Office of Science

Basic Energy Sciences

Core Research Activities

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Materials Chemistry

Portfolio Description

This program supports scientific research on materials with a focus on the *chemical synthesis, chemical control, and chemical dynamics* of material composition and structure across the range of length scales from atomic to mesoscopic, with a view to elucidating fundamental aspects of materials' structure-property relationships. Major scientific areas of interest include: fundamental aspects of the chemical assembly of material structures and control of multi-scale material morphology; synthesis and characterization of novel organic, inorganic, polymeric and composite materials; synthesis and characterization of complex fluids including ionic liquids; study and control of surface and interfacial chemistry and morphology; fundamental electrochemistry of materials; the study of the chemical dynamics and transformations of functional materials in operational environments; and the development of new, science-driven laboratory-based analytical tools and techniques for the elucidation of chemical processes in materials, particularly *in situ* or *in operando* in energy-relevant applications.

Unique Aspects

Research supported in this program advances knowledge in the materials sciences that underpins many energy-related technologies such as batteries and fuel cells; catalysis; energy conversion, transmission and storage; friction and lubrication; high efficiency electronic devices; photonic materials; light-weight, high-strength materials; and materials for advanced separations. The focus on chemistry-based formation and control of new materials and morphologies is complementary to the BES Biomolecular Materials research activity (that emphasizes discovery of materials and systems using concepts and principles of biology) and the Synthesis and Processing Science research activity (that emphasizes 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 scientific user 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 and DOE, and within the larger federal research enterprise:

- Within BES, this research activity sponsors – jointly with other core research activities, the Energy Frontier Research Center program, and the Joint Center for Energy Storage Research (JCESR), as appropriate – program reviews, Principal Investigators (PI) meetings, and programmatic workshops.
- There are active interactions with the DOE Offices of Energy Efficiency and Renewable Energy (EERE) and Fossil Energy (FE) through workshops, program reviews, PI meetings, and communication of research activities and highlights.
- Within the larger federal research enterprise, program coordination is through the Federal Interagency Chemistry Representatives, which meets annually, and the Interagency Polymer Working Group.
- 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 (NSTC) Nanoscale Science, Engineering, and Technology Subcommittee that leads the National Nanotechnology Initiative.

- Predictive materials sciences activities and the associated theory, modeling, characterization and synthesis research are coordinated with other federal agencies through the NSTC Subcommittee on the Materials Genome Initiative.
- There are particularly active interactions with the National Science Foundation (NSF) through workshops, joint support of National Academy studies in relevant areas, and communication about research activities.

Significant Accomplishments

The Materials Chemistry research activity has resulted in a variety of scientific accomplishments including the discovery of new superconducting materials, the discovery of the first organic magnet above room temperature, and the demonstration of new analytical techniques for surfaces and interfaces that have had significant impact in their respective fields.

Recent accomplishments include:

- The first demonstration of a metal organic framework material that shows both stable micropores and good charge mobility, relevant to energy storage technologies;
- The discovery of metal-containing polymers capable of white light emission, with significance for the future development of polymer-based solid-state lighting materials;
- A new understanding of the behavior of charged particles in ionic liquids that helps explain the low electrical conductivity of many ionic liquids and is expected to lead to the design of new and improved ionic liquids for energy-relevant applications;
- Demonstration of a method to completely polarize nuclei near optically polarized nitrogen-vacancy centers in diamond at room temperature, which can be applied to enhance the sensitivity of NMR/MRI experiments in bulk materials;
- Discovery and elucidation of the mechanism of dysprosium doping to boost the performance of a known thermoelectric material (TAGS-85) by 15%; and
- Fundamental studies on materials aspects of a micro-transfer printing process led to the development of micro-contact printed solar cells (and their commercialization by Semprius Inc.) that set the world record for high concentration photovoltaic module efficiency (33.9%) in January 2012.

Mission Relevance

The Materials Chemistry program supports research to generate fundamental knowledge based on the principles of chemistry about the creation, manipulation and functional behavior of materials that will underpin the future development of energy-relevant technologies including systems for energy storage, transformation, and utilization, with levels of performance superior to the current state of the art.

Scientific Challenges

The Materials Chemistry research activity seeks to explore and advance the frontier of accessible functional materials, through the application of the methods and principles of chemistry. Doing so requires addressing specific scientific challenges and opportunities, such as those identified in the BES Advisory Committee's reports, including *Directing Matter and Energy: Five Challenges for Science and Imagination* (report link) and *From Quanta to the Continuum:*

Opportunities for Mesoscale Science (report link). Challenges and opportunities identified in these reports include:

- Discovering new methods to design and perfect atom- and energy-efficient synthesis of revolutionary new forms of matter with tailored properties, taking advantage of the recent and ongoing development of theoretical methods and tools;
- Characterizing and controlling matter far away from equilibrium;
- Mastering defect mesostructure and its evolution by characterizing and controlling the patterns and evolution of mesoscale heterogeneity;
- Directing assembly of hierarchical functional materials through the integration of disparate materials classes across a range of length scales from molecular to macroscopic.

Each of these challenges and opportunities may potentially be addressed by the application of chemical principles to the design, synthesis and transformation of materials.

Projected Evolution

The overarching goal of materials chemistry research is to provide the *knowledge* needed to design and produce materials with tailored properties from first principles. This program will make progress towards that goal by emphasizing hypothesis-driven research on the chemistry-based synthesis of materials and/or morphologies that have the potential to enable next-generation energy-relevant technologies, and research on the chemical transformations occurring in functional materials in the operating environment. It will include the study of chemical processes that direct and control the covalent and non-covalent assembly of materials, discovery of synthetic methods to tailor the symmetry and dimensionality of crystalline and non-crystalline lattices, and the utilization of chemistry to control interfacial properties and interactions of materials. New approaches to the integration of theory and experiment leading to new materials design ideas and opportunities for predictive materials discovery may also be supported.

Biomolecular Materials

Portfolio Description

This activity supports fundamental research on the discovery, design and synthesis of functional materials, structures and materials aspects of energy conversion processes, based on principles and concepts of biology. Since biology provides a blueprint for translating atomic and nanoscale phenomena into mesoscale materials that display complex yet well-coordinated collective behavior, the major programmatic focus is on the hypothesis-driven creation of energy-relevant materials optimized for harsher, non-biological environments. Major thrust areas include: harnessing or mimicking the energy-efficient synthesis approaches of biology to generate new, optimized, energy-relevant materials; bioinspired self-, directed-, and active assembly approaches with control of assembly pathway mechanisms and kinetics to form materials that are far from equilibrium and display novel and unexpected properties; adaptive, resilient materials with self-repairing capabilities; and development of science-driven tools and techniques to achieve fundamental understanding of how these new materials and systems are formed and how they function in real time.

Unique Aspects

Basic research supported in this activity underpins DOE's mission to develop future, transformative energy technologies in areas such as energy conversion, transduction, and storage; light-weight/high-strength materials; efficient membranes for highly selective separations; and energy-efficient low temperature synthesis of materials. Current scientific thrusts balance grand challenge 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 biological principles and concepts is complementary to the focus on chemistry-based formation and control of new materials and morphologies of the Materials Chemistry research activity, and the emphasis on physical, rather than chemical, control of structure and properties, and on bulk synthesis, crystal growth, and thin films of the Synthesis and Processing Science research activity. The Biomolecular Materials activity's focus on the intersection of biology and materials sciences complements the BES Physical Biosciences activity, which focuses on biological aspects of capture, conversion, and storage of solar energy in plants and/or non-medical microbes. The researchers supported by the program benefit from significant use of BES-supported scientific user facilities with their advanced synchrotron x-ray, neutron scattering, electron microscopy and nanoscience tools.

Relationship to Other Programs

The Biomolecular Materials program is a vital interdisciplinary component of the materials sciences that interfaces materials sciences with biology. This interfacing results in active 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 the Energy Frontier Research Centers program, as appropriate – program reviews, contractor meetings, and programmatic workshops.
- There are active interactions with the DOE Office of Energy Efficiency and Renewable Energy (EERE) through workshops, program reviews, principal investigator meetings, and communication of research activities and highlights.

- Nanoscience-related projects in this activity are coordinated with the Nanoscience Research Center activities and reviews in the Scientific User Facilities Division within BES. 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.
- Predictive materials sciences activities and the associated theory, modeling, characterization and synthesis research are coordinated with other federal agencies through the NSTC Subcommittee on the Materials Genome Initiative.
- Active interactions with the National Science Foundation through workshops, joint support of National Academy studies in relevant areas, and communication about research activities.

Significant Accomplishments

The Biomolecular Materials research activity has produced several notable accomplishments that show promise of significant impact:

- Stiff polymeric materials able to spontaneously repair, a key feature of natural materials, without any external help from light, heat, or healing agents;
- The first "directed evolution" of an enzyme, capable of synthesizing semiconductors never before produced by living organisms, using a new cell-free approach;
- The fabrication of cell/silica composites and silica replicas using mammalian cells to direct complex structure formation, and the use of this process to reinforce cellular structures;
- A hybrid biological-organic solar converter that produces hydrogen from sunlight at a rate two to three times faster than that of natural photosynthesis;
- The first functional bio-nanoelectronic device that seamlessly integrates biological functions of membrane proteins with nanowire electronics;
- The first artificial solar cell that mimics the self-repair process used by plants as they convert light into energy; and
- An innovative biomimetic approach for directed formation and manipulation of colloidal assemblies that perform elaborate functions such as grasping, transporting and releasing cargo.

Mission Relevance

Research supported by the Biomolecular Materials activity underpins a broad range of energy technologies such as lighter and stronger materials to improve fuel economy, membranes for making separations and purification processes more efficient, energy-efficient synthesis and assembly of functional materials, and processes that can convert light, carbon dioxide, and water to fuels.

Scientific Challenges

Since biology has already figured out ways in which matter, energy, entropy, and information are organized and/or manipulated across multiple length scales, the challenge for us 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. 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* (report link):

- How do we design and perfect atom- and energy-efficient synthesis of revolutionary new forms of matter with tailored properties?
- How do remarkable properties of matter emerge from complex correlations of the atomic and electronic constituents and how can we control these properties?
- How can we master energy and information on the nanoscale to create new technologies with capabilities rivaling those of living systems?
- How do we characterize and control matter–especially very far away–from equilibrium?

Additional challenges directly correspond to the objectives laid out in the two recent BES reports, *From Quanta to the Continuum: Opportunities for Mesoscale Science* (report link) and *Computational Materials Science and Chemistry: Accelerating Discovery and Innovation through Simulation-Based Engineering and Science* (report link):

- Discovering, controlling, and manipulating complex mesoscale architectures and phenomena to realize new functionality
- The development and use of powerful new theory/modeling and physical/chemical characterization tools that can accelerate materials discovery.

Projected Evolution

Recent BES Basic Research Needs (and other) workshops and reports have clearly identified mastering the capabilities of living systems as a Grand Challenge that could provide the knowledge base to discover, design, and synthesize new materials with the precise control of complexity needed to yield totally new properties for next-generation energy technologies. Biomolecular Materials research activity will seek to advance the ability for materials to self-repair, self-regulate, sequester impurities, tolerate abuse, and produce, convert and store energy, with an emphasis on achieving mechanistic understanding of these new materials and systems. New approaches that will lead to predictable and scalable synthesis of novel, hierarchically structured polymeric, inorganic, and hybrid functional materials in vitro with controllable morphology, content, behavior and performance are sought. The activity will expand research on creating materials optimized for non-biological conditions (i) in which the components work in concert to initiate, maintain, cease functions, and communicate to coordinate collective behavior in response to multiple external signals; (ii) that are capable of spontaneous error-correcting formation and deformation; (iii) that undergo self-repair without external input; and (iv) that are capable of self-replication. This activity also will expand research to design and create next generation membrane materials with programmable selectivity and transport based on biological gating and pumping functions. Integration of theory and experiment to understand how materials complexity leads to new functionalities and the development of new design ideas and opportunities for accelerated discovery will also be emphasized.

Synthesis and Processing Science

Portfolio Description

This program supports scientific research on materials to understand the physical phenomena and unifying principles that underpin materials synthesis, including diffusion, nucleation, and phase transitions often using *in situ* diagnostics, and development of new techniques to synthesize materials with tailored structure and properties. An important element of this activity is the development of real-time monitoring tools that probe the dynamic environment and the progression of structure and properties as a material is formed. This information is essential to understand the underlying physical mechanisms and to gain atomic level control of material synthesis and processing. The emphasis is on the synthesis of complex thin films with atomic control; preparation techniques for high-quality single crystal and bulk materials with novel physical properties; understanding the contributions of the precursor states to the processing of bulk materials; and mild processing techniques for the assembly of nanostructured materials into larger scale structures.

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 activities 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. The focus on materials discovery and design by physical means is complementary to the BES Materials Chemistry and Biomolecular Materials research activities, which emphasize chemical and biomimetic approaches.

