the accurate and efficient description of processes relevant to the BES mission. Supported efforts are tightly integrated with the research and goals of the CPIMS and GPCP programs and many have wider crosscutting relevance, advancing goals of other BES chemistry, biochemistry and geochemistry programs. Common to all of these areas is the need for new approaches that go beyond standard representations to address excited-state dynamics, the inclusion of spin-dependent effects, the ability to model extremely anharmonic processes, and the ability to account for all types of energy exchange between various degrees of freedom. Also of

interest are methods that will advance modeling of weakly-bound systems and systems interacting with both polar and nonpolar solvents and/or environments.

Unique Aspects

The BES Chemical Physics Research activity is unique in its long term support of a number of fundamental chemical science areas, and in its integration of capabilities from research universities and DOE national laboratories that sustain long-term progress in difficult scientific areas as well as effective coupling to DOE missions:

- Through the GPCP program, DOE is the principal supporter of high-temperature chemical kinetics and gas-phase chemical reaction dynamics in the nation. This activity also has oversight for several national laboratory programs, including the Combustion Research Facility (CRF), a unique, multi-investigator research laboratory that have a strong collaborative visitor program and that promotes synergism between BES-supported basic research and the applied science and technology programs supported the Office of Energy Efficiency and Renewable Energy (EERE) and industry.
- The CPIMS program is unique is its relevance to DOE mission areas, providing a fundamental basis for understanding chemical reactivity in complex systems, such as those encountered in catalysis, energy storage, separations, and the environmental contaminant transport in mineral and aqueous environments. This program is a major supporter of basic research on chemical reactivity of molecular species in the liquid phase, on metal clusters, and at solid-gas and solid-liquid interfaces. Fundamental studies of reactive processes driven by radiolysis in condensed phases and at interfaces provide improved understanding of radiolysis effects and radiation-driven chemistry in nuclear fuel and waste environments.
- The CTC program is not a separate program but rather it is fully integrated with other BES research activities, contributing principally to the GPCP and CPIMS elements of the Chemical Physics portfolio, but also providing significant support to efforts spanning BES chemistry, biochemistry and geochemistry research. A unique component of this program is its support for extremely complex research that requires simultaneous development of theoretical and massively parallel computational implementation.

Relationship to Other Programs

Research under this activity complements research supported across the Office of Basic Energy Sciences, including Catalysis Science, Separations and Analysis, Heavy Element Chemistry, Atomic and Molecular Optical Science, Solar Photochemistry, and Geosciences. There is a particularly strong coupling between the CPIMS and Solar Photochemistry programs in the fundamental chemistry and physics of radiolytic processes in condensed media and at interfaces. The CTC program co-funds efforts with the Office of Advanced Scientific Computing Research (ASCR) where appropriate for the BES and ASCR missions, and has supported a number of Scientific Discovery through Advanced Computing (SciDAC) efforts. There are numerous linkages with combustion research conducted under various research programs within DOE EERE and DOE FE as well as combustion-related chemical physics research conducted by the Air Force Office of Scientific Research (AFOSR), Office of Naval Research (ONR), Army Research Office (ARO), National Aeronautics and Space Administration (NASA), National Institute of Standards and Technology (NIST), and the National Science Foundation (NSF). These linkages include common PIs and industry relationships in a number of programs, as well as the couplings described above fostered by the CRF. This activity provides substantial support for basic research to scientists at PNNL who utilize the William R. Riley Environmental Molecular Sciences Laboratory (EMSL), a national user facility operated by the DOE/SC Office of Biological and Environmental Research (BER). Experiments concerning ultrafast chemical imaging are supported at the Center for Nanoscale Materials at Argonne National Laboratory in coordination with the BES Scientific User Facilities Division. In FY 2009, support was provided for the following Gordon conferences: Dynamics at Surfaces, Time-Resolved Vibrational Spectroscopy, Electronic Spectroscopy and Dynamics, and Laser Diagnostics in Combustion. In FY 2010, support was provided for the Gordon conferences on Water Aqueous Solutions and Radiation Chemistry.

Significant Accomplishments
Impacts in fundamental science include the development of crossed molecular beams and ion imaging techniques that have spawned a generation of experiments in state-to-state chemical reaction dynamics and energy transfer, much of which has been supported by the chemical physics program. In addition, support from this activity resulted in the development of molecular beam and laser sputtering techniques for the study of atomic clusters as prototypical models for catalysis. More recently, ultrafast laser spectroscopy has provided important insights into hydrogen bonding and proton transport in water in nano-confined geometries. Support has yielded for the first time a conclusive link between the size of catalytic particles on a surface, the particle electronic properties, and the ability of particles to speed chemical reactions. Furthermore, recent advances in low-temperature scanning tunneling microscopy (STM) have been combined with temporally and spatially resolved spectroscopic tools such as ultrafast, two-photon photoemission, resulting in the discovery of long-lived electronic surface states that could lead to new ways to induce and control electronic excitation at surfaces, and have yielded an unprecedented view of the coupling of electronic and vibrational motion within a single molecule. Advanced probes of combustion environments have also yielded recent discoveries, such as the direct observation of reactions important in incipient soot formation and the recent discovery of the importance of enols in flame chemistry. This activity has played a major role in the development of quantum chemistry methodologies for accurate predictions of chemical properties. Advances in high resolution time-resolved spectroscopy have yielded information on intermediates and product state distributions with unprecedented isomeric specificity. These developments have led to theories and computer codes for the calculation of thermodynamic properties and chemical reaction rates in the gas phase as well as the properties of complex molecular systems in the condensed phase.

Mission Relevance
- The gas-phase portion of this activity contributes strongly to the DOE mission in the area of the efficient and clean combustion of fuels. The coupling of complex chemistry and turbulent flow has long challenged predictive combustion modeling. Truly predictive combustion models enable the design of new combustion devices (such as internal combustion engines, burners, and turbines) with maximum energy efficiency and minimal environmental consequences. In transportation, the changing composition of fuels, from those derived from light, sweet crude oil to biofuels and fuels from alternative fossil feedstocks puts increasing emphasis on the need for science-based design of modern engines.
- The condensed-phase and interfacial portions of this activity impacts a variety of mission areas by providing a fundamental basis for understanding chemical reactivity in complex

systems, such as those encountered in catalysis and environmental processes, along with activity that provides fundamental underpinnings relevant to energy production and storage. Surface-mediated chemistry research in this activity complements more directed efforts in heterogeneous catalysis. Condensed-phase and interfacial chemical physics research on dissolution, solvation, nucleation, separation, and reaction provides important fundamental knowledge relevant to the environmental contaminant transport in mineral and aqueous environments. Fundamental studies of reactive processes driven by radiolysis in condensed phases and at interfaces provide improved understanding of radiolysis effects in nuclear fuel and waste environments.

- The computational and theoretical portions of the portfolio aim to advance the Chemical Physics goals just described, and in addition to advance mission areas across the BES. For example, supported activates advance next-generation solar energy, sunlight-to-fuels, and energy storage concepts.

Scientific Challenges

Research in Chemical Physics is fundamental to meeting the grand challenges for basic energy sciences, as identified in the recent report on this topic from the Basic Energy Sciences Advisory Committee. Specific opportunities are to:

- Improve and expand experimental measurement of highly energetic, unstable molecules to diagnose complex reacting flows and, in more controlled environments, to determine molecular dynamics and reaction rates at elevated temperatures and pressures.
- Develop computational approaches of acceptable precision for the calculation of potential energy surfaces for ground and excited electronic states and their conical intersections for chemically important species including free radicals.
- Improve scaling with number of atoms to facilitate computation of properties and reactions of large molecules.
- Improve accuracy and throughput of methods for calculating chemical reaction rates from detailed chemical dynamics, including reactions without barriers for which statistical theories do not apply.
- Develop improved multiscale methods for dealing with systems exhibiting many orders of magnitude differences in spatial and temporal scales such as those found in turbulent combustion, catalysis, and condensed phase processes.
- Develop fundamental understanding of the mechanisms that underlie assembly of atoms into clusters and larger nanosystems for the rational design and synthesis of cluster-based nanoarchitectures with desired properties.
- Develop and apply new experimental methods for characterizing chemically active molecular scale structures and reaction mechanisms at interfaces.
- Characterize high-energy electron- and photon-stimulated processes at complex interfaces.
- Design quantitative models for condensed-phase solvation that include polarization, charge-transfer, and nano-confinement effects.
- Develop new theoretical time-domain and frequency-domain simulation tools for computing structural, transport, and optical properties of nanoscale systems.
- Develop methods to computationally determine how to externally control energy-, charge- and matter- transfer processes in chemical and molecular systems with low-energy sources of radiation or applied fields, small thermal swings, and/or relatively minor changes in the external environment.

