Office of Science

Basic Energy Sciences

Core Research Activities

October 2004

Basic Energy Sciences
Core Research Activities
FY 2003 - FY 2005 Budgets

(Numbers are from President's FY 2005 Budget Request.)

CRA #	BES Core Research Activities (CRAs)	BUDGETS FY 2003	FY 2004	FY 2005 Request
1	Experimental Condensed Matter Physics	37,205	40,500	42,449
2	Theoretical Condensed Matter Physics	16,993	17,000	17,975
3	X-Ray and Neutron Scattering	37,821	41,877	42,058
4 Sub.	Advanced Light Source	42,844	43,205	42,200
4 Sub.	Advanced Photon Source	90,894	93,410	97,400
4 Sub.	National Synchrotron Light Source	36,950	38,325	38,400
4 Sub.	Stanford Synchrotron Radiation Laboratory	25,903	30,305	28,100
4 Sub.	High Flux Isotope Reactor	36,838	37,805	39,832
4 Sub.	Radiochemical Engineering Development Center	6,515	6,305	6,300
4 Sub.	Intense Pulsed Neutron Source	16,714	16,655	17,222
4 Sub.	Manuel Lujan, Jr. Neutron Scattering Center	9,914	10,110	10,300
4 Sub.	Spallation Neutron Source	14,441	18,397	33,100
4	X-Ray and Neutron Scattering Facilities - TOTAL	281,013	294,517	312,854
5	Materials Chemistry and Biomolecular Materials	40,563	42,000	44,437
6	Structure and Composition of Materials	28,915	32,954	32,183
7	Mechanical Behavior and Radiation Effects	13,323	13,600	13,600
8	Physical Behavior of Materials	20,262	20,500	22,450
9	Synthesis and Processing Science	11,839	12,000	12,975
10	Engineering Research	15,297	14,038	13,500
11	Experimental Program to Stimulate Competitive Research	11,722	7,673	7,673
12 Sub.	Nanoscale Science Research Centers - Research	100	400	600
12 Sub.	ANL Nanoscience MIE	0	10,000	12,000
12 Sub.	Project Engineering and Design, Nanoscale Science Research Centers	11,850	2,982	2,012
12 Sub.	Nanoscale Science Research Center – The Center for Nanophase Materials Sciences, ORNL	23,701	19,882	17,811
12 Sub.	Nanoscale Science Research Center – The Molecular Foundry, LBNL	0	34,794	32,085
12 Sub.	Nanoscale Science Research Center – Center for Functional Nanomaterials, BNL	0	0	18,465
12 Sub.	Nanoscale Science Research Center – The Center for Integrated Nanotechnologies, Sandia National Laboratories/Los Alamos National Laboratory	4,444	29,674	30,897
12	Nanoscience Centers -TOTAL	40,095	97,732	113,870
13	Atomic, Molecular, and Optical (AMO) Science	13,379	13,401	13,401
14 Sub.	Chemical Physics Research	32,097	30,334	31,617
14 Sub.	Combustion Research Facility	5,935	5,967	6,169
14	Chemical Physics Research - TOTAL	38,032	36,301	37,786
15	Photochemistry and Radiation Research	24,853	28,502	29,477
16	Catalysis and Chemical Transformation	33,854	34,453	36,402
17	Separations and Analyses	14,547	13,517	16,441
18	Heavy Element Chemistry	9,974	9,375	9,375
19	Chemical Energy and Chemical Engineering	9,779	10,637	10,687
20	Geosciences Research	20,322	20,491	20,332
21 Sub.	Molecular Mechanisms of Natural Solar Energy Conversion	11,797	12,133	13,108
21 Sub.	Metabolic Regulation of Energy Production	18,665	19,195	18,695
21	Energy Biosciences Research - TOTAL	30,462	31,328	31,803

Research Activity: Experimental Condensed Matter Physics

Division: Materials Sciences and Engineering
Primary Contact(s): James Horwitz (james.horwitz@science.doe.gov, 301-903-4894)
Team Leader: William T. Oosterhuis
Division Director: Harriet Kung

Portfolio Description:

The portfolio consists of a broad-based experimental program in condensed matter and materials physics research emphasizing electronic structure, surfaces/interfaces, and the discovery of new materials. It includes the development and exploitation of advanced experimental techniques and methodology. The objective is to provide the understanding of the physical phenomena and processes underlying the properties and behavior of advanced materials. The portfolio includes specific research thrusts in magnetism, semiconductors, superconductivity, materials synthesis and crystal growth, and photoemission spectroscopy. The portfolio addresses well-recognized scientific needs, including understanding magnetism and superconductivity; the control of electrons and photons in solids; understanding materials at reduced dimensionality, including the nanoscale; the physical properties of large, interacting systems; and the properties of materials under extreme conditions.