Relationship to Other Programs

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

- Within BES, this research activity sponsors – jointly with other core research activities, the Energy Frontier Research Center program, and the Joint Center for Energy Storage Research (JCESR), as appropriate – program reviews, Principal Investigators (PI) meetings, and programmatic workshops.
- There are active interactions with the DOE Offices of Energy Efficiency and Renewable Energy (EERE) and Fossil Energy (FE) through workshops, program reviews, PI meetings, and communication of research activities and highlights.
- Nanoscience-related projects in this activity are coordinated with the Nanoscale Science Research Center user facilities 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 that leads the National Nanotechnology Initiative.

- Predictive materials sciences activities and the associated theory, modeling, characterization and synthesis research are coordinated with other federal agencies through the NSTC Subcommittee on the Materials Genome Initiative.
- The program also participates in the interagency coordination groups such the Interagency Coordination Committee on Ceramics Research and Development.
- Active interactions with the National Science Foundation through workshops, joint support of National Academy studies in relevant areas, and communication about research activities.

Significant Accomplishments

The Synthesis and Processing Science Research activity has many notable accomplishments. Some have already made an impact of scientific and technological significance:

- The discovery of superconductivity at the interface between metals and insulators was assisted by careful layer-by-layer defect controlled thin-film growth of superconducting oxide by molecular beam epitaxy.
- The evidence that even the thinnest silicon membranes are conductive provided the proper surface is present was supported through novel processing of silicon nano-membrane on insulator.
- The materials design of a tungsten photonic crystal opal structure used for thermal emission was enabled through first modeling and then fabrication.
- A newly developed theory of nanorod growth has guided experiments to realize the smallest well-separated metallic nanorods that can be used as air-tight glue for use in organic solar cell packaging.
- A liquid-crystalline dielectric fluid was shown for the first time to display a large electrocoloric effect near room-temperature that will enable efficient and environmentally friendly refrigerators to replace the vapor compression coolers.
- For the first time, high energy protons were used for real-time imaging of a large metal sample during melt and solidification without destroying the sample.
- For the first time, the design and discovery of new sulfur-rich highly ionic compounds as cathodes and electrolytes have enabled all-solid-state lithium-sulfur rechargeable batteries with high energy densities.
- Using a self-assembly process, porous graphene was developed into an electrode with high energy storage capacity for a lithium-air battery.

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 a wide range of semiconductors for solid state lighting and photovoltaics; light-weight metallic alloys and nanocomposites for transportation applications; novel, designer materials for electrical energy storage; and ceramics processing including high-temperature superconductors for near zero-loss electricity transmission. The research activity aims at providing new 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 high-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 advance understanding for the many challenges presently open in this field, including:

- Developing robust predictive thermodynamic and kinetic tools – How do we accurately incorporate dynamic processes and near-equilibrium phenomena into new or existing tools?
- Multiscale modeling of multi-phase functional materials – What new modeling approaches will enable us to accurately incorporate length scales of functional materials?
- Materials design and fabrication at the atomic scale to achieve tailored properties – How do we manipulate atoms at the atomic scale to achieve new functionality?
- *In situ* characterization of materials synthesis from the atomic to the micron scale – How do we measure *in situ* processes at their relevant length and time scales?

Finally, the BES Basic Research Needs workshop reports and the BES Advisory Committee's Grand Challenge report, *Directing Matter and Energy: Five Challenges for Science and the Imagination*, provide additional discussion on these and other challenges.

Projected Evolution

The Synthesis and Processing Science activity is encouraging hypothesis-driven proposals that integrate a creative experimental methodology with a first-principles theory-based approach that will accelerate progress in understanding and unifying principles for design, synthesis and discovery of new materials. Over the past few years, the activity has evolved an increasing interest in understanding nanoscale morphology, defect and dopant control in deposition processes, and complex chemical and structural materials growth. Over the next several years, these directions are expected to continue with a stronger focus on investigating fundamental mechanisms for bulk materials growth, new deposition techniques for organic and inorganic films, and organization of mesoscopic assemblies across a range of length scales, especially related to use-inspired clean energy research.

Experimental Condensed Matter Physics

Portfolio Description
This activity supports experimental condensed matter physics research, emphasizing the development of a detailed understanding of the relationship between the electronic structure and the properties of complex materials, both in bulk materials and thin films. Nanoscale structures and phenomena, and the impact of those structures on mesoscale properties, are core elements of the program. The focus is on systems whose behavior derives from strong correlation effects of electrons, anisotropy, or reduced dimensionality. Scientific themes include superconductivity, magnetism and spin physics, low dimensional electron systems, and nanoscale systems. Also supported is the development of techniques to characterize the electronic states and properties of materials under extreme conditions, such as in ultra-low temperatures (milli-kelvin) and in ultra-high magnetic fields (100 Tesla). As required to drive the discovery of new phenomena, this activity supports growth of single crystals of new materials.

Unique Aspects
This activity continues to support research on electronically complex materials, an area that impacts a wide range of other topics including superconductivity, magnetism, magnetoresistivity, and low-dimensional electron systems. 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. Research on the properties of materials in high magnetic fields utilizes the 100T multishot magnet (designed and built by BES), now located at the National High Magnetic Field Laboratory (NHMFL) at Los Alamos National Laboratory (LANL). This activity also supports research that involves using photoemission to investigate correlated electron systems. Internationally, this activity holds a position of world leadership in the areas of magnetism, superconductivity, materials characterization, 2D electron gases, and nanoscale science. New, exciting areas launched within this activity include studies on the evolution of condensed phase phenomena from ultra-cold atoms, topological insulators, and magnetic superconductors.

Relationship to Other Programs
The research in this activity 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. 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: Physical Behavior of Materials on superconductivity and magnetism; Synthesis and Processing Science on single crystal growth; X-ray and Neutron Scattering on photoemission studies of correlated electron systems; and Theoretical Condensed Matter Physics on nanostructures and low-dimensional systems. This research activity also sponsors – jointly with other core research activities and the Energy Frontier Research Centers program, as appropriate – program reviews, principal investigators (PI) meetings, and programmatic workshops.

The program also works with agencies outside of BES.

- There are active interactions with the DOE Office of Energy Efficiency and Renewable Energy (EERE) through workshops, program reviews, PI meetings, and communication of research activities and highlights.
- Nanoscience-related projects in this activity are coordinated with the Nanoscale Science Research Center user facilities 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 that leads the National Nanotechnology Initiative.
- Predictive materials sciences activities and the associated theory, modeling, characterization and synthesis research are coordinated with other federal agencies through the NSTC Subcommittee on the Materials Genome Initiative.
- The program has also supported topical studies by the National Research Council, including "Assessment of and Outlook for New Materials Synthesis and Crystal Growth", "Optics and Photonics: Essential Technologies for our Nation," and "High Magnetic Field Science".
- This program and the National Science Foundation (NSF) 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. Additional interactions with the NSF include joint support of National Academy studies in relevant areas and ongoing communication about research activities.

Significant Accomplishments

This activity has a long history of accomplishments. Among these are 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 first observation of superconductivity in a magnetically doped semiconductor (platinum antimony [$PtSb_2$] with ~1% Yb); and design/construction of the 100T multishot magnet (now operated by the NHMFL). The 100T magnet currently holds the world record for long pulse, high magnetic fields in a reusable magnet. In addition, the activity has supported much of the seminal work in the fields of high temperature superconductors and quasicrystals, efforts now pursued worldwide.

Recent accomplishments in the program include:

- The observation of Bose condensation of excitons doped double layer semiconductor structures.
- The characterization of BCS (Bardeen, Cooper, and Schrieffer), two-gap superconductivity in magnesium diboride (MgB_2).
- The first observation of the fractional quantum Hall effect in graphene.
- The first observation of the Hofstadter's butterfly energy spectrum in graphene and h-boron nitride moire superlattices.
- STM imaging of the formation of heavy fermions in cerium-cobalt-indium ($CeCoIn_5$).

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 physics of low dimensional systems, and understanding charge-orbital-spin interactions provide the scientific underpinnings for a broad range of 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 ongoing scientific challenges for experimental condensed matter physics are: the solution of the mechanism for high-temperature superconductivity; 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; understanding the influence of interfaces in determining the electronic properties of materials; and discovery and characterizations of topological states in materials. Low temperature physics continues to be important for the advancement of physics by providing the experimental conditions necessary to observe phenomena such as Bose–Einstein condensates, the quantum Hall effect, and superconductivity. High-magnetic-field research coupled with low temperature physics led to the discovery of the quantum and fractional quantum Hall effect and to the general area of novel quantum effects. The availability of very high magnetic fields over useable time scales offers the promise of both increasing the fundamental understanding of matter and of observing the effects of very high magnetic fields on materials properties. 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
This activity will include further work in developing a fundamental understanding of highly correlated systems and understanding phenomena that occur at the nanoscale, at low temperatures, and in very high magnetic fields. The program will expand to investigate phenomena that occur in mesoscale structures. The confinement of electronic behavior in mesoscale architectures (such as semiconducting quantum dots; metallic, magnetic, and ferroelectric nanocrystals; and lithographically patterned graphene sheets) results in new materials properties. Mesoscale science offers the opportunity to tune the degree of confinement to any arbitrary level and to connect multiple confined systems expressing different charge, spin, and mechanical degrees of freedom to produce new phenomena. The portfolio can be expected to continue thrusts in electronic structure, new materials, surfaces/interfaces, and development of experimental techniques, including the growth of thin films and single crystals to enable new physics. Efforts will continue to strengthen research in unconventional superconductivity, including the high-temperature cuprate superconductors, magnesium boride, and iron pnictide superconductors. In the last few years, the program has increased support for spin physics and nanomagnetism, topological states of matter, and graphene. 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. Major research areas include correlated electron systems, quantum phase transitions, magnetism, superconductivity, optical response, thermoelectric materials, and neutron and photon scattering. Research into fundamental material properties related to new or existing energy technologies, and theory targeted at aiding experimental technique design and interpretation of experimental results is also supported. The program includes modeling and simulation efforts in support of the interagency Materials Genome Initiative and research utilizing large scale computational science with joint funding from DOE's Advanced Scientific Computing Research (ASCR) program. Nanoscale and multi-scale modeling, as well as modeling at the mesoscale, are included.

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 there is likely 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 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. The Materials Genome Initiative has added a component of *validated* theory and modeling which includes data repositories aimed at increasing the rate of materials discovery. 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.

- Within BES, this research activity sponsors – jointly with other core research activities and the Energy Frontier Research Centers program, as appropriate – program reviews, contractor meetings, and programmatic workshops.
- The program actively collaborates with ACSR on research opportunities in large scale, advanced computational tools and resources.

- The BES commitment to advancing the frontiers of basic research is present in programmatic interactions with other DOE programs such as the Office of Energy Efficiency and Renewable Energy.
- Nanoscience-related projects are coordinated with the Nanoscience 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 (NSTC) Nanoscale Science, Engineering, and Technology subcommittee, which leads the National Nanotechnology Initiative.
- Predictive materials sciences activities and the associated theory, modeling, characterization and synthesis research are coordinated with other federal agencies through the NSTC Subcommittee on the Materials Genome Initiative.
- Active interactions with the National Science Foundation through workshops, joint support of National Academy studies in relevant areas, and communication about research activities.

Significant Accomplishments

The program has history of theoretical and computational advances which have contributed to the broad understanding of condensed matter physics. Examples are the so-called GW method which provided a first principles theory of the bandgap of semiconductors such as silicon, the prediction of topological insulators, the theory and design of photonic band gap materials, the development of software to predict x-ray absorption in materials and its use to obtain atomic geometry, the understanding of the critical role of vortices in superconductors, the prediction of the intensity optical absorption in semiconducting nanoparticles, and for advances in dynamical mean field theory, a widely used method for treating correlated electron materials, and its use to understand neutron scattering in actinides. Recent accomplishments include:

- Development of an accurate computational approach to the theory of excitons in semiconductors;
- A new strategy for increasing the magnetic field from superconducting magnets through vortex pinning; and
- Better understanding of the role of quantum phase transitions in high temperature superconductivity.

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 the nanometer or mesoscale 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 theory and computation which extend the understanding of strongly correlated materials including magnetic and superconducting materials and transition metal oxides. There is a growing interest in exotic states of matter such as the quantum Hall effect and topological insulators. Predictive theory and modeling as it relates to the Materials Genome Initiative will become more important, as will advanced computational techniques such as the Quantum Monte Carlo method. Time dependent and non-equilibrium phenomena, especially at the femtosecond time scale and in electron transport are important areas for future research. All of these have the potential to impact energy relevant technologies over the long term.

Physical Behavior of Materials

Portfolio Description

This activity supports basic research on the physical behavior of materials in response to electric, magnetic fields, electromagnetic fields, chemical environments, thermal excitation, size effects and the proximity effects of surfaces and interfaces. Emphasis is on bringing a better understanding to fundamental processes taking place between electric charges, photons, lattice vibrations, and other collective excitations in materials. Included within the activity is research to understand the role of crystal defects to semiconducting, superconducting, and magnetic properties; phase equilibria and kinetics of reactions in materials in unusual environments; and diffusion and transport phenomena. Basic research is also supported to develop new instrumentation, including *in situ* experimental tools to probe the physical behavior in real environments encountered in energy applications.