- Determine how such energy exchange, even when rare, is accomplished through resonant, nonresonant and dissipative processes
- Develop a means that addresses the manifestation of these effects over many temporal and spatial scales

Projected Evolution

The focus of the chemical physics program is the development of a molecular-level understanding of gas-phase, condensed-phase, and interfacial chemical reactivity of importance to combustion, catalysis, energy conversion and storage, and environmental preservation. The desired evolution is to predictive capabilities that span the microscopic to macroscopic domains enabling the computation of individual molecular interactions as well as their role in complex, collective behavior in real-world devices. Currently, increased emphasis in gas-phase chemical physics is on validated theories and computational approaches for the structure, dynamics, and kinetics of open shell systems, experimental measurements of combustion reactions at high pressures, better insight into soot particle growth and an improved understanding of the interaction of chemistry with fluid dynamics. In surface chemistry, continued emphasis is on the development of a structural basis for gas/surface interactions, encouraging site-specific studies that measure local behavior at defined sites. At interfaces, emphasis is on aqueous systems and the role of solvents in mediating solute reactivity. Expanding into the future, plans are to enhance the use of computer-generated mechanisms and models in combustion science, broaden efforts to molecular building blocks of emerging fuels, probe the chemical physics of energy transfer in large molecules, to explore the molecular origins of condensed phase behavior and the nature and effects of non-covalent interactions including hydrogen bonding, and to investigate temporally resolved interfacial chemical dynamics and charge transfer using advances in chemical imaging. Computational and theoretical efforts will continue to expand in scope, to span BES mission-relevant research in chemical sciences, geosciences and biosciences, while at the same time remaining tightly integrated with these efforts. A continuing emphasis on DOE mission impact will guide the selection of research opportunities, development of predictive capabilities, and interactions with other programs and organizations.

Solar Photochemistry

Portfolio Description

This activity supports molecular-level research on solar energy capture and conversion in the condensed phase and at interfaces. These investigations of solar photochemical energy conversion focus on the elementary steps of light absorption, electrical charge generation, and charge transport within a number of chemical systems, including those with significant nanostructured composition. Supported research areas include organic and inorganic photochemistry and photocatalysis, photoinduced electron and energy transfer in the condensed phase and across interfaces, photoelectrochemistry, and artificial assemblies for charge separation and transport that mimic natural photosynthetic systems. This activity, with its integration of physical and synthetic scientists devoted to solar photochemistry, is unique to DOE. Capital equipment funding is provided for items such as ultrafast laser systems, scanning tunneling microscopes, fast Fourier transform infrared and Raman spectrometers, and computational resources.

The program provides funding for approximately 60 university grants supporting about 100 graduate students and postdoctoral research associates, and partially supporting about 80 faculty members. There are 10 programs at DOE national laboratories supporting about 25 senior staff and 30 graduate students and postdoctoral research associates. Programs at the laboratories are multi-investigator efforts on problems that require extensive participation by senior experienced scientists and postdoctoral associates. In photochemistry, major research groups are supported in inorganic photochemistry and electron transfer at Brookhaven National Laboratory (BNL); in photoelectrochemistry at the National Renewable Energy Laboratory (NREL), Notre Dame, and Pacific Northwest National Laboratory (PNNL); and in photosynthesis at Argonne National Laboratory (ANL) and Lawrence Berkeley National Laboratory (LBNL). Many of the research efforts at the DOE national laboratories involve strong collaborative interfaces with university and industrial communities. Research in radiation chemistry is centered at specialized electron pulse radiolysis facilities at Notre Dame and BNL.

Unique Aspects

This activity is the dominant supporter of solar photochemistry research in the United States. Solar photochemical energy conversion is an important long-range option for meeting future energy needs. Increasing worldwide demands for energy will need to be met with technologies such as solar photoconversion that do not produce greenhouse gases. An attractive alternative to semiconductor photovoltaic cells, solar photochemical and photoelectrochemical conversion processes produce fuels, chemicals, and electricity with minimal environmental impact and with closed renewable energy cycles. Artificial photosynthesis can be coupled to chemical reactions for generation of fuels such as hydrogen, methane, or complex hydrocarbons. The activity also provides unique support for radiation science via specialized electron pulse radiolysis facilities at Notre Dame and BNL, which serve the academic research community, industrial users, and other Department of Energy national laboratories. Research in radiation sciences investigates fundamental physical and chemical effects produced by the absorption of energy from ionizing radiation. Fundamental studies of radiation science are of importance in understanding chemical reactions that occur in radiation fields of nuclear reactors, including in their fuel and coolants, and in the processing, storage, and remediation of nuclear waste. Such understanding is required for effective nuclear waste remediation and for design of next-generation nuclear reactors that might employ special media, such as supercritical fluids as coolants. The radiation chemistry of ionic liquids is relevant to their use as fuel-cycle separation solvents.

Relationship to Other Programs

The solar photochemistry research effort interfaces with several activities in BES: Photosynthetic Systems activities in biochemical aspects of photosynthesis; Chemical Physics in theoretical calculations of excited states and computational modeling; Physical Biosciences and Catalysis Science in investigations of electron transfer reactions in homogeneous and microheterogeneous solutions and advanced catalytic materials; and the Materials Sciences and Engineering Division efforts in fundamental photovoltaics research. The research is relevant to the DOE Office of Energy Efficiency and Renewable Energy (EERE) activities in its Solar Energy Technologies Program on photovoltaics and its Fuel Cells Technologies Program.

The radiation sciences activity is closely coordinated with the BES Condensed Phase and Interfacial Molecular Sciences in the physical and chemical aspects of radiolysis. The radiation science effort also coordinates with BES Catalysis Science in reaction kinetics in homogeneous solutions, and Mechanical Behavior and Radiation Effects in radiolytic damage to glasses and radiation-induced corrosion of structural materials. There are also important interfaces with the DOE Office of Environmental Management activities in waste remediation and Office of Nuclear Energy activities on nuclear reactors, and nuclear waste processing and storage.

Significant Accomplishments

Research in Solar Photochemistry has made significant advances in the understanding and control of the fundamental processes for harvesting the energy from sunlight. These include the light harvesting of solar photons, the subsequent separation of charge through electron transfer, and the generation of electric power or the catalytic production of fuels. Many of these advances are a consequence of past investigations of model photosynthetic systems and an emulation of how they perform these functions. Researchers have discovered unexpected quantum coherence in energy transfer within the light absorbing antenna complexes of natural photosynthetic systems. This coherence enables the absorbed light to spread out and sample the physical space occupied by numbers of light absorbing molecules in order to find the right place for the reaction for electron transfer charge separation. In research on quantum dot nanoparticles, scientists have predicted and confirmed the generation of two electron hole pairs through the absorption of a single photon. Concepts such as these have led to a vision for a new generation of solar cells, labeled "third generation," that will exceed the Shockley-Queisser limit on the efficiency of present solar cells. In systems for artificial photosynthesis, investigators have developed molecular models for light to chemical energy conversion. This work has refined the models of electron transfer and charge transport in organic complexes that are the backbone of advances in organic and polymeric "plastic" solar cells. Advances in homogeneous catalysis of photo-induced water splitting have led to the synthesis of many dozen inorganic catalysts within the past several years where the preceding decades had produced only one. A new field of catalysis for photon driven fuel production has been created with the study of molecules located at solid surfaces where charge transfer can induce catalytic action by either the solid or the molecule. Many novel nanostructures of semiconductor electrodes have been developed for the photoelectrolysis of water.