Unique Aspects:

The research on magnetism and magnetic materials has more emphasis and direction than in other federally supported programs. It focuses on hard magnet materials, such as those used for permanent magnets and in motors, and on exchange biasing, such as used to stabilize the magnetic read heads of disk drives. The Experimental Condensed Matter Physics (ECMP) activity continues to support research on electronically complex materials, an area that impacts a wide range of other topics including superconductivity, magnetoresistivity, low-dimensional electron systems, and magnetism including topics such as exchange bias and spin-polarized electron transport. The integrated photovoltaics program, consisting of research from this portfolio and technology from EE and EPRI, is both successful and a model for such integration. The combined projects in superconductivity comprise a concerted and comprehensive energy-related basic research program. The DOE laboratories anchor the efforts and maintain the integration with the EE developmental efforts. The LANL thermoacoustics program is unique, both scientifically and technologically. This work led to an R&D-100 award in 1999 and aspects are being developed commercially. The 100 T multi-shot magnet, under construction at LANL, is a multidisciplinary project in many different areas of materials design, materials research and high power systems. Two major areas research will be pursued upon completion of the magnet in 2005 which include magnetic field induced phase transitions in addition to nano-quantization and quantum size effect. The ECMP activity also has unique thrusts in photovoltaics and in photoemission investigations of superconductors. It is a source of new materials scientists through strong programs at LANL, SNL, Ames, ANL, BNL and Stanford**.** Internationally, the ECMP activity holds a position of world leadership in the areas of magnetism, superconductivity, materials characterization, and nanoscale science. It is dominant in photoemission characterization of cuprate superconductors. New, exciting areas launched within this activity in photonic band gap materials, 2-D electron systems, magnetic superconductors and quasicrystals are now pursued worldwide. Enhanced efforts are ongoing to generate high quality single crystals of new materials at Ames, ANL, BNL, ORNL and SSRL.

Relationship to Others:

This activity supports the National Academy of Science's Solid State Sciences Committee, which in turn serves as a coordinating mechanism nationally. Within DOE, the activity is coordinated through the Energy Materials Coordinating Committee. The ECMP activity interacts with the BES Condensed Matter Theory and Neutron and X-Ray Scattering activities. Research in photovoltaics is coordinated with the Chemical Sciences, Geosciences and Biosciences Division and with the Photovoltaics Technology Division of EE. The activity also supports projects jointly with DP, FE, EE/RE and EPRI. In the areas of magnetism, superconductivity, and research on the control of electrons and photons in solids, this activity provides more support than the National Science Foundation's Condensed Matter Physics program.

Significant Accomplishments:

The ECMP activity has a long history of accomplishments dating back to the 1950's and the first neutron scattering experiments at the Oak Ridge National Laboratory. Notable accomplishments include the discovery of ion channeling and the development of the field of ion implantation; the discovery of metallic and strained-layer superlattices; the establishment of the field of thermoacoustics and thermoacoustic refrigeration and heating; the invention of Z-contrast scanning transmission electron microscopy; the theoretical and predictive basis for photonic band gap materials; the tandem photovoltaic cell which holds the record for efficiency; the observation of stripes in superconductors; and, the invention of a Josephson junction scanning tunneling microscope and the first observation of superconductivity in a magnetically doped semiconductor ($PtSb_2$ with ~1% Yb). In addition, the activity has supported much of the seminal work in the fields of high temperature superconductors and quasicrystals, efforts now pursued worldwide.