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, superconductors, ferroelectrics, and magnetocaloric materials. Some specific examples include: the stability and morphology of materials in solution as function of pH and oxidation environment are investigated and methods are developed to understand and predict how structure selection can be modified by environment in aqueous solutions as in Li-ion batteries; a 3D metallic carbon that is stable under ambient conditions is predicted to exist that has building blocks of interlocking hexagonal carbon rings; a general analytical expression relating equilibrium fluctuations of the grain boundary shape and position to key parameters governing its motion coupled to a shear deformation is proposed for metals.

Relationship to Other Programs

This activity closely interacts with other programs in BES as well as other DOE activities and interagency coordination groups:

- Within BES, this research activity sponsors – jointly with other core research activities, the Energy Frontier Research Centers program, and the Joint Center for Energy Storage Research (JCESR), as appropriate – program reviews, principal investigators (PI) meetings, and programmatic workshops.
- There are active interactions with the DOE Office of Energy Efficiency and Renewable Energy (EERE) through workshops, program reviews, PI meetings, and communication of research activities and highlights.
- Nanoscience-related projects in this activity are coordinated with the Nanoscale Science Research Center user facilities 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 that leads the National Nanotechnology Initiative.

- Predictive materials sciences activities and the associated theory, modeling, characterization and synthesis research are coordinated with other federal agencies through the NSTC Subcommittee on the Materials Genome Initiative.
- The program also participates in the interagency coordination groups such the Interagency Coordination Committee on Hydrogen.
- Active interactions with the National Science Foundation through workshops, joint support of National Academy studies in relevant areas, and communication about research activities.

Significant Accomplishments

This activity has had broad impact in many classes of materials and phenomena. Some of the recent accomplishments include:

- A giant photonic Spin Hall effect was discovered when light is propagated through a metamaterial comprised of V-shaped antennas that follows a curved trajectory and drags light with different circular polarization in opposite transverse directions.
- The a.c. conductivity of a perfect dielectric was increased by more than 18 orders of magnitude within 1 femtosecond, allowing electric currents to be driven, directed and switched by the instantaneous light field without any material damage opening the way to ultra-high speed electronic signal processing in the petahertz (10^{15} hertz) domain range.
- An accurate magnetometer device was invented, based on a thin-film organic semiconductor diode, that is very low cost and yields better accuracies than existing sensors devices.
- Magneto-optical images have shown that high angle grain boundaries are the key critical current limiting factor in a superconductor $YBa_2Cu_3O_7$ film and enables future superconducting magnet energy storage.

Other accomplishments include: a technique to experimentally resolve a single individual magnetic spin on an atom using $KNbO_3$ nanowires that combine fluorescence and force microscopies; realization of the smallest feature size (100 nanometer gold) 3D metallic photonic crystal material; measuring thermoelectricity of a single individual molecule; and demonstration of 50-fold improvement in thermoelectric properties of silicon nanowires.

Mission Relevance

The research supported by this activity is necessary for discovery of novel material properties and improving materials reliability in chemical, electrical, and electrochemical applications, including 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 physical properties behavior is linked to these surroundings and exposure history is critical to the understanding of photovoltaics, fast-ion conducting electrolytes for batteries and fuel cells, corrosion, 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 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 photon-matter interactions, plasmonics, metamaterials and novel organic electronic materials will be considered. In addition, theory and modeling, taking advantage of the vast advances in computing speed and power, will be emphasized.

The long term goal of this program is to develop an atomistic understanding of 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-property relationship over multiple length scales, with emphasis at the atomic level, and by understanding the response of the nanometer and mesoscale 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 behavior of collections of these features at the mesoscale and onward 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. This program seeks to foster theory, modeling, and simulation activities that address charge and energy transfer; electronic structure calculation; exciton dynamics and transport; and spin dynamics in energy relevant materials. Developing and applying novel experimental techniques to these problems will be emphasized in coordination with the investment in theory and modeling.

Mechanical Behavior and Radiation Effects

Portfolio Description

This activity supports hypothesis-driven 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 fundamental studies of deformation of ultra-fine scale materials, radiation resistance of structural materials, and intelligent microstructural design for increased strength, formability, and fracture resistance in energy relevant materials. The goals are to develop the scientific underpinning for predictive models for the design of materials having superior mechanical properties and radiation resistance. This program will support research in these areas as well as research on unique synergistic effects of multiple environments on the strength, structural development, or failure of materials.

Unique Aspects

The ability to predict materials performance and reliability from a fundamental basis 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 fraction 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, such that researchers are now beginning to develop unified, first-principles models of deformation, fracture, and damage.

Relationship to Other Programs

The research in this activity has, at its heart, the influence of defects on properties of materials and as such underpins, or interacts with, a number of BES, DOE and other Federal government programs. Particularly 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 activity and Electron and Scanning Probe Microscopies research whose focus is on the relationship of structure to physical properties.

- Within BES and DOE, this research activity sponsors, jointly with other core research activities and Energy Frontier Research Centers program as appropriate, program reviews, contractor meetings, and programmatic workshops. Important links have been made with DOE research on nuclear energy, fusion energy, lightweight materials, defense programs and radioactive waste storage.
- The program also participates in the interagency coordination groups such the Interagency Coordination Committee on Ceramics Research and Development.
- 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 (NSTC) Nanoscale Science, Engineering, and Technology Subcommittee that leads the National Nanotechnology Initiative.

- Predictive materials sciences activities and the associated theory, modeling, characterization and synthesis research are coordinated with other federal agencies through the NSTC Subcommittee on the Materials Genome Initiative.

Significant Accomplishments

The Mechanical Behavior and Radiation Effects research activity has resulted in a variety of scientific accomplishments including the discovery of new materials that resist radiation damage; the understanding of new, tough ceramic materials; and the discovery of new analytical techniques and test methods that have impacted a number of research projects.

Recent accomplishments include:

- Based on a fundamental understanding of the role of fine-scaled precipitates, a new class of materials has been developed that can be used at relatively high operating temperatures without losing strength by microstructural evolution;
- Precise measurements of stress distribution during twinning of hexagonal close-packed materials, utilizing 3D x-ray diffraction to illustrate how these stresses are accommodated during compression;
- Developing a model for how specimen size and free surfaces affect the shape memory transitions in NiTi alloys using density functional theory;
- Demonstrating the effects of combined pressure and radiation on structural stability of ceramics such as $Gd_2Zr_2O_7$, in which irradiation under extreme pressures of a diamond anvil cell stabilized a non-equilibrium phase;
- Developed computational tools, along with synthetic and experimental capabilities, to design hybrid glasses with outstanding mechanical properties.

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; radioactive waste storage; 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

Irradiation and deformation can push materials out of equilibrium, creating a dynamic system that has unexpected behaviors. Examples include severe plastic deformation that leads to non-equilibrium and highly radiation-resistant particles in oxide-dispersion-strengthen alloys, and radiation flux that creates 3-dimensional patterns or unexpected phase separations/morphologies. These are challenging to study because of the non-equilibrium nature, but can have profound influence on the development of new understanding and superior materials.

Cooperative phenomena: What is missed when observing or modeling individual defects or processes in a linear fashion? Often 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, or application of more than one driving force. These processes include strain hardening, stress corrosion cracking, grain boundary sliding, and chemo-mechanical response.

Bridging the length and time scales, modeling, and measurement from atomic to continuum: 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) in a unified manner. This includes not only improved computational methods but also improved measurement techniques for full 3-dimensional analysis of microstructures.

Projected Evolution

Research opportunities that can be realized by the application of mechanics fundamentals to the general areas of self-assembly, physical behavior, and behavior under extreme environments (primarily environments that are experienced in current or future fission reactors) of structural materials will be emphasized. 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. Another area of emerging interest is evaluation of the impact on mechanical behavior of using nanoscale building blocks to fabricate longer length scale structures. In all topical areas, new opportunities arise by taking advantage of more powerful parallel computational platforms and new experimental tools. In addition to traditional structural materials, it is also important to understand deformation and failure mechanisms in other materials used in energy systems (e.g., membranes, coating materials, electrodes) so this will become an increasing part of the portfolio.

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 U.S. energy production, these are issues that need to be addressed at a fundamental level.

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 the BES-supported construction of the Linac Coherent Light Source (LCLS) and National Synchrotron Light Source-II (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 materials transformation through electronic structure excitation and subsequent energy transfer through various quantum mechanical structural pathways involving competing modes of ordering and energy dissipation. The aim of such ultrafast research is to investigate the details of dynamic events at the most fundamental time scales, leading to the understanding of emergent phenomena such as chemical reactions, the nucleation of defects in materials that result in the degradation of their properties, and 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 ferroelectric polarization domains, and non-equilibrium optical processing during material synthesis.

Relationship to Other Programs

Within the various DOE science and technology 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 x-ray scattering portfolio contributes to other program elements, including:

- 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.

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.

Coordination with other agencies includes:

- Joint funding (with NNSA) of the HPCAT beamline at the Advanced Photon Source optimized for high pressure condensed matter science.
- Predictive materials sciences activities and the associated theory, modeling, characterization and synthesis research are coordinated with other federal agencies through the National Science and Technology Council Subcommittee on the Materials Genome Initiative.
- Active interactions occur with the National Science Foundation through workshops, joint support of National Academy studies in relevant areas, and communication about research activities.

Significant Accomplishments

This 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 and nano-particles, 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 among the primary tools for characterizing the atomic, electronic, and magnetic structures of materials in relevant processing and energy conversion environments.

Scientific Challenges

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.

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 pumped 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 will be the integration and support of materials preparation (especially when coupled to *in situ* investigation of materials processing) as this is vital to careful x-ray 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. Emphasis will be on the application of neutron scattering, spectroscopy, and imaging as major tools for materials research primarily at BES-supported user facilities. Development of next-generation instrumentation concepts, innovative neutron optics, advanced high resolution detectors, rigorous modeling software tools, training next generation neutron scattering scientific community, and application of polarized neutrons for materials research are distinct aspects of this activity.

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 principal supporter of both the research and the instrumentation at the major U.S. neutron scattering facilities. It maintains strong fundamental research programs in materials and related disciplines at these facilities that serve to drive advancements in both the techniques and 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 in the world and a range of optimized neutron scattering instruments.

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

Relationship to Other Programs

This activity interacts closely with the BES Scientific User Facilities Division in the development of new instrumentation concepts and sophisticated software tools for data analysis and coordination on complementary scientific portfolios. It serves several BES-supported Energy Frontier Research Centers with focused research in the areas of superconductivity, magnetism, thermoelectrics, organic photovoltaics, materials under high pressure, structural materials under extreme conditions, and interfacial structure and dynamics for energy storage, hydrogen storage, carbon sequestration and catalysis. In addition, there are coordination activities with other federal agencies:

- Coordination with the National Institute of Standards and Technology’s Center for Neutron Research helps to ensure development of instrumentation and capabilities that best serve the broad neutron scattering user community.
- Nanoscience-related projects in this activity are coordinated with the Nanoscale Science Research Center user facilities and reviews in the BES Scientific User Facilities Division.
- Predictive materials sciences activities and the associated theory, modeling, characterization and synthesis research are coordinated with other federal agencies through the National Science and Technology Council Subcommittee on the Materials Genome Initiative.
- Active interactions with the National Science Foundation through workshops, joint support of National Academy studies in relevant areas, and communication about research activities.
- Coordination with other federal agencies on research instrumentation programs, especially in the funding of beam lines whose cost and complexity require multi-agency support.

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, fluids and magnetic materials.

Neutron scattering groups supported by this activity at the DOE national laboratories 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. Recent scientific accomplishments include:

- Phase diagrams for the recently discovered high temperature iron pnictide superconductors and heavy fermions;
- The first experimental determination of spin liquids, a new state of magnetism;
- Mechanisms responsible for the giant negative thermal coefficient materials and high performance thermoelectrics;
- Emergent magnetism at the interfaces of complex oxide heterostructures offering a new pathway for oxide spintronics;
- Rich phase behavior of protein-polymer block copolymers offering a new platform to assemble functional biomaterials at high concentrations; and
- Neutron focusing optics to increase neutron flux in the instruments.

Mission Relevance

The increasing complexity of DOE mission-relevant materials including superconductors, magnets, batteries, photovoltaics, thermoelectrics, metallic alloys and polymer nanocomposites requires ever more sophisticated scattering techniques to investigate the structure and dynamics at relevant length and time scales and to develop theories which can predict the behavior of these materials. Neutron scattering probes are among the primary tools for characterizing the atomic, electronic, and magnetic structures of materials. The activity is relevant to the behavior of matter in extreme environments, high pressure, shear and magnetic fields.