Mission Relevance

Solar photochemical energy conversion is an important option for generating electricity and chemical fuels and therefore plays a vital role in DOE's development of solar energy as a viable component of the nation's energy supply. Photoelectrochemistry provides an alternative to semiconductor photovoltaic cells for electricity generation from sunlight using closed, renewable energy cycles. Solar photocatalysis, achieved by coupling artificial photosynthetic systems for light harvesting and charge transport with the appropriate electrochemistry, provides a direct route to the generation of fuels such as hydrogen, methane, and complex hydrocarbons. Fundamental concepts derived from studying highly efficient excited-state charge separation and transport in molecular assemblies is also applicable to future molecular optoelectronic device development. Radiation chemistry methods are of importance in solving problems in environmental waste management and remediation, nuclear energy production, and medical diagnosis and radiation therapy.

Scientific Challenges

The major challenges in solar photoconversion have been outlined in a BES workshop on *Basic Research Needs for Solar Energy Utilization*. Among these challenges, knowledge gained in charge separation and long-distance electron transfer needs to be applied in a meaningful way to activation of small molecules such as CO_2 and H_2O via photocatalytic cycles to transform them into fuels. The major scientific challenge for photoelectrochemical energy conversion is that small band gap semiconductors capable of absorbing solar photons are susceptible to oxidative degradation, whereas wide band gap semiconductors, which are resistant to oxidative degradation in aqueous media, absorb too little of the solar spectrum. Ongoing research activities include multibandgap, multilayer cascade-type semiconductors, photosensitized nanoparticulate solids, and the study of the mechanism of multiple exciton generation (MEG) within nanoparticles. Experimental and theoretical studies on photosynthetic pigment-protein antenna complexes should lead to advances in design of efficient and robust artificial light-collecting molecular assemblies. Computational chemistry methods incorporating recent advances in calculation of excited states should be developed and applied in design of photocatalysts and molecular dynamics simulations in artificial photosynthesis. There are also challenges in fundamental understanding of photoconversion processes – energy transfer and the generation, separation, and recombination of charge carriers – in organic-based molecular semiconductors, which could lead to a new type of inexpensive and flexible solar cell. Fundamental studies on photochemical reaction pathways offer opportunities for less energy intensive and more environmentally benign processing of specialty chemicals and high volume industrial intermediates.

A recent workshop on *Basic Research Needs for Advanced Nuclear Energy Systems* has identified new directions, connections, and roles for radiation chemistry in the nuclear energy systems of the future. A common theme is the need to explore radiolytic processes that occur across solid-liquid and solid-gas interfaces, where surface chemistry can be activated and changed by radiolysis. Solid-liquid interfaces abound in nuclear reactors and high level radioactive wastes. Colloidal particles participate in gas production, gas retention, and in organic degradation of high level wastes. A more fundamental understanding of radiolytic reactions in heterogeneous media is needed in order to predict and control radiation chemical transformations in complex environmental systems.

Projected Evolution

In solar photochemistry, an increased emphasis on solar water splitting will explore new semiconductor and molecular systems for photoconversion. Also of emphasis are new hybrid systems that feature molecular catalysis at surfaces and new nanoscale structures for the photochemical generation of fuels. Modern combinatorial techniques will broaden and accelerate the search for new semiconductor and molecular structures. Novel quantum size structures, such as multiexciton generating quantum dots, hybrid semiconductor/carbon nanotube assemblies, fullerene-based linear and branched molecular arrays, and semiconductor/metal nanocomposites, will be examined that will allow for more complete and efficient use of the solar energy spectrum. Unresolved basic science issues in photocatalysis will be explored in coupling photoinduced charge separation to multielectron, energetically uphill redox reactions. Photoconversion systems will be investigated that are based on organic semiconductors and conducting polymers, which are inexpensive and easy to manufacture. An enhanced theory and modeling effort is needed for rational design of artificial solar conversion systems. Of particular interest is the calculation of factors controlling photoinduced long-range electron transfer, charge injection at the semiconductor/electrolyte interface, and photoconversion in biomimetic assemblies for solar photocatalytic water splitting.

Electron pulse radiolysis methods will investigate reaction dynamics, structure, and energetics of short-lived transient intermediates in the condensed phase. Fundamental studies on reactivity of nitrogen oxides in aqueous solution are pertinent to understanding radiolytic degradation of nuclear tank waste. Studies of solvent effects on free radical reaction rates in supercritical fluids are relevant to next-generation supercritical water-cooled nuclear power plants.

Photosynthetic Systems

Portfolio Description

This activity supports fundamental research on the biological conversion of solar energy to chemically stored forms of energy. Topics of study include light harvesting, exciton transfer, charge separation, transfer of reductant to carbon dioxide, as well as the biochemistry of carbon fixation and carbon storage. Emphasized areas are those involving strong intersection between biological sciences and energy-relevant chemical sciences and physics, such as in self-assembly of nanoscale components, efficient photon capture and charge separation, predictive design of catalysts, and self-regulating/repairing systems. Capital equipment funding is provided for items such as ultrafast lasers, high-speed detectors, spectrometers, environmentally controlled chambers, high-throughput robotic systems, and computational resources.

Unique Aspects

The Photosynthetic Systems program is the most prominent supporter of basic research in natural photosynthesis in the United States. This distinctive federal program brings together biology, biochemistry, chemistry, and biophysics to uncover the fundamental science of biological capture of sunlight and its conversion to and storage as chemical energy. Through its broad portfolio of projects at universities and DOE National Laboratories, the program will provide a critical scientific knowledge base that can inspire the roadmap for artificial photosynthesis and enable new strategies and technologies for more efficient generation of biomass as a renewal energy source.

Initiated with funding from its predecessor program (Energy Biosciences), the DOE Plant Research Laboratory (PRL) at Michigan State University is a unique facility jointly supported by the Photosynthetic Systems and Physical Biosciences programs. The PRL is devoted to fundamental plant biology research and the training of graduate students and postdoctoral researchers, the next generation of plant scientists who will provide the knowledge base for meeting future energy needs.

Relationship to Other Programs

The Photosynthetic Systems research effort interfaces with several activities within BES, including the Physical Biosciences program in the organizational and structural principles of cellular machinery as well as the Solar Photochemistry, Catalysis Science, and Biomolecular Materials programs in biomimetic and bioinspired photosynthetic systems. The basic research supported by the program also is relevant to biotechnology- and genomics-related programs in the DOE Office of Biological and Environmental Research, to the DOE Office of Fossil Energy, and to the DOE Office of Energy Efficiency and Renewable Energy, in particular, its activities in the Solar Energy Technologies Program on photovoltaics, the Biomass Program on algal feedstocks, and the Fuel Cell Technologies Program. The program collaborates and coordinates its activities with the National Science Foundation, U. S. Department of Agriculture, and National Institutes of Health in areas of mutual interest where there are multiple benefits.

Significant Accomplishments

Through its origin in the Energy Biosciences program, the Photosynthetic Systems program has a rich history of scientific impact. Among those accomplishments are the elucidation of the structure of the highly efficient light-harvesting chlorosome antenna complex, determination of the biosynthetic pathway for hydrogen production in photosynthetic bacteria, and characterization of critical components of the algal light-harvesting complex. Scientists supported by the program have received numerous awards and prizes including the 2006 Balzan Prize (Plant Molecular Genetics Award) for efforts in developing *Arabidopsis thaliana* as a model plant experiment system.

Mission Relevance

The impact of research in this activity is to uncover the underlying structure-function relationships and to probe dynamical processes in natural photosynthetic systems to guide the development of robust artificial and bio-hybrid systems for conversion of solar energy into electricity or chemical fuels. The ultimate goal is the development of bio-hybrid systems in which the best features from nature are selectively used while the shortcomings of biology are bypassed. Achieving this goal would impact DOE's efforts to develop solar energy as an efficient, renewable energy source. Knowledge generated by this research may also guide the enhancement of photosynthetic efficiency which would significantly impact DOE's efforts to produce advanced biofuels.