Mission Relevance:

This activity provides direct research assistance to the technology programs in EE (photovoltaics, superconductivity, power sources, thermoacoustics), FE (thermoacoustics), and DP (photoemission, positron research, and electronic and optical materials). In addition, it supports, more fundamentally, several DOE technologies and the strategically important information technology and electronics industries through its results in the fields of semiconductor physics, ion implantation and electronics research; the petroleum recovery efforts of FE and the clean-up efforts of EM through research on granular materials and on fluids; the OTT through research on advanced materials and magnets; energy conservation efforts through research on ion implantation, ultra-hard materials, superconductivity, thermoelectrics, and power source component materials; and DP through research on advanced laser crystals and weapons-related materials.

Scientific Challenges:

Among the immediate on-going scientific challenges are: the solution of the mechanism for high temperature superconductivity; the understanding of “stripes” in correlated electron systems; the understanding of novel quantum effects and of “emergent phenomena,” that is, new phenomena that emerge when the complexity of a system grows with the addition of more particles; the development of a very high-magnetic field research program to exploit the 100T and 60T magnets at LANL; research in nanoscale science; low-temperature physics; and the continued development of a materials synthesis and crystal growth capability in this country. Quality materials lie at the heart of quality measurements: a thrust to develop a core competence in the synthesis of new materials and the growth of crystals is underway and it will continue to be a priority. High-magnetic-field research coupled with low temperature physics led to the discovery of the quantum Hall effect and to the general area of novel quantum effects. The availability of very high magnetic fields over useable time scales, as will be afforded by the new magnets at LANL, offers the promise of both increasing the fundamental understanding of matter and of observing the effects of very high magnetic fields on materials properties. This will undoubtedly lead to the discovery of new and exciting physics. Similarly, low temperature physics continues to be important for the advancement of physics by providing the experimental conditions necessary to observe phenomena such as BEC, the quantum Hall effect, and superconductivity. Developing and understanding matter and materials at the nano- and subnanoscale is a critical need because electronic, optical, and magnetic devices continue to shrink in size. Ballistic transport in quantum wires exceeding 5 μm in length may provide the basis for quantum computing.

Funding Summary:

Dollars in Thousands

FY 2003	FY 2004	FY 2005 Request
37,205	40,500	42,449

Performer	Funding Percentage
DOE Laboratories	77%
Universities	23%

These are percentages of the operating research expenditures in this area; they do not contain laboratory capital equipment, infrastructure, or other non-operating components.

ORNL has the largest single program in the portfolio, comprising approximately 22% of the overall effort. ANL is second at 18%, followed by, in order, 9% at LBNL, 8% at Ames, and 7% BNL. Of particular note are: (1) the integrated and successful research (this activity) and technology (EE) program in photovoltaics at NREL; (2) LBNL with its world-class collection of “electronics” research, including molecular electronics based upon carbon species; and (3) LANL, where the thermoacoustics effort with joint funding from FE shows promise as a commercial technology, the project on photoemission spectroscopy of actinides has joint funding with DP, and the 100T magnet project. The forty-nine currently active university grants are distributed among forty universities in twenty-seven states and Puerto Rico. Included are one HBCU and one HSI.

Projected Evolution:

The Experimental Condensed Matter Physics activity will include further work at the nanoscale; the development of a very high magnetic field research program; and continued development of the materials synthesis and crystal growth thrust. The portfolio can be expected to continue thrusts in electronic structure, new materials, surfaces/interfaces, and experimental techniques. For example, sum frequency generation is a new technique that is now being used to probe the electronic and vibrational structure of chiral molecules on surfaces. Femtosecond time-resolved magnetooptical, tehahertz and x-ray diffraction techniques will be used to study the coupled dynamics of charge carriers along with the associated lattice deformations in high temperature superconductors, colossal magneto-resistance manganites and charge density wave conductors. The subtopics also will be the similar, e.g., magnetism, low dimensional electron systems, and new materials. Low temperature physics and superconductivity both are important. Low temperature physics underlies several other areas of opportunity and presents issues of its own. Superconductivity, specifically high temperature superconductivity, continues to be a potentially revolutionizing technology. The goal for the former is to augment the investment in low temperature physics when possible. In superconductivity, the goal is to identify the most pressing scientific issues and ensure the level of effort is consistent with the priorities. New investigations in the Casimir force will be initiated. The attractive force between two surfaces in a vacuum predicted over 50 years ago, could affect everything from micromachines to unified theories of nature.