Scientific Challenges

Strongly Correlated Electron Materials – 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, thermoelectrics, spintronics, and magnets, remains a great challenge; inelastic neutron scattering, diffraction and imaging will play major roles in the studies of these materials.

Matter Under Extreme Conditions – Extreme temperature (both ultrahigh and ultralow), pressure, magnetic and electric fields, shear and combinations thereof are important parameters for material synthesis as well as to tune the material properties. Highly optimized neutron scattering spectrometers with novel sample environments will enable *in situ* studies at high pressures. Similarly, scattering experiments at high magnetic fields can be used to study materials during phase transitions, allowing separation of magnetic field effects as well as to simulate effects normally observed via doping.

Multi-component Complex Materials – Interfaces play strong roles in the behavior of these materials. The role of individual constituents on the emergent behavior in these materials can be readily probed using unique contrast variation techniques. Highly optimized instruments at the SNS will enable the science with smaller samples with unprecedented resolution, accuracy, and sensitivity under various parametric conditions.

Projected Evolution

The Neutron Scattering activity will continue its stewardship role in fostering growth in the U.S. neutron scattering community in the development of innovative time-of-flight neutron scattering and imaging instrumentation concepts and their effective utilization for transformational research. A continuing theme will be the integration and support of materials preparation as this is vital for relating neutron structural measurements to materials properties.

Electron and Scanning Probe Microscopies

Portfolio Description

This activity supports basic research in materials sciences that utilizes and advances electron and scanning probe microscopy and spectroscopy techniques to address forefront challenges related to atomic, electronic, and magnetic structures and properties of materials. This activity also supports the development of new instrumentation concepts and quantitative techniques, including ultrafast electron diffraction and imaging techniques, for basic science and materials characterizations for energy applications. The goal is to develop a fundamental understanding of materials through advanced microscopy and spectroscopy.

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 the structure, chemistry and physical properties of materials at near-atomic length scales. High spatial resolution in electron and scanning probe microscopy and spectroscopy provides unique opportunities to characterize atomic and mesoscale 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, Synthesis and Processing, Physical Behavior, Materials Chemistry, Biomolecular Materials, Mechanical Behavior and Radiation Effects, Catalysis, Energy Frontier Research Centers, and the DOE Experimental Program to Stimulate Competitive Research. In addition, interactions outside of BES include:

- With the DOE Office of Energy Efficiency and Renewable Energy through activities in solar energy, hydrogen and energy storage technologies.
- Nanoscience-related projects in this activity are coordinated with the Nanoscale Science Research Center user facilities 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 that leads the National Nanotechnology Initiative.
- Predictive materials sciences activities and the associated theory, modeling, characterization and synthesis research are coordinated with other federal agencies through the NSTC Subcommittee on the Materials Genome Initiative.
- Active interactions occur with the National Science Foundation through workshops, joint support of National Academy studies in relevant areas, and communication about research activities.

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 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 development of the Embedded Atom Method to study defects in materials, which revolutionized computational materials science by permitting large scale simulations of materials structure and evolution; the successful correction of electron microscope lens aberrations that allowed the first spectroscopic imaging of single atoms within a solid; the development of dynamic transmission electron microscopy, which couples high time resolution (~nanoseconds) with high spatial resolution (~nanometers), providing a unique tool for probing and understanding materials dynamics; and the visualization of electronic structure at the nanometer and atomic scale by spectroscopic imaging scanning tunneling microscopy which contributed to the understanding of the electronic transport mechanisms for superconductivity.

Recent accomplishments include:

- The discovery of the first solid-state triple point in vanadium dioxide.
- A new mechanism of thermal transport using electron thermal microscopy.
- The direct observation of nanoscale ferroelectric switching in real-time.
- New insights on the superconductivity of heavy fermions and magnetic superconductors through the developments of state-of-the-art scanning tunneling microscopy techniques.

Mission Relevance

This activity is relevant to materials research and energy technologies through the structural and functionality determination of mesostructured materials for a wide range of energy generation and use technologies. The nation’s long-term energy needs present many fundamental challenges that require 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 atomic, electronic, and magnetic structures found in advanced materials; electron and scanning probe microscopies and associated spectroscopy are among the primary tools for characterization of these structures. Analysis of the surface and interior of nano- or meso-scale structures related to the functionality of materials often require *in situ* and *in operando* microscopy techniques under various environments.

Scientific Challenges

Researchers addressing major scientific challenges supported by this activity require utilization of advanced, innovative imaging and spectroscopy to solve forefront scientific problems in understanding materials properties and functionality. Relevant research challenges are: imaging functionality at the near-atomic or mesoscale; development of a fundamental understanding of electron scattering and nanoscale ordering phenomena in matter; utilization of high-resolution, quantitative analysis of nano- and mesoscale materials to understand the origin of macroscopic properties and enable the design of high-performance materials; understanding the correlation between electrons and spins at nanoscale, and their dynamics and transport properties; determination of interface structures and understanding the link between surface/interface/defect structures and materials properties; combining electron and scanning probes to study complex properties; probing the local properties of materials at the atomic or molecular scale with *in situ* and *in operando* microscopy in the end-use application environment; development of time-resolved microscopy with high spatial, temporal and energy resolutions to study the atomic level mechanisms during structural or phase transformations; and the application of first principles theory to understand the data obtained from microscopy instrumentation and how to use this information to predict the structures of real materials.

Projected Evolution

The emphasis of the program will be basic research for the fundamental understanding of materials using advanced microscopy and spectroscopy techniques. This program will use currently available electron and scanning probe microscopy capabilities; develop new, innovative instrumentation and techniques; and use advanced scattering, imaging and spectroscopy methods to understand functionality, fundamental processes and dynamics of materials at the near-atomic to mesoscopic length scales.

To address forefront scientific challenges, new state-of-the-art experimental and theoretical techniques will need to be developed. This activity will continue to support the development and use of advanced microscopy instrumentation/techniques, and the associated theoretical tools to understand the experiments, for research on imaging materials functionality and understanding the properties of materials. New advances are needed in time-resolved microscopy and related spectroscopy, in high-resolution analyses of energy-relevant soft matter and for quantitative *in situ* analysis capabilities under perturbing parameters such as temperature, stress, chemical environment, and magnetic and electric fields. The combination of multiple probes in a single experiment is expected to address complex and challenging materials science problems. Significant improvements in resolution and sensitivity in microscopy and related spectroscopy techniques will provide an array of opportunities for groundbreaking science.

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 objectives are addressed through three funding mechanisms: (1) Implementation Grants, (2) State-Laboratory grants and (3) participation in the DOE Office of Science Early Career Research Program. 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. Further information on the Early Career Research Program may be found at its website. This program is science-driven and supports the most meritorious proposals based on peer review and programmatic priorities.

Relationship to Other Programs

The activity interfaces with all other research activities within BES. It is also responsive to programmatic needs of other program offices within DOE. In addition, EPSCoR grants support graduate students, undergraduates, and postdoctoral associates, and encourage them to be trained in frontier energy research areas by using the 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. Recent accomplishments include:

- Bridging Basic Energy Sciences and Vehicle Technologies was investigation of the solid electrolyte interphase or SEI, a complex layer that forms from the decomposition products in the electrolyte of a lithium-ion battery. To address long-standing difficulties in understanding the SEI including its composition, formation mechanism and functioning, researchers combined a novel microscopy technique with multi-nuclear magnetic resonance (NMR) to analyze the structure and composition of the SEI. While many results suggest that upon additional cycling and aging, the structure, composition, and thickness of the anode SEI change, these experiments show the initial composition could be relatively simpler than earlier believed.

- Researchers provided the first experimental confirmation that a current of electrons with the same spin alignment (a pure spin current) in a thin metal film can penetrate neighboring metal layers in a multilayer structure and cause switching of the magnetization direction (e.g., magnet polarity) in the bottom layer. The experiments demonstrated that spin current can produce a rotation of the magnetization within the film plane in addition to the commonly observed rotation of the magnetization out of the film plane.

Mission Relevance

The core activity interfaces with all other core activities within the Office of Science and DOE and in many cases provides bridging between interests of science and energy technology. 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

The National Academy of Sciences conducted a recent evaluation of EPSCoR and EPSCoR-like programs supported by the Federal Government. While responses to this report are under discussion, the report's recommendation for (resuming) cost sharing will be acted on in the next DOE EPSCoR funding opportunity announcement. The scientific emphasis for EPSCoR grants will continue to evolve with the strategic directions for DOE and the scientific directions of the subprograms for DOE's basic research and technology programs

X-ray Scattering Facilities

Portfolio Description

This activity supports the operation of five synchrotron radiation light sources. Four of the light sources are storage ring-based sources: 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 Lightsource (SSRL) at the Stanford Linear Accelerator Center (SLAC). The fifth light source, the Linac Coherent Light Source (LCLS) at SLAC, is a free electron laser which provides 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 are the most advanced facilities of their kind in the world. Together, they serve over 11,000 users annually from academia, Department of Energy (DOE) national laboratories, and industry, a number that has nearly doubled in the past decade and that can double again in the next decade as current facilities and those under construction are fully instrumented. These light sources represent the largest collection of such facilities operated by a single organization in the world. Conception, design, construction, and operation of these facilities 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 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 the Office of Fusion Energy Sciences, and with other areas of 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 is establishing more frequent contacts with international user facilities such as ESRF, XFEL, SPring-8, and others. The objectives are to share experiences and to make optimal use of present facilities.

Significant Accomplishments

During the past three 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 insertion devices that provide 10 to 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 exceeded its original designed performance specifications and all six experimental stations have successfully been commissioned and are available for users. Recent research at the light source facilities supported by BES, other agencies, industry, and private sponsors includes:

- Time-resolved soft x-ray transmission microscopy measurement revealing the strength and duration of trains of electric and magnetic pulses affect the circulation of a magnetic vortex that may lead to the possibility of magnetic memory bits with four states instead of two, improving storage capacity as well as energy efficiency
- *In situ* x-ray diffraction studies to investigate and map out the process-structure-property relationships in CuInGaSe materials, the active material in the solar shingles leading to the development of the first-of-its-kind commercial 'Solar Singles', Powerhouse^{TM} Solar Shingles, by Dow Chemical
- Coherence diffraction imaging measurement using intense, coherent, and ultrashort x-ray pulses revealing vibration modes in gold nanoparticles at trillionths of seconds time scale with never-before-seen details; and
- Particularly significant was the award of the 2012 Nobel Prize in Chemistry for studies on G-protein–coupled receptors (GPCRs) which cells use to pick up signals from the outside world such as tastes, flavors and sights, and to communicate with mobile messengers from inside the body, such as hormones and neurotransmitters.

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, and chemical change. 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 large scale powerful facilities that are not possible to develop, construct and operate by individual institutions and/or companies. Such highly sophisticated and expensive tools are by their nature centralized and staffed with specialists that provide expertise to the user community 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 are reflected in the large number of publications appearing annually in the most important scientific journals.

Scientific Challenges

First, 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. Second, optimal utilization of the LCLS coherent short-wavelength x-ray source will require continued development of new capabilities and advanced optics, instruments, and detectors.

Projected Evolution
X-ray scattering will continue to play a central role in the growth of BES programmatic science. The facilities will need continuous growth and advancement in terms of upgrades, new 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 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 (50 femtoseconds in standard operation with planned improvements that will further reduce the pulse length to <5 femtoseconds), 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 create plasmas.

Neutron Scattering Facilities

Portfolio Description

This activity supports the operation of three neutron scattering facilities: 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 pulsed spallation neutron source in existence.

Unique Aspects

The DOE neutron scattering facilities are the most advanced facilities of their kind in the world. Together, they serve over 1,300 users annually from academia, Department of Energy (DOE) national laboratories, and industry. These neutron scattering sources represent the largest collection of such facilities operated by a single organization. Conception, design, construction, and operation of these facilities are among the core competencies of the BES program.

Relationship to Other Programs

- This activity has very strong interactions with many areas of BES programmatic research. This includes research in condensed matter and materials physics, chemistry, soft matter materials, geosciences, high-pressure science, environmental sciences, engineering, biosciences, and many other disciplines.
- Interaction also exists with other parts of the Office of Science, notably the Office of Biological and Environmental Research, and the Office of Nuclear Physics with other areas of DOE, notably the National Nuclear Security Administration, and the Office of Energy Efficiency and Renewable Energy.
- There are frequent contacts with other federal agencies in order to better coordinate efforts in optimizing beamlines and instruments. This activity is establishing more frequent contacts with national and international user facilities such as NIST, ILL, ISIS, J-Parc, and the future ESS. The objectives are to share experiences and to make optimal use of present facilities.
- In addition to scattering research, HFIR has ongoing programs 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.