Scientific Challenges

Plants, cyanobacteria, and algae use solar energy to convert water and carbon dioxide into chemical energy, i.e. energy-rich organic molecules such as carbohydrates, fat, and protein, which can be collectively termed biomass. Nature has had approximately 3 billion years to modify and refine photosynthesis, a time period 10- to 100-fold longer than humans have had to evolve their complicated biochemical machinery. Understanding nature's complex design for converting sunlight into chemical energy remains a grand challenge for increasing solar energy utilization and enhancing carbon fixation. Despite research efforts, a detailed understanding is still lacking of the structure of the oxygen-evolving complex, the mechanism of action of Rubisco, and the energy dissipation of reactive oxygen species. Molecular, biochemical, and biophysical studies of the mechanisms of the photosynthetic apparatus are much needed, particularly pertaining to light harvesting and energy transduction as well as to the maintenance of the biological integrity of these systems including defect tolerance and self-repair. Another critical research need is increased understanding of the temporal and spatial dynamics and regulation of photosynthesis. Photon absorption and harvesting occur on a femtosecond time scale; charge separation and electron transport on a nano- to picosecond time scale; and photocatalysis and carbon-carbon bond formation on a micro- to millisecond time scale – while presenting experimental and technical challenges, appreciation of the kinetics of each of these processes can provide important insight into natural photosynthetic mechanisms and how they might be altered for use in biomimetic systems for instance. Such fundamental knowledge of natural photosynthesis can play a critical role in the development of renewable, cost-effective, and environmentally-sustainable energy systems and supplies.

Projected Evolution

In FY 2009, the prior Energy Biosciences program evolved into two complementary and synergistic programs: 1) Photosynthetic Systems and 2) Physical Biosciences. Both programs support unique areas of fundamental research on plant and microbial systems. While it is envisioned that the Photosynthetic Systems program will remain tightly integrated with the Physical Biosciences program, the program also anticipates that solar energy utilization research will be enhanced through complementary efforts and greater coordination of its activities with the Solar Photochemistry, Catalysis Science, and Biomolecular Materials programs within BES, as well as with other Offices in DOE in selected areas where programmatic synergies are achievable.

Advances in genomics technologies such as metabolomics along with increased availability of plant genomic sequences provide new opportunities to leverage the strengths of the Photosynthetic Systems program in molecular biology and biochemistry with powerful capabilities in imaging and computation. This will allow an unprecedented biophysical understanding at the nanoscale of photosynthesis and related processes such as carbon fixation. Research will continue to emphasize understanding and control of the weak intermolecular forces governing molecular assembly in photosynthetic systems; understanding the biological machinery for cofactor insertion into proteins and protein subunit assemblies; adapting combinatorial, directed evolution, and high-throughput screening methods to enhance fuel production in photosynthetic systems; characterizing the structural and mechanistic features of new photosynthetic complexes; and determining the physical and chemical rules that underlie biological mechanisms of repair and photo-protection.

Physical Biosciences

Portfolio Description

This activity combines experimental and computational tools from the physical sciences with biochemistry and molecular biology. A fundamental understanding of the complex processes that convert and store energy in living systems is sought. Research supported includes studies that investigate the mechanisms by which energy transduction systems are assembled and maintained, the processes that regulate energy-relevant chemical reactions within the cell, the underlying biochemical and biophysical principles determining the architecture of biopolymers and the plant cell wall, and active site protein chemistry that provides a basis for highly selective and efficient bioinspired catalysts. Capital equipment is provided for items including advanced atomic force and optical microscopes, lasers and detectors, equipment for x-ray or neutron structure determinations, and Fourier transform infrared and nuclear magnetic resonance spectrometers.

Unique Aspects

Physical Biosciences is a unique federal program devoted to funding fundamental science that applies the tools of physical science to address biological phenomena underlying the production and conservation of energy in plants and non-medical microbial systems – including the archaeal kingdom. It occupies an essential niche within DOE's Office of Science, lying at the interface between the life sciences and the chemical and physical sciences. Accordingly, this activity promotes multi- and cross-disciplinary research activities required for the development of bio-inspired energy-relevant technologies and processes.

In addition to its broad portfolio of funded projects in universities and at the DOE National Laboratories, this activity sponsors the Complex Carbohydrate Research Center (CCRC) at the University of Georgia. The CCRC is internationally acclaimed, not only for research excellence, but also for its leadership in providing analytical support and training for the carbohydrate chemistry community. In conjunction with the Photosynthetic Systems program, the Physical Biosciences program also supports the DOE Plant Research Laboratory (PRL) at Michigan State University. The PRL is devoted to fundamental research in plant biology and has a long history of training the next generation of plant scientists.

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Relationship to Other Programs

This research activity interfaces with several complementary activities within BES, including the Photosynthetic Systems program in the area of natural photosynthesis, carbon fixation and metabolism; with the Catalysis Science program in the area of biomimetic catalysis; with Separations and Analysis in the area of analytical tool and technology development; and with Biomolecular Materials in the area of synthesis of novel bio-inspired materials. This activity also supports and complements basic research relevant to the DOE Office of Biological and Environmental Research (BER), in particular for its activities in imaging and biomass conversion technologies; the DOE Office of Energy Efficiency and Renewable Energy (EERE), in particular the Biomass Program's efforts to enhance microbially-mediated conversions of lignocellulosic and other plant feed stocks; the DOE Office of Fossil Energy and the DOE Office of Environmental Management. The program collaborates and coordinates its activities with the National Science

Foundation, U. S. Department of Agriculture, and National Institutes of Health in areas of mutual interest where there are multiple benefits.

Significant Accomplishments

Through its origin in the Energy Biosciences program, the Physical Biosciences program has a strong record of scientific impact as exemplified by its support of research that was instrumental in defining *Archaea* as the third kingdom of life. Other significant accomplishments include: The determination of the biosynthetic pathway for methane production from CO_2 and molecular hydrogen, the elucidation of the biochemistry and genetic regulation of plant lipid synthesis, and the determination of the structure of many of the polysaccharide components of the plant cell wall, as well as many important aspects of its supramolecular structure. The recognition of scientists supported by the program is illustrated by numerous awards and prizes, including the 2008 Wolf Foundation Prize in Chemistry for the unique coupling of single molecule spectroscopy with electrochemistry.

Mission Relevance

The research provides basic structure/function and mechanistic information necessary to accomplish bio-inspired solid-phase nanoscale synthesis in a targeted manner, i.e., design and control of the basic architecture of energy-transduction and storage systems. This impacts numerous DOE interests, including improved biochemical pathways for biofuel production, next generation energy conversion/storage devices, and efficient, environmentally benign catalysts.

Scientific Challenges

The application of physical science and computational tools to increase our understanding of biological systems will enable important new insights into structure/function and chemical mechanisms required to develop new energy capture, conversion, and storage systems and technologies. Analysis of both spatial and temporal dynamics and their subsequent integration into coherent and testable models represent a significant scientific challenge, but also present new opportunities. For instance, understanding aspects of lipid biosynthesis and deposition in membranes as well as storage vesicles would benefit substantially from such integrated approaches, and will lead to new strategies for increasing the energy-rich lipid content of target organisms. Probing the organizational principles of biological energy transduction and chemical storage systems exemplifies another substantial programmatic challenge. In this regard, the use of advanced molecular imaging and x-ray or neutron scattering methods will provide new and essential insights into cell wall and other supramolecular architectures, as well as into the sophisticated structures of enzyme complexes, leading to novel bio-inspired materials and renewable sources of energy.

Projected Evolution

In FY 2009, the prior Energy Biosciences program evolved into two complementary and synergistic programs: 1) Photosynthetic Systems; and 2) Physical Biosciences. Both programs support unique areas of fundamental research on plant and non-medical microbial systems. While it is envisioned that the Physical Biosciences program will remain tightly integrated with the Photosynthetic Systems program, the program also anticipates greater coordination of its activities with the Catalysis Science, Separations and Analysis, and Biomolecular Materials programs within BES, as well as with other Offices in DOE in selected areas where programmatic synergies are achievable.