Research Activity: Theoretical Condensed Matter Physics

Division: Materials Sciences and Engineering
Primary Contact(s): Dale Koelling (Dale.Koelling@science.doe.gov , 301-903-2187)
Team Leader: William Oosterhuis
Division Director: Harriet Kung

Portfolio Description:

The Theoretical Condensed Matter Physics activity includes a broad spectrum of theoretically research complementing all parts of the Materials Science and Engineering Division. Research areas include structure and properties of quantum dots and nanotubes, two dimensional electron gas, quantum transport, tribology at the atomic level, superconductivity, magnetism, and optics. A significant effort within the portfolio is the development of advanced computer algorithms to treat many-particle systems. An important facilitating component is the Computational Materials Science Network (CMSN), which enables groups of scientists from DOE laboratories, universities, and (to a lesser extent) industry to address materials problems requiring larger-scale collaboration across disciplinary and organizational boundaries.

Unique Aspects:

New areas of materials science are being identified and studied. New technology is enabling a much closer examination of the existing ones. This healthy progress dictates that new theories be developed and that established ones be reexamined and possibly extended. A very important contribution of the theorist is enforcing a rational, consistent understanding of experimental observations so that we can go forward. Often, this involves working out implications of a theory for a specific material or situation. In materials, this can be an extremely difficult task because of the very many atoms involved. Many conceptual tools such as quasiparticles, entities defined to examine phenomena at different length scales, or summary statistical approaches have been developed. Further development of such conceptual tools continues to be a very important aspect of this theoretical program. However, for many phenomena now being studied, large scale computation must be utilized to perform the complex calculations dictated by the fundamental theory or to perform the simulations of systems with many interacting components. The rapid advance in computational capabilities now enables research at such a level of sophistication that computational science has become a "third way of doing science", but at a price. The complexity of such research very often requires larger groups of collaborating researchers from a diversity of disciplines. One response has been formation of the Computational Materials Science Network to assemble multi-disciplinary groups of scientists from DOE laboratories, universities, and industry to collaborate on computational materials science projects. At present, CMSN consists of five sub-projects: Excited States and Response Functions (testing the accuracy of current levels of fundamental theory); Microstructural Effects on the Mechanics of Materials (computational study of the fundamental basics of metallurgy); Fundamentals of Dirty Interfaces: From Atoms to Alloy Microstructures (the development of microstructure in heterogeneous materials); Magnetic Materials Bridging Basic and Applied Science (an attempt to interconnect different scales of magnetic behavior from quantum mechanical electronic behavior all the way to continuum micro-mechanical properties); Predictive Capability for Strongly Correlated Systems (an attempt to advance capabilities in many body theory).

Relationship to Others:

This activity interacts with all the other research activities within the Division of Materials Science and Engineering driven by mutual interest Also, because the computational resources at the National Energy Research Scientific Computing facility utilized by the division are administered here, there is an enhanced awareness of opportunity. Within DOE, frequent interaction occurs with the Mathematics, Information and Computer Sciences division. Information on university grants is shared with NSF, peer reviews are sometimes shared, and on occasion there is joint funding of grants. On the international level participation in organizing and steering committees is frequent, as are exchanges of experts between foreign and domestic institutions.

Significant Accomplishments:

Consistent with the emphasis on nanoscience enabled by developments in technology and computational techniques, notable achievements in this area have been made within the Condensed Matter Theory activity.
Research into low dimensional materials has revealed exciting new information and has pointed to new possibilities in creating new tailored materials and devices. Highlights include:

1. By judiciously attaching molecules to nanoclusters, one can guide them to assemble in a specified manner. (The rule book remains to be written but it is under construction.)
2. Gold nanoparticles behave much more like their platinum group neighbors in the periodic table including exhibiting interesting catalytic behavior. When passivated by dodecane thiols, they can self-assemble into nanocrystalline superlattices with unique properties.
3. Nanocrystalline diamond can form with a bucky-ball-like surface reconstruction. The carbon nanoparticles exhibit very weak quantum confinement unlike silicon and germanium.
4. Silicon nanotubes can be formed by stabilization with a core of nickel atoms. Unlike carbon, silicon nanotubes are not stable without such help.