Significant Accomplishments

Since the late 1940s, BES and its predecessors have 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. DOE has developed research reactors and spallation sources as high-flux neutron sources for neutron scattering research including diffraction, inelastic scattering (spectroscopy), reflectivity, and imaging and helped pioneer virtually all the instruments and techniques used at these facilities world-wide. Because of the neutral charge and magnetic moment of the neutron, neutrons penetrate most materials with minimum absorption and, via their scattering from both the nuclei and the magnetic electrons of a sample under study, three-dimensional atomic and magnetic structures can be obtained. In addition, thermal neutrons have energies comparable to phonon and magnon excitations in solids, and thus can provide dynamic information via inelastic scattering. Neutrons possess other unique properties including sensitivity to light elements, which is invaluable to polymer, biological, and pharmaceutical research.

Neutron scattering studies have been crucial to a detailed understanding of many materials and properties including:

- The structure and dynamics of new classes of high temperature superconductors,
- The structures proteins utilizing the light element sensitivity of the technique in concert with light source data,
- The development of higher strength magnets for more efficient electric generators and motors and to better magnetic materials for computer hard drives,
- The determination of complex polymer structures,
- Porous materials including oil-bearing shales, and
- Non-destructuve property measurements of automotive gears, brake disks, airplane wings, engines and turbine blades utilizing the high penetrating power of neutrons.

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 atoms in materials, and how the materials behave under the influence of external perturbations such as temperature, pressure, magnetic or electric field, and chemical change. 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 large scale powerful user facilities that are not possible to develop, construct and operate by individual institutions and/or companies. Such highly sophisticated and expensive tools are by their nature centralized and staffed with specialists that provide expertise to the user community to optimize the scientific benefit 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 are reflected in the large number of publications appearing annually in the most important scientific journals.

Scientific Challenges

As new areas of science open up that are impacted by neutron scattering research, new instrumentation capabilities must be developed at the neutron scattering facilities and must undergo a continual upgrade and refinement process to provide optimal capabilities for the user program and to enable world-class scientific research. Much of the current and future developments focus on increased effective intensity using new detector technology, increased resolution using long wavelength neutron beams, and new sample environment capabilities.

Projected Evolution

Neutron scattering will continue to play a central role in the growth of BES programmatic science. The set of instruments associated with these facilities provides unique scientific and technical capabilities that serve the needs of the scientific community. These facilities necessarily must be kept in an optimal operational condition with increasing availability of user time in order to maintain and increase the tremendous scientific achievements they have facilitated.

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 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 or co-located except at major user facilities. These facilities are routinely made available on a scientific merit basis to the broad research community. There are five NSRCs:

- Center for Functional Nanomaterials (CFN) at Brookhaven National Laboratory
- Center for Integrated Nanotechnologies (CINT) at Los Alamos National Laboratory and Sandia National Laboratories
- Center for Nanophase Materials Sciences (CNMS) at Oak Ridge National Laboratory
- Center for Nanoscale Materials (CNM) at Argonne National Laboratory
- The Molecular Foundry (TMF) at Lawrence Berkeley National Laboratory

Unique Aspects

Nanotechnology is the understanding and control of matter at dimensions of roughly 1 to 100 nanometers (one billionth of a meter), where unique phenomena enable new applications. At these size scales, small numbers of atoms, molecules, and supramolecular structures exhibit new phenomena which produce novel electronic, optical, chemical and structural macroscopic properties. To discover, understand and synthesize nanostructures, NSRCs make available sophisticated research tools for nanoscience and nanotechnology 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 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 phenomena and 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 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.
- BES 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.

Significant Accomplishments

All five NSRC facilities entered full user operations between FY 2006 and FY 2008. In the operations phase of the NSRCs, user activity has increased substantially from four operational centers with nearly 800 unique users in FY 2007 to the present five operating centers serving 2,300 users in FY 2013. Since their inception the NSRCs have served over 11,200 users and are essentially at capacity. Many new and exciting discoveries have emerged in a wide range of nanoscience areas. Research highlights include:

- The electron beam directed assembly of polymers with features relevant to terabit per square inch magnetic storage media,
- Novel metamaterials for next generation terahertz flat optics,
- Unprecedented spatial resolution hard xray optics for nanotomography,
- Precision polymer deuteration processes for neutron beam probing of soft material folding behavior, and
- Formation of the first 2D supramolecular organic framework with honeycomb periodicity using a novel solution-based self-assembly approach.

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 National Science and Technology Council (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 are in full operation phase. NSRC scientists have established significant major capabilities and leadership in several areas of nanoscience and work effectively with the large user community and their collocated beam facilities. The NSRCs had their Triennial Reviews in FY2012. The number of user proposals has steadily increased and acceptance rates have begun to decrease showing that the Centers are near or at capacity for their funding level. Publication productivity in high-impact journals and the increasing user demand are signs that the NSRCs have been assimilated into the national scientific infrastructure. The NSRCs are expected to perform as world-leading institutions, excelling both in scientific impact and productivity and in working with users.

Electron-beam Microcharacterization Centers

Portfolio Description

The electron-beam microcharacterization centers (EBMCs) operate as national user facilities and work to develop next-generation electron-beam scattering and diffraction instrumentation, and conduct corresponding research. One-of-a-kind signature and world-class instrumentation are available including scanning, transmission, and scanning transmission electron microscopes; atom probes and related field ion instruments; related surface characterization apparatus; scanning probe microscopes; ancillary tools such as spectrometers, detectors, and advanced sample preparation equipment. These facilities are routinely made available on a scientific merit basis to the broad research community.

There are three EBMCs:

- Electron Microscopy Center for Materials Research (EMC) at Argonne National Laboratory (ANL)
- National Center for Electron Microscopy (NCEM) at Lawrence Berkeley National Laboratory (LBNL)
- Shared Research Equipment (ShaRE) program at Oak Ridge National Laboratory (ORNL).

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, a single one. Furthermore, the use of these charged particles allows electromagnetic control and lensing of electron beams resulting in spatial resolution better than interatomic separations (i.e., approaching or less than 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. The EBMCs have a broad range of capabilities and are accessible without usage fees for non-proprietary work, with instrument time and staff support allocated on the basis of peer review of proposals.

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 prior to FY 2007, called the Structure and Composition of Materials program at that time.
- There are also strong interactions with other BES user facilities, particularly with the collocated Nanoscale Science Research Centers. The electron beam centers are used by

researchers funded by BES, other parts of the Office of Science, other parts of the Department of Energy, and numerous other federal agencies and industry.

- BES 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.

Significant Accomplishments

Major historical accomplishments for the electron-beam characterization centers have spanned improvements in resolution and other performance measures, development of unique capabilities, and outstanding scientific results.

- 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) are such examples; all constituted world-leading instruments in demonstrated lateral spatial resolution. TEAM 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.
- 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, have 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 the suite of EMBC 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:

- Determining the atomic and nanoscale origins of macroscopic properties, for developing new high-performance materials ranging from those used in structural applications to those used in microelectronics
- Elucidating the underlying science involved in chemical processes such as catalysis and charge transport
- Probing the interfaces between hard and soft matter in operating 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

A BES workshop will be held in February 2014 on the “Future of Electron Diffraction and Scattering” to identify the scientific frontiers that are addressable by the next generation of electron probes.

Projected Program Evolution

The EBMCs are in full operation phase and the scientists have established significant major capabilities and leadership in several areas of electron probe science and characterization. They work effectively with the large user community, and their collocated NSRC (Nanoscale Science Research Center) and beam facilities. 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; high 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. There is strong mission alignment and scientific complementarity between the EBMCs and NSRCs. As such, the EBMCs will merge with their respective collocated NSRCs in FY 2015 to produce combined nanoscience research capabilities that are unique in the world.

Accelerator and Detector Research

Portfolio Description

This activity supports basic research in accelerator physics, x-ray and neutron detectors, and advanced x-ray optics instrumentation. Accelerator research is the cornerstone for the development of new technologies that will improve the 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 in research leading to a new and more efficient generation of photon and neutron detectors and in x-ray optics, both are overlooked but crucial components in the optimal utilization of the neutron or photon beams. Research includes studies on creating, manipulating, transporting, and diagnosing ultra-high brightness electron beam behavior from its origin at a photocathode to propagation through undulators, and to transporting, analyzing and detecting x-ray beams. Studies on achieving sub-femtosecond free electron laser (FEL) pulses are also undertaken. Demonstration experiments are being pursued in advanced FEL seeding techniques, the study of methods to control the spectral properties of an x-ray self-amplified spontaneous emission (SASE) FEL using amplitude and phase mixing and other optical manipulations to reduce the cost and complexity of seeding harmonic generation FELs. Theoretical and experimental studies on collective electron effects are also supported.

Unique Aspects

Technological advances require new materials and chemical processes for novel and improved sources of energy. 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. 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. 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 Research 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, biosciences, and much more.
- There is an ongoing collaboration with the Advanced Scientific Computing Research program to support code development relevant to beam dynamics and to develop tools and codes addressing the exponential growth of experimental data at the BES facilities.
- This activity also interacts with other DOE offices, especially in the funding of capabilities whose cost and complexity require shared support.
- This activity collaborates with the National Science Foundation on Energy Recovery Linac research.
- There are ongoing industrial interactions through the DOE Small Business Innovation Research and Small Business Technology Transfer (SBIR/STTR) Program awards for the

development of advanced accelerator technology, x-ray and neutron detectors, and x-ray optics instrumentation.

Significant Accomplishments

- This activity was a major supporter of theoretical and experimental studies that led to realization of the Linac Coherent Light Source (LCLS). Theoretical and simulation studies addressed many of the fundamental physics questions concerning SASE FELs and high-brightness beams leading to successful experiments.
- An advanced ^{3}He neutron detector prototype was developed that is capable of measuring pulse height distributions with the highest energy resolution in this mode and covering large areas as required by many neutron source instruments.
- Coded source neutron microscopy has been demonstrated at 25 times magnification, improving resolution and reducing scattering noise in existing limited-resolution imaging detectors.
- A new concept to generate multiple simultaneous spikes in an x-ray FEL spectrum by periodic modulation of the undulator magnetic field has been demonstrated. This allows the generation of two-color spectra and the unique exploration of molecular systems.
- An innovative *in situ* and *in operando* x-ray analysis system was developed to fully explore and analyze the physics and chemistry of photo-cathode materials.
- A program that explores the application of 3D techniques to the difficult problem of integrating x-ray sensors of high-resistivity silicon and readout application specific integrated circuits of low-resistivity silicon has achieved the first successful three-dimensionally integrated chip for photon science. When fully developed these sensors will be capable of handling synchrotron radiation at energies up to 100 keV with 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 electron gun was successfully built under the specifications of repetition rates up to 1 MHz, small beam size, and high charge per bunch.

Mission Relevance

The Accelerator and Detector Research program supports the most fundamental of research needs 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 higher-precision, more efficient detectors capable of acquiring data several orders of magnitude faster than state-of-the-art detectors, and advanced x-ray optics that offer higher precision and higher accuracy in order to fully exploit 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.
- Sponsor research to support the BES Advisory Committee recommended light source to provide high repetition rate, ultra-bright, transform limited, femtosecond x-ray pulses over a broad photon energy range with full spatial and temporal coherence.
- Development of components suitable for diffraction-limited storage rings with beamlines, optics, and detectors compatible with the increase in brightness afforded by upgraded storage rings.
- 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.
- Low-background, high-spatial-resolution neutron detectors, and replacement of Helium-3-based detectors.
- Development of x-ray optics instrumentation that can compensate for detector limitations to enhance the combined spatial, temporal and energy resolution of experimental data.
- Special emphasis on R&D leading to more energy efficient machines and devices that go beyond the most common methods of particle acceleration.

Projected Evolution

X-ray and neutron scattering will continue to play a central role in the growth of BES programmatic science. The Spallation Neutron Source (SNS) will be the most powerful neutron spallation source in the world for years to come. Future FEL light sources are expected provide high repetition rate, ultra-bright, transform-limited, femtosecond x-ray pulses over a broad photon energy range, with full spatial and temporal coherence.

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 radiofrequency (RF) systems, and photon beams of enhanced temporal coherence, such as produced by improved seeding techniques or x-ray oscillators, in the case of FELs. 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. Higher neutron flux capabilities at the SNS 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. Finally, R&D emphasizing energy efficient machines and strong collaborations among the national laboratories and universities will allow a cost-effective, coordinated, and interdisciplinary approach to research and development in accelerators, detectors and x-ray instrumentation.

Atomic, Molecular, and Optical Sciences

Portfolio Description

This activity supports theory and experiments to understand structural and dynamical properties of atoms, molecules, and nanostructures. 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. The study of energy transfer within isolated molecules provides the foundation for understanding chemical reactivity, the processes of energy transfer that make and break chemical bonds. Topics include the development and application of novel, ultrafast optical probes of matter, particularly with x-rays; the interactions of atoms and molecules with intense electromagnetic fields; and studies of collisions and many-body cooperative interactions of atomic and molecular systems. Capital equipment funding is provided for items such as lasers and optical components, 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 Atomic, Molecular, and Optical Sciences (AMOS) program are critical components of the fundamental science effort of the Department of Energy (DOE), and research conducted at Basic Energy Sciences (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.