Future impact is, in general, envisioned through increased use of physical science and computational tools (ultrafast laser spectroscopy, current and future x-ray light sources, and quantum chemistry) to probe spatial and temporal properties of biological systems. Combined with efforts in molecular biology and biochemistry, this will give us an unprecedented architectural and mechanistic understanding of such systems and allow the incorporation of identified principles into the design of bio-inspired synthetic or semi-synthetic energy systems. The application of such tools to the detailed study of individual enzymes (and multi-enzyme complexes) will enable the design of improved industrial catalysts and processes (e.g. more cost-effective, highly-efficient, etc) through a more complete understanding of structure and mechanistic principles. One such priority area for the program is achieving a greater understanding of the active site chemistries of multi-electron redox reactions (e.g. CO_2 reduction). Another unique aspect of biological systems is their ability to self-assemble and self-repair. These capabilities occur via complex processes that are not well-understood, and enhanced efforts will be devoted to the identification of the underlying chemical/physical principles that govern such behaviors. Still another area of emphasis for the program lies in the application of these same tools to achieve a more detailed understanding of the structure – and dynamics – of complex biological nanomaterials such as plant cell walls, biological motors, and cytoskeletal and other assemblies involved in energy capture, transduction, and storage.

Catalysis Science

Portfolio Description

This activity develops the fundamental scientific principles enabling rational catalyst design and chemical transformation control. Research includes the identification of the elementary steps of catalytic reaction mechanisms and their kinetics; construction of catalytic sites at the atomic level; synthesis of ligands, metal clusters, and bio-inspired reaction centers designed to tune molecular-level catalytic activity and selectivity; the study of structure-reactivity relationships of inorganic, organic, or hybrid catalytic materials in solution or supported on solids; the dynamics of catalyst structure relevant to catalyst stability; the experimental determination of potential energy landscapes for catalytic reactions; the development of novel spectroscopic techniques and structural probes for *in situ* characterization of catalytic processes; and the development of theory, modeling, and simulation of catalytic pathways. Capital equipment funding is provided for items such as ultrahigh vacuum equipment with various probes of interfacial structure, spectroscopic analytical instrumentation, and specialized cells for *in situ* synchrotron-based experiments, and computational resources.

Unique Aspects

This activity funds the largest fraction of basic research in catalysis in the Federal government. It seeks to cross the barriers between heterogeneous, homogeneous, and bio catalysis. The integration promotes synergism among disciplines and innovation in fundamental approaches as well as applications. Multidisciplinary approaches are encouraged by means of multi-PI grants. This program encourages the use of large-scale facilities at DOE national laboratories to significantly advance catalysis research.

Relationship to Other Programs

This activity is closely coordinated with several programs within BES. The Condensed Phase and Interfacial Molecular Science program, a part of the Chemical Physics activity, supports fundamental aspects of interfacial science, surface chemistry, and quantum mechanical theory, molecular modeling, and simulation of catalytic-related phenomena. The Solar Photochemistry activity supports complementary aspects of photocatalysis and photoelectrocatalysis, while the Physical Biosciences activity supports aspects of enzymatic catalysis. The Separations and Analysis activity supports the synthesis of organic and inorganic materials relevant also to catalysis. The Heavy Elements Chemistry activity supports the design and synthesis of ligands and coordination compounds of lanthanides. The Materials Synthesis activity covers among others, materials of interest for catalysis. The BES synchrotron facilities have beamlines used by catalysis science researchers, in particular the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL), the Advanced Photon Source (APS) at Argonne National Laboratory (ANL), and the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL). In addition two BES Nanoscale Science Research Centers (NSRCs) have thrust areas that provide unique capabilities for the synthesis and characterization of nanoscale catalysts.

Within DOE, the activity of Catalysis produces research outcomes of relevance to programs of the Office of Energy Efficiency and Renewable Energy and the Office of Fossil Energy. These programs have collaborated during the review of proposals in relevant initiatives, such as the Hydrogen Fuel Initiative.

The catalysis portfolios of other federal agencies are typically restricted to particular applications or dispersed across the agency. The National Science Foundation (NSF) funds heterogeneous catalysis mainly within their engineering directorate; and it funds homogeneous and bio catalysis mainly within their Mathematical and Physical Sciences directorate. The National Institutes of Health (NIH) funds the health-related applications of homogeneous, enzymatic, and bio catalysis; the Environmental Protection Agency (EPA) funds environmental remediation catalysis; and the Defense agencies support catalysis for military applications.

Mission Relevance
Catalytic transformations impact an enormous range of DOE mission areas. Particular emphasis is placed on catalysis relevant to the conversion and use of fossil and renewable energy resources and the creation of advanced chemicals. Catalysts are vital in the conversion of crude petroleum and biomass into clean burning fuels and materials. They control the electrocatalytic conversion of fuels into energy in fuel cells and batteries and play important roles in the photocatalytic conversion of energy into chemicals and materials. Catalysts are crucial to creating new, energy-efficient routes for the production of basic chemical feedstocks and value-added chemicals. Environmental applications of catalytic science include minimizing unwanted products and transforming toxic chemicals into benign ones, such as the transformation of chlorofluorocarbons into environmentally acceptable refrigerants.

Significant Accomplishments
Major breakthroughs over the past three decades have resulted as a consequence of basic catalysis research funded by this core research activity. In particular, the molecular-level understanding of catalytic processing of hydrocarbons led to many new concepts explaining the functioning of metallic and non-metallic catalysts. Consequently, such understanding led to novel catalyst designs, accelerating the development of practical catalysts, some of which are in industrial use today. Examples are new families of synthetic zeolites and noble metal alloys for petroleum reforming catalysis; mixed sulfides and phosphide for hydroprocessing; mixed metal oxides and supported metal nanoparticles for the processing of combustion exhaust pollutants; etc. This activity has also led to fundamental advances in the catalysts required for the selective oxidation of hydrocarbons for the manufacturing of monomers, fine chemicals, and fuel additives. One of the most significant accomplishments in homogeneous catalysis was the development of practical catalysts for the metathesis of unsaturated compounds, a reaction that is ubiquitous in organic synthesis and was highlighted by a recent Nobel Prize. The discovery of single-site metallocene catalysis in the polymerization of alkenes led to new processes for the widespread fabrication of polymers, and recognition of its major author with a National Medal of Science. The development of new methods to study the surface science of catalysis also led to a National Medal of Science for its major author. The low-temperature N_2 activation (the crucial step in ammonia synthesis) with organometallic complexes was attained. Researchers in this program have been widely honored by scientific societies, as they have received most of the awards in Organometallic Chemistry given by the American Chemical Society, and most of the fundamental catalysis awards given to U.S. academics by the North American Catalysis Society.

Scientific Challenges

The grand challenge for this area of research is the *a priori* molecular-level design and synthesis of catalysts with controlled reactivity and long-term stability. Such knowledge is of relevance for the production of catalysts that convert natural resources into energy or desired products in an energetically efficient and environmentally benign manner. A special focus is the identification of new carbon-neutral pathways for the catalytic conversion of biologically-derived feedstocks. Those challenges can be met by coordinating fundamental research on chemical synthesis, structural characterization, mechanistic and kinetics studies, and theory-modeling and simulation.

In inorganic synthesis, the molecular control of structure, shape, and functionality, must be pursued by means of rationally designed modular ligands. In solid state synthesis, emphasis is placed on catalytic materials with nanoscale control of composition, homogeneity, shape, and structure, and in particular, hybrid organometallic-inorganic porous materials able to catalyze the conversion of multifunctional molecules with high selectivity and durability under reaction conditions. Traditional routes of surface chemistry, aqueous-solution chemistry, and high-temperature chemistry are complemented by softer routes, such as surface-functionalization of nanoparticles with coordination compounds. Organic or biological strategies may then be used to arrange the particles into preconceived patterns possessing unique molecular recognition properties (for example, size, shape, chirality, and hydrophobicity). The interfacial interactions with anchoring ligands, supports, and solvent spheres generate fundamental challenges for exacting characterization but also ways of tuning the reactivity and stability of catalytic materials.

The characterization of synthetic catalysts demands higher spatial and time resolution under *ex situ* and *in situ* conditions. Both electronic and atomic structures must be correlated with secondary and macrostructure and their time-resolved evolution. The kinetically significant intermediates must be discriminated from those that are mere spectators. This is a particularly crucial need in solid-mediated catalysis and biocatalysis.