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

Dynamic mean-field theory, which is exact for infinite dimensions, has been successfully coupled with three dimensional band theory. The resulting hybrid theory has been used to elucidate the spin polarization of CrO_2 --- a famous magnetic recording material that might find new use is spintronics. A competition between quasiparticle behavior and local –moment behavior is found.

A way has been found to see diffraction data for molecules adsorbed on surfaces. The conventional methods of low energy electron diffraction will not work: the molecules produce no Bragg spots because they are randomly distributed on the surface. However, it has been shown that the information is present in the intensity variation of the spots originating from the substrate. The resulting technique has successfully revealed the geometry of small hydrocarbons on a palladium surface.

The origin of the light-induced conductivity in the transparent oxide $12CaO\cdot 7Al_2O_3$ is traced to electrons excited off H ions present. To accomplish this, it was first necessary to accomplish calculating the Coulomb gap leading to hopping conductivity.

Progress has been made on the question of how to treat core-hole effects in x-ray absorption spectra by a collaboratory research team of the Computational Materials Science Network. The team, which focuses on Excited States and Response Functions, brought together experts of all applicable approaches to compare against each other and elucidate the formal relationships between them. What resulted was an excellent prescription for success but with identified places for improvement. This is needed not only for fundamental understanding of the details of x-ray absorption phenomena but technological applications --- an example of which is the measurement of the thickness of integrated circuit interconnects.

Mission Relevance:

The program's ultimate purpose is to understand the properties of existing materials and to reveal new ones that are more efficient in producing, storing, and using energy. To this end, the programs in this portfolio have the common goal of achieving a basic understanding of matter at all scales ranging all the way from the atomic to the bulk. The experimental and theoretical programs work closely together, but there are also more independent modes of research. The theorists try to establish a theoretical basis for experimentally observed results, which almost always suggests further experiments, and thus leads to new results. New experiments and experimental techniques are often suggested. New science is also produced by simulating processes on computers. "Computer experiments" can be performed which are difficult or impossible perform in the laboratory. They are also much easier to dissect and to vary the conditions in order to isolate the effective mechanisms. For example, the behavior of the surface layers of materials sliding on each other and a new understanding of the role of lubricants has been obtained in this way. Other examples include investigations into the behavior of electrons flowing in nano wires and nanotubes and in the properties of matter at extreme conditions of temperature and pressure.

Scientific Challenges:

The close relationship between the experimental and theoretical programs dictates that many challenges are common to both. Examples are exploring the behavior of complex systems, investigating nano-scale systems, and understanding superconductivity. New ways of conceptually visualizing and characterizing phenomena will broaden our horizons. Stripes occurring in cuprate superconductors and two dimensional electron gasses are an excellent example. Bridging length scales is a major thrust. The tactic of dividing up the effects in materials according to the length scale at which they occur has greatly facilitated our understanding. But for the theorists, this creates the problem of how to pass needed information between the different constructs used at the different length scales. Only in that way can one calculate parameters rather than make phenomenological fits. Such is the basis for improved understanding and greater precision of our modeling. It is a continuing major goal on which limited progress has been made. Bridging time scales is similarly important but far less progress has been made. Basic theory improvements are also needed. For example, density functional theory is our most computationally tractable many body theory but it defines many functionals both for the ground state or ensemble energy and separately for the properties that must be determined. Whereas knowledge of the exchange-correlation functional for the ground state energy is reasonably advanced, knowledge of all other functionals is still quite rudimentary. Other many body approaches, although far more computationally intensive, provide important information and require further development. Improvements are also needed in our computational tools. Materials theory is a very heavy consumer of computer resources even if not so visibly as other disciplines. (This is because materials theory deals with many dissimilar problems rather than a few overarching ones.) The materials community could very productively make use of vast increases in computational capability. Because the phenomenal growth due to hardware improvements is actually overshadowed by those due to clever algorithm design, further improvements in "tool development" will significantly impact future development of science in a qualitative way.