Relationship to Other Programs

- The program supports experiments involving 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.
- A close working relationship exists with the National Science Foundation (NSF) Atomic Molecular and Optical Physics Programs. These programs co-fund studies by the National Academies in relevant areas and the National Academies' Committee on Atomic, Molecular, and Optical Sciences (CAMOS).

Significant Accomplishments
The AMOS activity has been a major supporter of experimental and theoretical studies of the fundamental properties of atoms, ions, and small molecules and of collisional 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 third 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 fourth 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 accomplishments in the program include:

- Generation of ultrashort x-ray pulses from table-top, laser-based sources to provide complementary capabilities to x-ray free electron lasers.
- High harmonic generation in gases has been used to shift laser light from the infrared or visible to extreme-ultraviolet and soft x-ray wavelengths.
- Optical manipulation of the harmonics has been used to produce isolated extreme ultraviolet pulses shorter than 100 attoseconds in duration.
- AMOS scientists were deeply involved in commissioning and early experiments at the LCLS. Results at this facility include inner-shell photoionization of atom and molecules, single-particle imaging of nanoparticles, inner-shell lasing, and non-linear x-ray spectroscopy.

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, free-electron laser, and nanoscience facilities. Similarly, studies of formation and evolution of highly-excited states of atoms, molecules, and nanostructures provide 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, 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 scientists will continue to have a prominent role at BES user 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 complex chemical systems. Experimental and theoretical AMOS tools will be used in the study of low-energy electron-molecule interactions in the gas and condensed phases.

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. Also supported are new opportunities to attain predictive understanding of chemical reactivity, 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, (2) Condensed Phase and Interfacial Molecular Science, and (3) Computational and Theoretical Chemistry. Each program area has a core focus, and there are significant synergies among them:

- *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 energy-relevant chemical, physical, and electron-driven and photon-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. 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. 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 mesoscale systems, such as the effects of solvation on chemical structure and reactivity.
- *Computational and Theoretical Chemistry (CTC)* research emphasizes development and integration of new and existing theoretical and computational approaches for the accurate and efficient description of processes relevant to the BES energy mission. Of special interest is foundational research on computational design of molecular- to meso- scale materials and processes, and on next-generation simulation of processes that are so complex that efficient computational implementation must be accomplished in concert with development and testing of theories and algorithms. As such, 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 well beyond standard representations to address excited-state dynamics, low-energy diffusive effects, 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 matter and radiation in vacuum and in solvated 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, enabling long-term progress in difficult scientific areas as well as effective coupling to DOE missions:

- Synergy among the three program areas is a hallmark of the Chemical Physics portfolio. Methods, tools, and knowledge developed in each area inform the others, and many supported efforts bridge the three program areas; this synergy is pronounced in concerted collocated efforts supported at Pacific Northwest and Lawrence Berkeley National Laboratories, and at the Combustion Research Facility (CRF).
- The program is uniquely positioned to undertake joint theoretical, computational and experimental efforts. Such a capability is essential for validating and improving models and methods used to design chemical processes, which are increasingly complex and data-intensive.
- The GPCP program 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 CRF, a unique, multi-investigator research laboratory that has 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.
- The CTC program 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 and coordinates and leverages efforts with other agencies and facilities. These interactions include:

- *Gas Phase Chemical Physics:* The GPCP program and DOE EERE support coordinated combustion research efforts at the CRF and at Argonne National Laboratory (ANL). The GPCP program works with 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) as an active member of the Multi-Agency Coordinating Committee on Combustion Research (MACCCR) to host an annual Fuels Research Review as well as combustion workshops. These linkages include common principal investigators and industry relationships in a number of programs, joint workshops, and coordination meetings. GPCP supports the Chemical Physics Beamline at the Advanced Light Source (ALS).
- *Condensed Phase and Interfacial Molecular Science:* There is a strong coupling between the CPIMS and Solar Photochemistry programs in the fundamental chemistry and physics of radiolytic processes in condensed media and at interfaces. Support is provided for basic research to scientists at Pacific Northwest National Laboratory who utilize the William R. Riley Environmental Molecular Sciences Laboratory, a national user facility operated by the DOE/SC Office of Biological and Environmental Research. 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. Support is provided for the Molecular Environmental Science Beamline at the ALS.
- *Computational and Theoretical Chemistry:* 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 and participated in efforts with the technical community and other agencies to foster advanced approaches to design of materials and chemistry. These efforts have included workshops on BES-relevant Scientific Discovery through Advanced Computing, workshops on materials and chemistry by design, and workshops aimed at understanding the increasing role of computational chemistry in industry.

Significant Accomplishments

- Impacts in fundamental science include the development of 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. The capabilities have been extended to the development of molecular beam and laser sputtering techniques for the study of atomic clusters as prototypical models for catalysis.
- 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. Advances in high resolution time-resolved spectroscopy have yielded information on intermediates and product state distributions with unprecedented isomeric specificity.
- 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 Criegee reaction kinetics important in combustion and atmospheric chemistry.
- Development of high-fidelity engine simulations has demonstrated the importance of molecular scale dynamics, e.g. quantum tunneling, on engine performance.
- This activity has played a major role in the development of quantum chemistry methodologies for accurate predictions of chemical properties. 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.
- Development and application of new approaches to density functional and traditional wavefunction-based methods for predicting energetic processes involving ground- and excited-electronic states. These developments allow BES researchers to predict excited-states in large light-harvesting complexes, address thermal and electronic transport through molecules, quantify dynamics associated with multiple carrier generation, investigate conversion of visible light into chemical energy and address plasmon-driven chemical reactions. They have also led to new approaches for non-destructive spectroscopic evaluation and interrogation of chemical conversion and separation systems and for unprecedented approaches to probing potential energy surfaces in mesoscale systems such as metal-organic frameworks.

Mission Relevance

- The GPCP 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 CPIMS 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 CTC activity aims to advance the Chemical Physics goals just described and also advance mission areas across BES. For example, supported activities 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 include:

Gas Phase Chemical Physics

- 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 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 methods of uncertainty quantification and model reduction to enable high-fidelity predictive combustion models.
- Understanding the interaction of chemistry and fluid dynamics in turbulent combustion conditions.
- Role of multiphase chemistry in combustion, including fuel aerosols and soot particle formation and growth.

Condensed Phase and Interfacial Molecular Science

- 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 a structural basis for understanding gas/surface interactions, encouraging site-specific studies that measure local behavior at defined sites.
- Understand the molecular origins of condensed phase behavior and the nature and effects of non-covalent interactions including hydrogen bonding and proton transport.
- Develop new experimental and theoretical tools that push the horizon of joint space-time resolution needed to probe chemical behavior selectively at interfaces and in solution.

Computational and Theoretical Chemistry

- Improve efficiency for quantum-mechanical based simulations of chemical and molecular processes that impact the BES mission. Such improvements are achieved through multi-scale coupling, melding of chemical-, physical- and mathematical- methods, or improved parallelization.
- Develop new theoretical time-domain and frequency-domain simulation tools for computing structural, transport, and optical properties of nanoscale systems in polarizable environments.
- Develop methods to computationally determine how to externally control both resonant and non-resonant energy-, charge-, spin- 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.

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 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. 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.

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. 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 DOE 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. This research is required for effective nuclear waste remediation, fuel-cycle separation, and for design of next-generation nuclear reactors.

Relationship to Other Programs

The Solar Photochemistry research effort interfaces with several activities in BES as well as within DOE.

- Within BES, research efforts are coordinated with 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.
- This research activity sponsors – jointly with other BES research activities as appropriate – program reviews, principal investigators' meetings, and programmatic workshops.
- Many projects within solar photochemistry coordinate efforts with the Joint Center for Artificial Photosynthesis Energy Innovation Hub, as well as with the many relevant Energy Frontier Research Centers active in solar energy research.

- The work of solar photochemistry 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 in the Solar Photochemistry program is closely coordinated with the BES Condensed Phase and Interfacial Molecular Sciences in the physical and chemical aspects of radiolysis.
- There are also important interfaces between the radiation sciences activity and 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

Significant advances in this program are found 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 result from past investigations of model photosynthetic systems and their emulation. Researchers have discovered unexpected quantum coherence in energy transfer within the light absorbing antenna complexes of natural photosynthetic systems, which enables the absorbed light to spread out and sample the physical space of the chromophores and find the right place for electron transfer charge separation.
- In research on quantum dot nanoparticles, scientists have predicted and confirmed the generation of two electron hole pairs through absorption of a single photon. A vision for a new generation of solar cells has been envisioned, labeled “third generation,” that will exceed the Shockley-Queisser limit on present solar cell efficiencies.
- 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 thousand inorganic catalysts within the past several years. A new field in photon driven fuel production has been created with the study of molecules located at solid surfaces where new pathways exist for charge transfer-induced catalysis.
- Many novel nanostructures of semiconductor electrodes have been developed for the photoelectrolysis of water and reduction of CO_2 to multi-carbon compounds. This research in Solar Photochemistry has formed the basis of the Joint Center for Artificial Photosynthesis Energy Innovation Hub and of a half dozen Energy Frontier Research Centers focused on solar photoconversion.

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. 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 transport needs to be applied to activation of small molecules such as CO_2 and H_2O via photocatalytic cycles to transform them into fuels. The principles of this research are being extended to the problem of nitrogen fixation. The major scientific challenge for photoelectrochemical energy conversion is that semiconductors capable of absorbing solar photons are susceptible to oxidative degradation in water, whereas oxide semiconductors resistant to oxidative degradation absorb too little of the solar spectrum. Ongoing research activities include multibandgap, multilayer cascade-type semiconductors, photosensitized nanoparticulate solids, and the study of multiple exciton generation within nanoparticles. Experimental and theoretical studies on quantum coherence in light antenna complexes should lead to 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 energy transfer and the generation, separation, and recombination of charge carriers in organic-based molecular semiconductors, which can lead to a new type of inexpensive and flexible solar cell. A workshop on *Basic Research Needs for Advanced Nuclear Energy Systems* 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. These interfaces abound in nuclear reactors and high level radioactive 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

An increased emphasis on solar fuels production will require new semiconductor and molecular systems for photoconversion. Of emphasis are new hybrid systems that feature molecular catalysis at surfaces and new nanoscale structures for the photochemical generation of fuels. Novel quantum size structures, such as hybrid semiconductor/carbon nanotube assemblies, fullerene-based linear and branched molecular arrays, and semiconductor/metal nanocomposites, must be examined. 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. In these efforts, an enhanced theory and modeling effort is needed for rational design of artificial solar conversion systems. In radiation chemistry, 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.

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, and biochemistry of carbon fixation in plants, algae, and photosynthetic microbes. An emphasis is placed on research that intersects biological sciences and energy-relevant chemical sciences and physics, such as in efficient photon capture and charge separation, self-assembly of nanoscale components, 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 provides a critical scientific knowledge base that can inspire the roadmap for artificial photosynthesis and enable new approaches 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 has been 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. Its multidisciplinary research program is focusing on complex questions in photobiology, carbon fixation, and high energy redox reactions and makes use of novel high-throughput, non-invasive phenotyping technologies being developed at the PRL.

Relationship to Other Programs

The Photosynthetic Systems program interfaces with several activities within BES as well as within DOE and other federal agencies.

- Within BES, research efforts are coordinated with the Physical Biosciences program, particularly in areas of carbon fixation and organizational and structural principles of the cellular machinery; the program also interacts with the Solar Photochemistry, Catalysis Science, and Biomolecular Materials programs in bioinspired and biomimetic photosynthetic systems and components.
- This research activity sponsors – jointly with other core research activities and the Energy Frontier Research Centers program as appropriate – program reviews, principal investigators' meetings, and programmatic workshops.
- The basic research supported by the program also collaborates with the genomics- and biotechnology-related programs in the DOE Office of Biological and Environmental Research and the DOE Advanced Research Projects Agency-Energy.

- This activity interacts with the DOE Office of Energy Efficiency and Renewable Energy through its activities in the Solar Energy Technologies program on photovoltaics, the Biomass program on algal and plant feedstocks, and the Fuel Cell Technologies program.
- The program collaborates and coordinates its activities with the National Science Foundation, 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. 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. Building on that strong foundation, research in the Photosynthetic Systems program has made significant advances in our fundamental understanding of how nature captures energy from sunlight and converts that energy into chemical energy for the cell.