The study of reaction mechanisms is promoted by the synergistic use of theory, simulation, and experimentation. In particular, identification and structural characterization of the reaction intermediates still remains a challenge for most reactions. Classical labeling, trapping, and molecular probe experiments must be complemented with time-resolved *in-situ* spectroscopy in order to acquire information on bonding dynamics. The development of chemo-, regio-, and stereo-selective reactions is of primary importance to the advancement of the science of catalysis, since these reactions present the highest demands on catalysts. While high selectivity has been obtained with homogeneous catalysts in selected instances, heterogeneous or hybrid catalysts require substantially more study, possibly with help from biomimetics and the use of cascade or tandem reactions.

Catalysis of bond cleavage and reformation has, for the most part, been restricted to hydrocarbons (CC, CH bonds), halogenated compounds (CX bonds), and nitrogen- and sulfur-containing compounds (CS, CN bonds). Moreover, past and current research has also addressed the selective addition of oxygen, hydroxyl, or nitrogen to hydrocarbon and aromatics. For homogeneous catalysis, one of the challenges is to carry out these selective reactions under solvent-less conditions or in supercritical media or ionic liquids, while maintaining stability. For heterogeneous catalysis, the challenge is to work at extremely high temperature with high selectivity, or extremely low temperature with high activity. New challenges for all types of catalysts have arisen in activating molecules and materials derived from biorenewable resources.

Projected Evolution

The science of catalytic chemistry is still emerging. A wealth of experimental information has been accumulated relating catalytic structure, activity, selectivity, and reaction mechanisms. However, for phenomenological catalysis to evolve into predictive catalysis, the principles connecting those kinetic phenomena must be more clearly and thoroughly identified.

Better understanding of the reactivity of matter will result from more complete integration of experiment and theory, reproducible synthesis of single-site catalysts, and thorough characterization of catalysts and reactions by means of cooperation among groups with complementary expertise in synthesis, structural characterization, intermediate and transition state characterization, dynamics simulation, and kinetics determination.

The convergence of heterogeneous, homogeneous, and biocatalysis is evolving. Ideas and approaches motivated by biological reaction systems will be used to derive new biomimetic homo- or heterogeneous analogues. Examples are the use of long-range or secondary structure and structural flexibility to affect both selectivity and also activity of inorganic catalysts. The mechanisms and pathways for charge transfer and rearrangements following non-thermal activation, such as electrochemical and photochemical activation, will also be addressed.

In the immediate future, research will focus on the chemistry of inorganic, organic, and hybrid porous materials, the nanoscale self-assembly of these systems, and the integration of functional catalytic properties into nanomaterials. New strategies for design of selective catalysts for fuel production from both fossil and renewable biomass feedstocks will be explored. Increased emphasis will be placed on the use of spectroscopy and microscopy to probe both model systems in vacuum and realistic catalytic sites. Research on catalytic cycles involved in electrochemical energy storage and solar photocatalytic fuel formation will receive increased emphasis.

Heavy Element Chemistry

Portfolio Description

This activity supports research in the chemistry of the heavy elements, including actinides and some fission products. The unique molecular bonding of the heavy elements is explored using theory and experiment to elucidate electronic and molecular structures, bond strengths, and chemical reaction rates. Additional emphasis is placed on the chemical and physical properties of actinides to determine solution, interfacial, and solid-state bonding and reactivity; on determining chemical properties of the heaviest actinide and transactinide elements; and on bonding relationships among the actinides, lanthanides, and transition metals. Capital equipment funding is provided for items such as instruments used to characterize actinide materials (spectrometers, diffractometers, etc.) and equipment to handle the actinides safely in laboratories and at user facilities.

Unique Aspects

This activity represents the only source of funding for basic chemical research in the actinides and transactinides in the United States. Its major emphasis is to understand the underlying chemical and physical principles that determine the behavior of these elements. The activity is primarily based at national laboratories because of the special facilities needed in order to handle these radioactive materials safely. The education of undergraduates, graduate students, and postdoctoral researchers in radiochemistry at national laboratories and universities is an important responsibility of this activity.

Relationship to Other Programs

This activity provides the fundamental understanding of the properties of the actinides and fission product elements that support DOE missions in advanced nuclear energy, stewardship responsibilities for defense programs, and environmental clean-up. The heavy element chemistry program conducts unclassified basic research on all the actinide and transactinide elements, while applied programs (nuclear energy, environmental, stockpile stewardship) generally limit their investigations to the chemical and material properties of specific elements and systems of strategic programmatic interest. This activity is coupled to the BES Separations and Analysis activity, to actinide and fission product chemistry research in DOE’s Environmental Remediation Sciences Program, and to nuclear fuel cycle research within DOE's Office of Nuclear Energy.

Significant Accomplishments

Heavy element chemistry had its genesis in the Manhattan project. Early goals were to discover new elements and to determine their chemical and physical properties from microscale and tracer experiments. Processes for the separation of plutonium from uranium and fission products on an industrial scale were then developed. The chemistry of the elements through einsteinium (Es, atomic number 99) has been determined with small but weighable quantities. For the elements heavier than Es in the periodic table, tracer techniques and one-atom-at-a-time chemistry have been developed and carried out through element 108 to determine chemical properties. Organometallic chemistry has been enriched by discovery of many unique organoactinide compounds.

Taken together, the results from this activity have repeatedly confirmed the Seaborg hypothesis that the actinides are best represented in the periodic table as a 5f element series placed under the 4f (lanthanide) series. Interpretations of spectroscopic results have provided thermodynamic quantities such as oxidation-reduction potentials and enthalpies of reactions. Specific electronic transitions determined in this activity have proven useful to develop processes for laser isotope separation of uranium and plutonium. Magnetic measurements show the light actinide metals have delocalized 5f orbitals and resemble d-orbital transition metals, whereas the 5f electrons become localized at americium, element 95; thus the heavier actinide metals exhibit behavior similar to the rare earth metals.

Mission Relevance

This activity represents the nation's only funding for basic research in actinide and long-lived fission products, especially technicium, and is broadly relevant to the DOE mission. Knowledge of the chemical characteristics of actinide and fission-product materials under realistic conditions provides a basis for advanced fission fuel cycles. Fundamental understanding of the chemistry of these long-lived radioactive species is required to accurately predict and mitigate their transport and fate in environments associated with the storage of radioactive wastes.

Scientific Challenges

The role of 5f electrons in bond formation remains the fundamental topic in actinide chemistry and is the central focus for this program. The 5f orbitals participate in the band structure of metallic and ceramic materials that contain the light actinides. Theory and experiment show that 5f orbitals participate significantly in molecular actinide compounds, for example, compounds required for advanced nuclear energy systems. Molecular-level information on the geometry and energetics of bonding can now be obtained at the Nation's synchrotron light sources and from multi-photon laser excitation studies. These tools enable studies of actinides in the gas phase, as clusters, and at interfaces between solutions and surfaces of minerals and colloids in solution. Actinide and fission product samples must be handled in special facilities because of their radioactivity, which limits the types of experiments that can be safely conducted.

Sophisticated quantum mechanical calculations that treat spin-orbit interactions accurately need further development so that they can predict the properties of molecules that contain actinides. Development and validation of computer codes yield fundamental information about actinide species that are difficult to study experimentally, predict the electronic spectra of important species, and correlate electronic properties with molecular structure. Improved modeling of actinide transport requires understanding of the processes describing sorption on surfaces such as colloidal particles. Surface complexation models can predict the migration of radioactive species; experimental validation of the theoretical properties of models will be the key to understanding the role of the 5f electrons. This activity supports research in heavy element chemistry at universities, encouraging collaborations between university and laboratory projects. Twenty-four undergraduate students, chosen competitively from universities and colleges throughout the United States, are taught actinide chemistry and radiochemistry each summer in programs at Brookhaven National Laboratory and San Jose State University. Graduate and postdoctoral students are educated to provide personnel for the technological challenges associated with the heavy elements.