Funding Summary:

Dollars in Thousands

FY 2003	FY 2004	FY 2005 Request
16,993	17,000	17,975

Performer	Funding Percentage
DOE Laboratories	75%
Universities	25%

The program provides funding for 54 university grants supporting about as many students and partially supporting about 60 faculty and senior staff. There are approximately 70 postdocs fully or partially supported by this CRA. This program supports research at LBNL, AMES, BNL, ANL, LLNL, MRS, LANL, ORNL, and NREL. Programs at the laboratories are multi-investigator efforts on problems that require extensive participation by experimental and theoretical scientists. Many of the research efforts at national laboratories involve interfaces with the university and industrial communities and with user facilities. Additionally, about $1.4M is provided for projects of the Computational Materials Science Network.

Projected Evolution:

Materials will be modeled with ever-greater sophistication and realism and complexity. Needs and opportunities will drive the effort inexorably in this direction. Science at the nanoscale will continue a major example, although it is only one of many. With the Chemistry Division, a cooperative effort will be begun with Mathematics, Information, and Computer Sciences seeking to enhance our capabilities to model and simulate at the nanoscale. As a way to bring together teams adequate to address the more complex problems envisioned, the Computational Materials Science Network will be enhanced.

Research Activity: X-Ray and Neutron Scattering

Division: Materials Sciences and Engineering
Primary Contact(s): Helen M. Kerch (Helen.Kerch@science.doe.gov; 301-903-2346)
Team Leader: William Oosterhuis
Division Director: Harriet Kung

Portfolio Description:

This activity supports basic research in condensed matter and materials physics using neutron and x-ray scattering capabilities primarily at major BES-supported user facilities. Research is aimed at achieving a fundamental understanding of the atomic, electronic, and magnetic properties of materials and their relationship to the physical properties of materials. Both ordered and disordered materials are of interest as are strongly correlated electron systems, surface and interface phenomena, and behavior under environmental variables such as temperature, pressure, and magnetic field. Development of neutron and x-ray instrumentation is a major component of the portfolio.

Unique Aspects:

The Department's history and mission has played an important role in BES's current position as the Nation's steward of major neutron and x-ray 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. Similarly, synchrotron facilities stemmed from particle accelerators that were developed for high-energy physics research. As part of its stewardship responsibilities, BES maintains strong fundamental research programs in materials and related disciplines that are carried out at these facilities by the laboratory, university, and industrial communities. This activity has evolved from the pioneering, Nobel prize-winning efforts in materials science to the current program that encompasses multiple techniques and disciplines. The activity also supports the research that has motivated the largest BES construction projects in recent years - the ALS, APS, and SNS. BES is a major supporter of both the research and the instrumentation at these and other facilities. Neutron and x-ray scattering are well-established techniques for investigating the microscopic properties of materials. With the advent of both high brightness x-ray beams produced by third generation synchrotron radiation facilities and intense pulsed neutron beams provided by accelerator-based neutron sources, a number of totally new capabilities will become possible.

Neutron Scattering. Neutron scattering provides information on the positions, motions, and magnetic properties of solids. With unique characteristics such as sensitivity to light elements, neutron scattering has proven to be invaluable to polymer and biological sciences. The high penetrating ability of neutrons allows property measurements and nondestructive evaluation deep within a specimen. Neutrons have magnetic moments and are thus uniquely sensitive probes of magnetic species within a sample. The wavelength of neutrons used in scattering experiments is commensurate with interatomic distances, and their energy (meV) is comparable to both lattice and magnetic excitations (phonons and magnons) making them an ideal probe for both structure and dynamics.

X-ray Scattering. The unique properties of synchrotron radiation – high flux and brightness, tunability, polarizability, high spatial and temporal coherence, along with the pulsed nature of the beam – afford a wide variety of experimental techniques in diffraction and scattering, spectroscopy and spectrochemical analysis, imaging, and dynamics.