- Elucidation of the structure of the highly efficient light-harvesting chlorosome antenna complex and characterization of critical components of the algal light-harvesting complex are revealing the structure and molecular components important for light capture.
- Studies of photosynthetic reaction centers have identified regions important for controlling the directionality of charge separation and the efficiency of electron transfer.
- In characterizing the structure/function relationships in photosystem I, scientists are uncovering the fundamental mechanisms of photochemical proton-coupled electron transfer reactions, potentially leading to breakthroughs for coupling photons to fuels in photosynthetic hybrid systems.
- A study of photosystem I components from algae resulted in the development of a biohybrid complex that could produce hydrogen five times more efficiently than observed previously.
- A critical advance has been development of innovative methodologies for collecting simultaneous x-ray diffraction/x-ray emission spectroscopy data from photosystem II using femtosecond pulses from an x-ray free electron laser. Using these cutting-edge techniques, scientists achieved the unprecedented simultaneous imaging of the atomic and electronic structures of photosystem II, gaining critical insights into water oxidation.
- Complementary approaches probing charge transfer mechanisms and pathways in photosystem II are revealing how water molecules are directed to, bound, and activated by the oxygen-evolving complex. Through these studies, a more complete picture is being developed of the energy and electron transfer processes in natural photosynthesis.

Mission Relevance

The impact of research in this activity is to uncover the underlying structure-function relationships and to probe dynamic processes in natural photosynthetic systems. Such fundamental knowledge can guide the development of robust artificial and biohybrid systems for conversion of solar energy into electricity or chemical fuels. Through this understanding, solar fuel systems can be designed which selectively use the best features from nature while bypassing the shortcomings of biology. Achieving this goal would impact DOE’s efforts to develop solar energy as an efficient, renewable energy source. Further, the knowledge generated by this research may guide the improvement of photosynthetic efficiency in plants, algae, and microbes which would significantly enhance 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 continue to be 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. Increased understanding of the temporal and spatial dynamics and regulation of photosynthesis is another critical research need. 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 biohybrid and artificial systems for instance. Such fundamental knowledge of natural photosynthesis can play a significant role in the development of renewable, cost-effective, and environmentally-sustainable energy systems and supplies.

Projected Evolution

Advances in genomics technologies such as metabolomics along with increased availability of plant genomic sequences provide 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. The program will continue to emphasize research to understand the structural and mechanistic features of photosynthetic complexes; determine the mechanisms behind photon capture and charge transfer; characterize and control the weak intermolecular forces governing molecular assembly in photosynthetic systems; understand the biological machinery for cofactor insertion into proteins and protein subunit assemblies; uncover the biochemical mechanisms that can enhance fuel production in photosynthetic systems to build on results from combinatorial, directed evolution, and high-throughput screening methods; and determine 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 plants, algae, and non-medical microbes is sought. Research supported includes studies that investigate the principles and 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 the structure/function of the active sites of energy-relevant proteins that provide 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 fundamental science that applies the tools of physical science to address biological phenomena underlying the production and conservation of energy in plants, algae 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 has been 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. The multidisciplinary research program at the PRL is focusing on complex questions in photobiology, carbon fixation, and high energy redox reactions. As part of this research, the PRL is developing and using novel high-throughput, non-invasive phenotyping technologies.

Relationship to Other Programs

This research activity interfaces with several complementary activities within BES as well as within DOE and other federal agencies.

- Within BES, research efforts are coordinated with the Photosynthetic Systems program in the areas of natural photosynthesis, carbon fixation, and the organizational and structural principles of the cellular machinery; with the Catalysis Science program in the area of enzyme and biomimetic catalysis; with the Separations and Analysis program in the area of analytical tool and technology development; and with the Biomolecular Materials program in the area of synthesis of novel bio-inspired materials.

- This research activity sponsors – jointly with other core research activities and the Energy Frontier Research Centers program as appropriate – program reviews, principal investigators' meetings, and programmatic workshops.
- This activity also supports and complements basic research relevant to the DOE Office of Biological and Environmental Research, in particular for its activities in imaging and biomass conversion technologies; the DOE Office of Energy Efficiency and Renewable Energy, in particular with Biomass Program efforts to enhance microbially-mediated conversions of lignocellulosic and other plant feed stocks; and the Advanced Research Projects Agency-Energy, in particular related to its efforts to develop new technologies for methane utilization and to enhance the capabilities of plants to store solar energy as plant lipids.
- 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. 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. Significant accomplishments of the program include:

- The determination of the biosynthetic pathway for methane production from CO_2 and molecular hydrogen, which led to the discovery and structural determination of many unique cofactors involved in archaeal electron transfer pathways. Mechanistic studies are now providing insights that will aid the design of novel catalysts.
- The elucidation of the biochemistry and genetic regulation of plant lipid synthesis, as well as enzyme structure/function studies that have identified the catalytic basis for the introduction of various modifications at precise points on a fatty acid chain. Current studies in this area are providing important information needed to increase the production of energy-rich lipids in oil seeds as well as aerial tissues.
- The determination of the structure of many of the complex polysaccharide components of the plant cell wall, as well as many important aspects of its supramolecular structure, have guided strategies aimed at improving the conversion efficiencies of plant biomass to fuel molecules.
- The elucidation of the specificities and insights into the mechanisms of numerous plant membrane transporters has opened up new opportunities to improve the properties and sustainability of plants being considered as future energy crops.
- Studies of hydrogenase structure, function, and biosynthesis have provided information on the assembly and mode of action of complex metal-organic cofactors and gated electron flow that are critical for the production of hydrogen in biological systems.

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
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 principles behind the rational design of catalysts and the deliberate control of chemical transformations. The chemistry of most interest pertains to the conversion of energy resources. Medicinal and human chemistry are outside the scope of this activity. Research includes the elucidation of catalytic reaction mechanisms and kinetics; the synthesis of catalytic sites, molecular ligands, metal clusters, and reaction environments designed to tune 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 specific to catalytic pathways.

Unique Aspects

This activity funds a large fraction of the basic research in catalysis science in the Federal government. In particular, it supports novel research into energy-specific catalytic chemistry, and into plant-derived chemistry and hybrid solid-state/organic chemistry. The newer advances require complex expertise in different areas of science and engineering, seldom possessed by single individuals, hence this activity has funded small teams dedicated to interdisciplinary research. An important element of this activity is the emphasis on maximizing the atom and energy efficiency of the transformation of natural or man-made chemical resources. Such optimization usually demands the discovery of new chemical pathways not present in nature; hence bio-inspiration is important but insufficient for progress. Control of catalytic pathways requires not only new catalysts, but also finely tuned processes that must be developed specifically for the intended chemical applications. While advanced materials synthesis, enhanced by molecular-level theory and new in-situ instrumentation, is key to designing new catalysts, they are not sufficient for the discovery of more efficient and long-lived chemical transformations. To specifically pursue efficiency, researchers in this program synergistically combine approaches used in heterogeneous, homogeneous, or bio catalysis, and reaction engineering, usually pushing the individual frontiers. For operando and in-situ characterization of working reactions, catalysis researchers must increasing resort to techniques with high spatial and time resolution and molecular-level sensitivity, and they also participate in the advancement of such techniques. Most instruments are lab-based but DOE facilities are utilized as needed.

Relationship to Other Programs

- The Condensed Phase and Interfacial Molecular Science program and the Computational and Theoretical Chemistry program support some aspects of interfacial science, surface and solution chemistry, quantum mechanical theory, molecular modeling, and simulation of catalytic-related phenomena.
- The Solar Photochemistry activity supports some aspects of photocatalysis and photoelectrocatalysis, while the Physical Biosciences activity does so for enzymatic catalysis.
- The Separations and Analysis activity and the Materials Discovery, Design and Synthesis Team support the synthesis of organic and inorganic materials relevant also to catalysis.
- The BES synchrotron facilities have beamlines customized for catalysis science researchers.

- Two BES Nanoscale Science Research Centers (NSRCs) have thrust areas that provide unique capabilities for the synthesis and characterization of nanoscale catalysts.
- Several EFRCs and the Joint Center for Artificial Photosynthesis Hub support investigators and topics relevant to catalysis.
- The Catalysis Science activity produces research outcomes of relevance to programs of the Office of Energy Efficiency and Renewable Energy, and the Office of Fossil Energy. Other federal agencies also support catalysis research, but not comprehensively: National Science Foundation (NSF), National Institutes of Health (NIH), Environmental Protection Agency (EPA), and the Defense Department agencies.

Significant Accomplishments
Researchers funded by this activity have received numerous awards from national and international scientific societies. They have innovated on the molecular-level understanding of catalytic processing of hydrocarbons and carbohydrates, for example:

- Selective oil reforming and hydroprocessing pathways with new families of synthetic zeolites and noble metal alloys, mixed sulfides and phosphides;
- Selective oxidation of hydrocarbons for the manufacturing of synthetic fuels, commodity and specialty chemicals, with novel mixed metal oxides and supported metal nanoparticles;
- High-yield metathesis of unsaturated compounds with new organometallic transition metal complexes, a ubiquitous reaction that brought a Nobel Prize to two PIs;
- Polymerization of alkanes and alkenes with novel single-site metallocene catalysis, responsible for a large fraction of all oil-derived and biomass-derived industrial polymers, which led to a National Medal of Science to a program PI;
- Selective and high-yield rearrangement of C-C, C-O, and C-H bonds in organic molecules, thanks to atomic-level control of nanoparticle composition, support interface, and reconstruction, which evolved from classical surface science and merited a National Medal of Science to a program PI;
- Low-temperature nitrogen splitting and CO activation with novel organometallic complexes and heterogeneous catalysts, a highly sought breakthrough. Nitrogen splitting is the essential step in the synthesis of ammonia and fertilizers; and water-gas shift via CO oxidation with water is responsible for the synthesis of most industrial hydrogen. Ammonia and hydrogen production account for over 5% of the world's energy use.

Mission Relevance
Catalytic transformations impact a large range of DOE mission areas. Particular emphasis is placed on catalysis relevant to the conversion and use of fossil and renewable energy resources, such as the conversion of crude petroleum and biomass into clean burning fuels and materials. Catalysts are used in fuel cells and batteries as well as photocells. Catalysts are essential for energy-efficient routes for the production of basic chemical feedstocks and value-added chemicals, as well as for minimizing the production of unwanted products.

Scientific Challenges
The unique challenge for Catalysis Science is to predict and control catalytic reaction mechanisms and rates in order to design new and more efficient ways to convert natural or man-made products. A special focus is the identification of carbon-neutral pathways for the catalytic conversion of biomass-derived feedstocks, which are characterized by multiple chemical

functionalities. New hybrid organometallic-inorganic porous catalysts are able to match in their structure the multifunctionality required by the feed. To synthesize such catalysts, traditional 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 achieve unique molecular recognition properties (for example, size, shape, chirality, and hydrophobicity). The interfacial interactions provoked by ligands, supports, and solvent spheres generate ways of tuning the reactivity and stability of catalytic materials.

The characterization of synthetic catalysts demands 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. In particular, characterization of the reaction intermediates and pathways typically resorts to labeling, trapping, and molecular probe experiments 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 challenging, particularly with heterogeneous or hybrid catalysts, sometimes demanding the use of cascade or tandem reactions. For homogeneous catalysis, one of the long-term 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.

Projected Evolution

The science of catalytic chemistry is still emerging. Much experimental information has been accumulated relating catalytic structure, activity, selectivity, and reaction mechanisms. Phenomenological catalysis is however evolving into predictive catalysis by means of integration of experiment and theory, reproducible synthesis of single-site catalysts, and thorough characterization of catalysts and reaction mechanisms. The convergence of heterogeneous, homogeneous, and biocatalysis is progressing. Examples are the use of long-range or secondary structure and structural flexibility to affect both selectivity and also activity of inorganic catalysts, or the use of non-thermal activation, such as electrochemical and photochemical activation. At present, research is leading to the substitution of noble and rare elements by non-precious and abundant elements or compounds. New chemical functions are being achieved by utilizing mesoscale or collective properties of materials. Natural products of fossil and renewable origins are being converted into common intermediates that serve as platforms for the energy-carrier and chemical industries of the future. Catalytic cycles for electro- or photo- activation of abundant chemicals are also receiving special attention.

Heavy Element Chemistry

Portfolio Description

This activity supports basic research on the fundamental chemistry of the elements beyond actinium (those elements with an atomic number greater than 89); typically uranium, neptunium, plutonium, americium, and curium. The goal of this activity is to understand the underlying chemical and physical principles that determine the behavior of the actinides and transactinides elements. The unique molecular bonding of the heavy elements is explored using theory and experiment to elucidate electronic and molecular structure as well as reaction thermodynamics. Emphasis is placed on resolving the *f*-electron challenge; the chemical and physical properties of these elements to determine solution, interfacial, and solid-state bonding and reactivity; fundamental transactinide chemical properties; and the fundamental science underpinning the extraction and separation of the actinides. While the majority of the research supported by this activity is experimental, theoretical proposals are considered such as more adequately describing quantum-mechanically spin-orbit interactions and relativistic effects, which integrate closely with existing experimental research. Synthetic research is pursued within this this activity on molecules that contain heavy elements and on ligand development to separate and sequester heavy elements. Spectroscopic research on the chemical bonding and reactivity of all manner of energy-relevant molecules is also pursued within this activity. Capital equipment funding is provided for items such as instruments used to characterize actinide materials and equipment to handle the actinides safely in laboratories and at user facilities.