Projected Evolution

At the frontier of the periodic table, theoretical chemists predict the properties of actinides and transactinides in gaseous molecules, clusters in liquids, and solid species, using modern calculation tools such as density functional theory. Because most actinide species have partly filled 5f electron subshells and all have highly charged nuclei, both spin-orbit and relativistic effects must be included in the calculations. Sophisticated quantum mechanical calculations of actinide compounds and actinide species in environmental media are being developed. Heavy Element Chemistry research pursues advances in gas-phase chemistry that explore new reactivity patterns, providing benchmarks for theoretical calculations.

Support of research to understand the chemical bonding of elements that have 5f electrons leads to fundamental understanding of separations processes and to the design and synthesis of preorganized chelating agents for the separations of particular actinide ions. Research in bonding, reactivity, and spectroscopic properties of molecules that contain heavy elements and of actinides in environmentally relevant species aids the development of ligands to sequester actinides in the environment and to remove toxic metals from the human body. Better characterization and modeling of the interactions of actinides at liquid-solid and liquid-liquid interfaces, including mineral surfaces under environmentally relevant conditions, improve separations processes that are essential for advanced nuclear fuel cycles.

Separations and Analysis

Portfolio Description

This activity supports fundamental research covering a broad spectrum of separation concepts, including membrane processes, extraction under both standard and supercritical conditions, adsorption, chromatography, photodissociation, and complexation. Also supported is work to improve the sensitivity, reliability, and productivity of analytical determinations and to develop new approaches to analysis in complex, heterogeneous environments, including techniques that combine chemical selectivity and spatial resolution to achieve chemical imaging. This activity is the nation's most significant long-term investment in the fundamental science underpinning actinide separations and mass spectrometry. The overall goal is to obtain a thorough understanding, at molecular and nanoscale dimensions, of the basic chemical and physical principles involved in separations systems and analytical tools so that their full utility can be realized. Capital equipment funding is provided for items such as lasers for use in sample ionization and chemical imaging, advanced mass spectrometers with nanoprobes, confocal microscopes for sub-diffraction limit resolution, and computational resources.

Unique Aspects

This activity represents the Nation's most significant long-term investment in solvent extraction, ion exchange, and mass spectrometry. The supported research is characterized by a unique emphasis on underlying chemical and physical principles, as opposed to the development of methods and processes for specific applications.

Relationship to Other Programs

The activity is closely coupled to the Department's stewardship responsibility for actinide and fission product chemistry and to its clean-up mission. It emphasizes the separation and analysis of actinide and fission product elements and their decay products and is therefore naturally coordinated with the BES Heavy Element Chemistry Program. Similarly, elements of the analysis science portfolio benefit from cooperation with the BES Catalysis Science, Chemical Physics, Materials Chemistry, and Atomic, Molecular, and Optical Science Programs. The basic nature of the research has led to advances in technologies ranging from those that support nuclear non-proliferation efforts to those connected with advanced nuclear energy systems.

Significant Accomplishments

This activity is responsible for such recent notable contributions as the concept of host-guest complexation, which was recognized with the 1987 Nobel Prize in Chemistry; the use of the inductively coupled plasma (ICP) for emission and mass spectrometry; the development of the TRUEX process based upon fundamental research on ligand design; the development of SIMION, a program to simulate the motion of ions in fields, that has become the standard tool internationally for development of ion lens; and, more recently, the development of a new calixerene ligand that complexes Cs^+ that is based on design and development work performed by BES researchers at Oak Ridge National Laboratory (ORNL) and that is being used to clean up waste tanks at Savannah River National Laboratory (SRNL). The success of the Manhattan Project was, in large part, due to our ability to develop industrial-scale processes for separating plutonium from irradiated fuel. Thus began the intense interest of the Department of Energy and its predecessor agencies in the science that underlies separation processes. The missions of the Department have evolved, and it must now face the legacy of accumulated wastes from the cold war era and the growing emphasis on alternative energy sources. Knowledge of molecular-level processes is required to characterize and treat the extremely complex mixtures associated with cleanup and to predict the fate of associated contaminants in the environment.

Likewise, the Department and its predecessors were also driven to develop analytical methodologies to support their early missions. Nuclear and radiochemical analyses were supported and refined by developments in analytical separations, such as solvent extraction and ion exchange. A need for reliable potentiometric titration prompted the first use of operational amplifiers in analytical chemistry and led to a revolution in electrochemistry. Mass separation was required for assay in the form of mass spectrometry and, in the form of the calutron, served as the first method for the production of macroscopic quantities of separated isotopes of uranium and other elements. As with separation science, improved understanding of the underlying science is required to meet the analytical challenges presented by the legacy of the cold war, alternative energy sources, and the future challenges of the Department as its missions and responsibilities continue to evolve.

Mission Relevance

Work is closely coupled to DOE's stewardship responsibility for transuranic chemistry; therefore, separation and analysis of transuranic isotopes and their radioactive decay products are important components of the portfolio. Knowledge of molecular-level processes is required to characterize and treat extremely complex radioactive mixtures in, for example, new nuclear fuel systems, and to understand and predict the fate of radioactive contaminants in the environment. Separations are essential to nearly all operations in processing industries and are also necessary for many analytical procedures.

Scientific Challenges

Challenges in separation science include the development of a deeper understanding of processes driven by small energy differences. These include self-assembly and molecular recognition, crystallization, dispersion, coalescence, and hysteresis in transport properties of glassy polymer membranes. The development of fundamental principles to guide ligand design for atomic and isotopic specific recognition and separations is also required. These, in turn, pose challenges to analysts to generate the understanding required to characterize amorphous materials through analysis of scattering data or other methods. Other analytical challenges include single-molecule detection and direct observation of bimolecular interactions and reactions. A deeper understanding of laser-material interactions as well as ionization and excitation sources for optical and mass spectrometric analyses is also required. Significant challenges are posed by elucidation of principles to underlie diagnostics at interfaces between synthetic materials and biomolecules, at oxide-aqueous interfaces, and to monitor spatial and temporal processes in and on the surfaces of living cells. Though understanding at the molecular level is required, there is currently insufficient knowledge to extend that understanding from the molecular level to the nanoscale, to mesoscale, and finally, to macroscale phenomena. Pursuit of that knowledge presents a major challenge to this activity.

This activity provides funding for about 50 university grants supporting, at any given time, on the order of 60-70 students and 25-30 postdoctoral fellows. In addition, 14 programs at national laboratories support numerous senior staff, and additional students and postdoctoral fellows. Programs at the laboratories are typically multi-investigator efforts on problems that require extensive collaboration by experienced scientists. These programs act as the focal point for specific research efforts vital to the DOE mission. This BES activity supports research programs at ORNL, Argonne National Laboratory (ANL), and Pacific Northwest National Laboratory (PNNL), with smaller efforts at Ames Laboratory, and Lawrence Berkeley National Laboratory (LBNL). Many of the research efforts at the national laboratories involve collaborations with the university and industrial communities.

Projected Evolution

Separations research will continue to advance the understanding of multifunction separations media; supramolecular recognition (using designed, multi-molecule assemblies to attract specific target species); synthesis of new porous materials and control of interface properties at the nanoscale; ligand design and synthesis of extractant molecules; mechanisms of transport and fouling in polymer and inorganic membranes; solvation in supercritical fluids; field-enhanced mixing; and drop formation.

Analytical research will pursue the elucidation of ionization and excitation mechanisms for optical and mass spectrometry; single molecule detection, characterization, and observation; nano- and molecular-scale analytical methods; laser-based methods for high-resolution spectroscopy and for presentation of samples for mass spectrometry; characterization of interfacial phenomena, with emphasis on chromatography; surface-enhanced Raman spectroscopy; and use of quadrupole ion traps to study gas-phase ion chemistry.

An expanded activity will support work to understand the underlying science needed to achieve true chemical imaging, i.e., the ability to selectively image selected chemical moieties at the molecular scale and to do so with temporal resolution that allows one to follow physical and chemical processes.

Geosciences Research

Portfolio Description

This activity supports basic experimental and theoretical research in geochemistry and geophysics. Geochemical research emphasizes fundamental understanding of geochemical processes and reaction rates, focusing on aqueous solution chemistry, mineral-fluid interactions, and isotopic distributions and migration in natural systems. Geophysical research focuses on new approaches to understand the subsurface physical properties of fluids, rocks, and minerals and develops techniques for determining such properties at a distance; it seeks fundamental understanding of wave propagation physics in complex media and the fluid dynamics of complex fluids through porous and fractured subsurface rock units. Application of x-ray and neutron scattering using BES facilities plays a key role in the geochemical and geophysical studies within this activity. The activity also emphasizes incorporating physical and chemical understanding of geological processes into multiscale computational modeling. Capital equipment funding is provided for items such as x-ray and neutron scattering end stations at BES facilities for environmental samples and for augmenting experimental, field, and computational capabilities.

Unique Aspects

The activity contributes to the solution of Earth Science-related problems in multiple DOE mission areas by providing a foundation of scientific understanding for them. Examples of these applications include (but are not limited to): the potential for geophysical imaging of permeability; reactive fluid flow studies to understand contaminant transport and remediation, and geothermal energy production; and coupled hydrologic-thermal-mechanical-reactive transport modeling to predict geological repository performance. The DOE applied activities focus on solutions to existing problems in the near-term (0-5 years) but seek fundamental research results as the foundation for their directed research and development efforts in the longer-term, both from the national laboratories and from the university community. In particular, the Geosciences activity provides funding for long-term crosscutting research efforts at national laboratories, which are directly and immediately transferred to the applied programs when needed.

Relationship to Other Programs

The Geosciences activity in BES provides the majority of individual investigator basic research funding for the Federal government in areas with the greatest impact on unique DOE missions such as high-resolution Earth imaging and low-temperature, low-pressure geochemical processes in the subsurface. BES focuses on a narrower range of fundamental issues than NSF. DOE user facilities in geosciences, particularly synchrotron x-ray beamlines, are available to all of the geosciences community within the United States. BES research activities focus primarily upon the physical and chemical properties of geo-systems with a cognizance of critical biological interactions. This contrasts with research programs in the Office of Biological and Environmental Research (BER), which primarily focus on biological interactions with the physical and chemical properties of geo-systems, and on DOE site-specific issues. The BES geosciences activity is closely coordinated with applied programs focused on geological CO_2 sequestration within the Office of Fossil Energy (FE) and geothermal energy within the Office of Energy Efficiency and Renewable Energy (EERE).

Significant Accomplishments

The GSECARS beamline has been built and commissioned (in collaboration with NSF-EAR) as a center for high-resolution analytical geochemistry for the whole Earth sciences community, including multiple DOE applied program users. The Geosciences activity also supports BESSRC at the Advanced Photon Source (APS) and X26a at the National Synchrotron Light Source (NSLS). Geosciences supported investigators have been selected in a highly competitive process to design and build one of six facility-supported beamlines at the NSLS-II facility at Brookhaven National Laboratory. Geosciences research projects, unique BES supported laboratory facilities, and BES funded workshops on Basic Research Needs for Geosciences and in topical areas are the foundations for identifying research opportunities for research and development integration activities between the Office of Science and the applied program offices. Recent Geosciences workshops have produced broadly applicable publications on geosciences user facilities, reactive fluid flow and transport modeling, and geophysical processes and properties that can be imaged for environmental applications. These documents promote BES activities to the science community in areas of importance for the DOE and publicize DOE research interests to the broader science community. Geosciences investigators led a National Academy of Sciences study of grand challenges for the earth sciences which was published in March 2008 as *Origin and Evolution of Earth: Research Questions for a Changing Planet*. Investigators sponsored by this activity have published major review volumes on Synchrotron Science related to Geosciences, Molecular Modeling applied to Geosciences, Nanophases in the Shallow Earth Environment, Biomineralization, Isotope Geochemistry, Isotopic Geochemistry, and Molecular Geomicrobiology, and have published a number of recent textbooks.

Mission Relevance

This activity provides the basic research in geosciences that underpins the nation's strategy for understanding and mitigating the terrestrial impacts of energy technologies and thus is relevant to the DOE mission in several ways. It develops the fundamental understanding of geological processes relevant to geological disposal options for byproducts from multiple energy technologies. Knowledge of subsurface geochemical processes is essential to determining the fate and transport properties of harmful elements from possible nuclear or other waste releases. Geophysical imaging methods are needed to measure and monitor subsurface reservoirs for hydrocarbon production or for carbon dioxide storage resulting from large-scale carbon sequestration schemes.

Scientific Challenges

Understanding the natural heterogeneity of geochemical and geophysical properties, processes, and rate laws is critical to managing improved production of the Earth's energy resources and safe disposal of energy-related wastes. Improved imaging and tracking of geochemical processes at the atomic (angstrom) scale using synchrotron x-rays and neutrons is critical for progress in understanding geochemical systems. New investigations are needed at the smallest scales to study electronic properties, geochemical reactivity, solute properties, and isotopic distributions in both inorganic and organic systems. Facilities such as the Linac Coherent Light Source (LCLS) will provide unique capabilities for Geosciences investigators to probe natural reactivity processes at ultrafast times to provide a new paradigm for understanding geological reaction rates. Mineral-fluid-biological systems are also new targets for systematic examination. Understanding pristine natural systems and DOE-specific sites requires improving our capabilities to make and understand high-resolution geochemical and geophysical measurements experimentally and in the field and to model them. Understanding mineral surface-particle-fluid interactions is the key to predicting the fates of contaminants in the environment or predicting nuclear waste-site performance. Improved high-resolution geophysical imaging will underlie new resource recovery, tracking of contaminants, and predicting and tracking repository performance, whether for nuclear or energy-related wastes (such as CO_2). In addition, new research on high-pressure/high-temperature mineralogical systems will create new opportunities to study and manipulate fundamental mineral and mineral-fluid properties and interactions. Upgrading national laboratory and university investigator experimental, field instrumentation and computational capabilities with new instrumentation and facilities is a continuing challenge. Even with new improved analytical equipment, technical challenges will continue in mastering data-fusion approaches to multiple-technique measurements, such as combined x-ray and neutron analyses or combined seismic-electromagnetic measurements. Computational capabilities driven by the PC-cluster approach with new higher speed chips (3GHz and greater) will enable optimization of clusters for individual molecular dynamics, seismic, electromagnetic, geomechanical, and hydrologic modeling techniques and provide unique support to experimental analysis.

Projected Evolution

In the near term, geosciences research continues its basic activity in fundamental rock physics, fluid flow, and analytical, theoretical and experimental geochemistry. It continues national laboratory and university projects focusing on understanding the significance of commonly observed natural nanophases and nanoparticles in shallow earth systems and how they contribute to mineral-fluid interactions. The activity continues working with various groups on investigating uses of neutron imaging in Geosciences.

In the mid-term, the activity initiates new research efforts on imaging of earth processes with attention devoted both to improved small-scale imaging (geochemistry focus) using x-ray sources, neutron sources, and scanning microscopy, and large-scale imaging (geophysics focus) of physical properties through understanding intrinsic attenuation within seismic and electromagnetic imaging. New energy waste storage options will require high-resolution monitoring and verification at a new level of sophistication. New high-pressure/high-temperature research activities begin to investigate how physical and chemical properties in the Earth vary with depth and Earth dynamics. The GSECARS and BESSRC at the Advanced Photon Source (APS) begin their second decade as the premier synchrotron user facilities for the earth sciences community, pioneering approaches that can be exported to designing other facilities such as the National Synchrotron Light Source II (NSLS II). They will expand research efforts in nanogeosciences to understand the role of nanophases in geological systems and efforts on understanding the geophysical and geochemical challenges of predicting the fate and transport of CO_2 as sequestration in deep geological formations is tested as a technology option to mitigate greenhouse gas emissions.

In the longer term, Geosciences activities will link analytical capabilities with computational capabilities at the nano-, micro- and macro-scales to provide understanding of geochemical processes occurring at natural time and length scales. Geosciences activities will provide robust understanding of what can be measured remotely at depth by geophysical means and will increase both the depth of current resolution and the resolution at any depths of interest. Geosciences activities will pioneer the use of neutrons to understand geological processes.