Unique Aspects

This activity represents the only Federal, non-applied research program focused primarily on the chemistry of the actinide elements. All of the research sponsored through this activity is peer-reviewed and unclassified. Federal support of heavy element chemistry began with the Manhattan Project as the elements beyond uranium were unknown before then. Since then, this activity has been continuously supported in some manifestation throughout the Atomic Energy Commission years up to the present-day Department of Energy due to its importance to energy and defense. The long term support of this activity to researchers investigating the fundamental properties of the actinides has been crucial to maintain U.S.-based leadership in this critical field. Actinide researchers are supported through other Federal programs (such as the NSF and DOD), but aside from this activity, there is no program that identifies fundamental heavy element chemistry as a research thrust.

Relationship to Other Programs

- Improved knowledge of the fundamental properties of the heavy elements has a direct positive impact on many other Department of Energy missions, including but not limited to advanced nuclear energy, nuclear proliferation detection, defense program stewardship, and environmental remediation.
- This activity uniquely supports unclassified basic research on all the actinide and transactinide elements, while the more applied programs (nuclear energy, environmental, nuclear forensics, stockpile stewardship) limit their investigations to the chemical and material properties of specific elements and systems of strategic programmatic interest.

- This activity is closely coordinated with the BES Separations and Analysis activity, and is highly synergistic with the Catalysis program and Computational and Theoretical Chemistry program, as well as the Subsurface Biogeochemical Research program in the Office of Biological and Environmental Research and to nuclear fuel cycle research funded through the Office of Nuclear Energy.
- This activity sponsors research that is performed at many BES User Facilities; typically the Advanced Light Source (ALS), the Stanford Synchrotron Radiation Lightsource (SSRL), and the Advanced Photon Source (APS). Computational research is also supported that makes use of ASCR User Facilities.
- Related actinide nonproliferation research is pursued within the Office of Nonproliferation R&D of the National Nuclear Security Administration, the Basic Research program of the Defense Threat Reduction Agency, and at the National Technical Nuclear Forensics Center at the Department of Homeland Security.
- Based on programmatic priorities, this activity program does not fund research on: the processes affecting the transport of subsurface contaminants, the form and mobility of contaminants including wasteforms, projects aimed at optimization of materials properties including radiation damage, device fabrication, or biological systems, which are all more appropriately supported through other Department of Energy programs.

Significant Accomplishments
Early goals of this activity were to discover new elements and to determine their chemical and physical properties from microscale and tracer experiments, similar to the techniques that must still be used for the heaviest of elements due to their low-production rate. For the elements heavier than einsteinium in the periodic table, tracer techniques and one-atom-at-a-time chemistry have been developed and carried out to determine chemical properties. Organometallic chemistry has been enriched by discovery of many unique organoactinide compounds. Continual progress has been made on elucidating the novel and unique chemistry of the elements directly relevant to energy-production (the major actinides).

Recent accomplishments in the program include:
- Interpretations of spectroscopic results have provided thermodynamic quantities such as oxidation-reduction potentials and enthalpies of reactions.
- Molecular-level information on the geometry and energetics of bonding can now be obtained at 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.
- Measurements show the light actinide metals have delocalized 5f orbitals and resemble d-orbital transition metals, whereas the 5f electrons become localized at americium (halfway down the actinide series), resembling the rare-earth elements; although recent studies have shown divergent properties that indicate this largely uninvestigated field of chemistry is not a straightforward extrapolation from lighter actinide to heavier.
- The nuclear magnetic resonance of plutonium-239 has finally been measured, which could be the beginnings of the brand-new, fruitful field of plutonium NMR research.
- The exceptional computational challenge imposed by so many electrons and relativistic electron energies has spurred the development of innovative theoretical treatments.

Mission Relevance
This activity is broadly mission relevant to the Department of Energy and represents the nation's only program focused uniquely on the fundamental research on the elements beyond actinium. Knowledge of the chemical characteristics of the heavy elements 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 the environment. Knowledge of the physical properties of defense-relevant elements is required to develop technologies to counter proliferation of weapon-useable nuclear material. Better characterization and modeling of the interactions of actinides at liquid-solid and liquid-liquid interfaces is motivated by improving the separations processes that are essential for improved nuclear fuel cycles.

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. Resolving the role of the f-electrons is one of the three grand challenges identified in *Basic Research Needs for Advanced Nuclear Energy Systems* report of the Basic Energy Sciences Workshop (2006) and echoed in the report from the Basic Energy Sciences Advisory Committee: Science for Energy Technology: Strengthening the Link between Basic Research and Industry (August 2010). 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. The majority of this activity is pursued at the national laboratories or coordinated directly with them because of the infrastructure needed to handle these materials safely. Research in heavy element chemistry at universities through single-investigator grants is supported, encouraging collaborations between university and laboratory projects. 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 and 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.

Projected Evolution
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. At the frontier of the periodic table, theoretical chemists predict the properties of actinides and transactinides using modern calculation tools. Sophisticated quantum mechanical calculation techniques that take into account both spin-orbit and relativistic effects of actinide compounds and actinide species in environmental media are being developed.

Separations and Analysis

Portfolio Description
This activity supports fundamental research to enable predictive understanding, at molecular and nanoscale dimensions, of the basic principles involved in chemical recognition, separation, and analysis. A range of multidisciplinary experimental and computational approaches is employed, inspired by the potential for discovery of new concepts in a broad spectrum of current mission-relevant separation and analysis applications. Separation approaches include those using membranes, adsorption/desorption, complexation, extraction under both standard and supercritical conditions, chromatography and photodissociation. Chemical analysis research goals include improved sensitivity and applicability of ambient imaging mass spectrometry, and new approaches to analysis in complex, heterogeneous environments. Special emphasis is focused on techniques that combine chemical selectivity, spatial resolution and temporal resolution to achieve chemical imaging at the molecular- and nanoscale. Capital equipment funding is provided to enable measurement of separation/recognition properties, and components such as lasers, advanced mass spectrometers, nanoprobes, and microscopes for chemical imaging research.

Unique Aspects
This activity represents the Nation's most significant long-term investment in solvent extraction, ion exchange, and mass spectrometry. The combined activity with Heavy Element Chemistry is the nation's most significant long-term investment in the fundamental science underpinning actinide separations. 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 separations-related activity coordinates closely with the Heavy Element Chemistry Program to support the Department's stewardship responsibility for actinide and fission product chemistry and to its clean-up mission.
- Similarly, elements of the Separations and Analysis portfolio benefit from cooperation with the BES Computational and Theoretical Chemistry, Catalysis Science, Condensed-Phase and Interfacial Molecular Science, Geosciences and Materials Chemistry Programs. The analysis research, in particular, is coordinated with a broad range of BES programs benefiting from advanced chemical imaging.
- A number of BES Energy Frontier Research Centers support investigators and topics of relevance to this activity.
- Other federal agencies support investigators and topics that are mutually complementary. Participation in program management working groups assures coordination across the DOE in related areas such as fuel cells and carbon capture/sequestration.

Significant Accomplishments
This activity is responsible for such 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.

More recent accomplishments include:

- A new calixerene ligand-based separations process that complexes Cs+ based on research and development work performed by BES researchers at Oak Ridge National Laboratory is being used to clean up waste tanks at Savannah River National Laboratory.
- Significant contributions to the discovery of metal-organic framework (MOF) materials for carbon capture and other gas separations.
- New approaches to ion separations have resulted in related applications (e.g. patents applicable to desalination).
- A revolution in ambient and imaging mass spectrometry is having very broad impacts in the analysis community.
- New approaches for aerosol and particulate analysis that are impacting the atmospheric and climate change research communities.

Mission Relevance

Early relevance to the Manhattan Project and nuclear defense has broadened to cleanup of accumulated legacy wastes from the cold war era, improved efficacy and energy efficiency in industrial chemical and energy production, the growing emphasis on alternative energy sources and climate change, and on the separations and analysis requirements of the nanoscale revolution.

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, adsorption/desorption, crystallization, dispersion, coalescence, and transport properties of new membrane concepts and materials. The development of fundamental principles to guide design and synthesis of ligands, adsorbents, and self-assembled complexants and membranes are also required. These, in turn, pose challenges to analysts to characterize these and related amorphous materials through analysis of scattering data or other methods. Other analytical challenges include direct observation of molecular scale interactions, self-assembly and chemical 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.

Projected Evolution

Separations research will continue to advance the understanding and control of the atomic and molecular interactions between target species and separations media, and the resulting molecular structures, dynamics, kinetics and transport properties resulting in desired meso- and macroscopic functionalities. Particular current interests include such topics as supramolecular recognition; synthesis of new porous materials; interfacial properties at the nanoscale; ligand design and synthesis of extractant molecules; mechanisms of transport and fouling in polymer and inorganic membranes; solvation in fluids and their interfaces; and drop formation. This fundamental research is motivated by a desire to advance discovery and predictive design of future chemical separations-related concepts enabling efficient and multifunctional capabilities for a broad range of processes. Examples include membrane processes (e.g. separation, reactive separation, and fuel cell membranes), complexation, extraction under both standard and supercritical conditions, ionic liquids, selective adsorption and efficient release using materials such as MOFs, and limited fundamental aspects of chromatography.

Analytical research will pursue the elucidation of ionization, chemical interactions, and excitation mechanisms for optical and mass spectrometry that enable temporal and chemical observation and characterization at the nano- and molecular-scale of systems relevant to DOE's energy interests. One focal point of this research is the underlying science needed to achieve true chemical imaging, i.e., the ability to selectively image desired chemical moieties at the molecular scale with temporal resolution that elucidates physical and chemical processes relevant to energy science.

Additional evolution of the program is anticipated from the growing DOE mission emphasis on alternative energy sources, climate change, and on exploiting the nanoscale revolution for scientific discovery and mission applications. Based on programmatic priorities, this activity does not support areas directly overlapping those supported by complementary programs in DOE or other agencies or any engineering scale up or development of narrowly defined processes, devices or sensors, or research that is directed toward medical applications.

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 an important 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.

Unique Aspects

Society and industry rely on the earth to provide energy resources, or the materials to synthesize energy systems, and to be the ultimate repository of energy wastes safely and cost effectively. 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 better understand hydrocarbon transport, contaminant transport and remediation, and geothermal energy production; and coupled hydrologic-thermal-mechanical-reactive transport modeling to predict geological repository performance. The DOE technology programs activities tend to focus on solutions to existing problems in the nearer-term. This activity seeks fundamental research results that can serve as the foundation for the technology programs directed research and development efforts in the longer-term, both from the national laboratories and from the university community. In particular, the BES Geosciences activity provides funding for long-term cross-cutting research efforts at national laboratories, which are directly and immediately transferred to the applied programs as needed.

Relationship to Other Programs

- 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.
- The BES Geosciences activity is closely coordinated with applied programs focused on geological CO_2 sequestration within the Office of Fossil Energy (FE) and on geothermal energy within the Office of Energy Efficiency and Renewable Energy (EERE). It provides fundamental support in improving understanding of geochemical reactivity, subsurface flow and high resolution geophysical imaging to other DOE mission programs such as Environmental Management and Legacy Management.
- The BES Geosciences program also supports the National Research Council's Board on Earth Sciences and Resources and its study committees.

Significant Accomplishments

BES Geosciences has pioneered the use of synchrotron science and neutron science applications in the Earth sciences at the NSLS, APS, ALS, SSRL and SNS since their inception.

- The GSECARS beamline has been built and commissioned (in collaboration with NSF) as a center for high-resolution analytical geochemistry for the whole Earth sciences community, including multiple DOE applied program users. The Geosciences activity currently also supports other beamline activities at the Advanced Photon Source (APS) and at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory.
- Geosciences-supported investigators are significantly involved in plans for several new beamlines at the NSLS-II facility, and the program has provided seed funding for beamline transitions from NSLS I to NSLS II.
- 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. These workshops have also produced broadly applicable publications pertinent to geosciences topics of current interest.

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 a number of ways. Performance assessments of energy and environmental systems can't be tested with any usual engineering approach. They have to rely upon conceptual and computational predictions of those systems over geological periods of time (decades to centuries to millennia), and over technological spatial scales (kilometers), based on geological observations. This activity develops the fundamental understanding of geological processes relevant to energy materials production and for geological disposal options for byproducts from multiple energy technologies. This new knowledge will be critical to developing robust monitoring, verification and accounting metrics for regulatory approaches to new energy technologies, and as the foundation for consent-based waste disposal approaches. 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. 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 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). 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. New computational capabilities enabled by new high performance computing architectures will be important contributors to optimization of geological modeling approaches for individual molecular, 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 fluid-rock-particle interactions including natural nanophases and nanoparticles in shallow earth systems and how they contribute to mineral-fluid reactivity. The activity continues working with various groups on investigating uses of synchrotron and 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. GSECARS and other BES Geosciences supported synchrotron beamlines begin their second decade as the premier synchrotron user facilities for the earth sciences community, including bringing their expertise to new end stations at NSLS-II. The activity 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.