Relationship to Others:

This activity interacts closely with research instrumentation programs supported at other federal agencies, especially in the funding of beamlines whose cost and complexity require multi-agency support. The activity works in concert with the Instrumentation for Materials Research -- Major Instrumentation Projects (IMR-MIP) at the National Science Foundation and the NIST Center for Neutron Research (NCNR) in the Department of Commerce to develop instruments and capabilities that best serve the national user facility needs. A coordinated effort between the Department of Energy (DOE) and the National Science Foundation (NSF) is ongoing to facilitate the full utilization of the nation's neutron scattering facilities under the auspices of the Office of Science and Technology Policy's Interagency Working Group on Neutron Science. Interaction with ISIS and ILL in the training of post-doctoral fellows and neutron detector development is also underway. In FY2003, the program coordinated with the DOE's SBIR Program which resulted in 6 Phase I and 2 Phase II awards in the area of neutron detectors, monochromators and other scattering instrumentation.

Significant Accomplishments:

Neutron Scattering. This activity supported the research of Clifford G. Shull at Oak Ridge National Laboratory that resulted in the 1994 Nobel Prize in Physics for the development of the neutron diffraction technique. Shull's work launched the field of neutron scattering, which has proven to be one of the most important techniques for elucidating the structure and dynamics of solids and fluids. The program supports major efforts in neutron scattering centered primarily at the DOE laboratories- Ames, ANL, BNL, ORNL, LANL- and these groups have pioneered virtually all the instruments and techniques in neutron scattering, spectroscopy, and imaging.

X-ray Scattering. As in the neutron scattering effort, the program supports large research groups that utilize synchrotron radiation to understand the intrinsic properties of materials. These groups have contributed to the development of such powerful techniques as magnetic x-ray scattering, inelastic x-ray scattering, extended x-ray absorption fine structure (EXAFS), x-ray microscopy, microbeam diffraction, time-resolved spectroscopy and others.

Recent accomplishments include the development of ^3He spin filters for the production of polarized neutrons, the first evidence of icosahedral ordering in liquid metals by in-situ x-ray diffraction, the first measurements of local deformation in bulk materials on the mesoscale using combined x-ray microscopy and nanoindentation, the demonstration of the existence of electron-lattice polarons in colossal magnetoresistive manganites via single crystal x-ray and neutron scattering, the confirmation of stripe domains in ferroelectric thin films as shown by in-situ x-ray diffraction, and the formation of "nanowater wires" in zeolites by applying simultaneous pressure and temperature using a hydrothermal diamond anvil cell.

Mission Relevance:

To understand the physical properties of any material, one needs to begin with its structure. The fundamental understanding of the structure and behavior of matter contributes to the Nation's science base and underpins DOE's broad energy and environmental mission and responsibilities. X-ray and neutron scattering are the primary tools for characterizing the atomic, electronic and magnetic structures and excitations of materials. The increasing complexity of such energy-relevant materials as superconductors, semiconductors, and magnets requires ever more sophisticated, specific, and sensitive X-ray and neutron scattering techniques to extract new and useful knowledge and develop new theories for the behavior of new materials. The scientific importance of x-ray and neutron science has been broadly recognized as some 15 Nobel Prizes (14 in x-rays; 1 in neutrons) have been based on research utilizing these tools. Additionally, neutrons will play a key role in the President's Hydrogen Fuel Initiative as they provide atomic- and molecular-level information on structure, hydrogen diffusion, and interatomic interactions, as well as the nanoscale and macroscopic morphologies that govern useful properties in catalysts, membranes, proton conductors, hydrogen storage materials, and other materials and processes related to hydrogen production, storage, and use.

Scientific Challenges:

Programmatic Challenges:

Neutron Scattering. The ongoing enhancements at the HFIR will not only increase the nation's neutron scattering capacity, but, in many cases, will provide instruments with resolution and flux on sample that is equal to or greater than existing benchmark instruments. The SNS will push instrument capacity and performance even further. One challenge for this activity will be to support an increased research effort in neutron scattering to take full advantage of the improved sources and to prepare for the SNS. Another includes maintaining the strength of the DOE lab-based neutron scattering groups and rebuilding strength in neutron sciences in the academic community. Education and training of the next generation of neutron scientists - especially those familiar with instrumentation and performance of TOF methods - remains a high priority.

X-ray scattering. Major instruments at the synchrotron light sources have a lifetime of 7-10 years. Thus a challenge to the program is to provide support for the 10-15% of the instruments which must be upgraded or replaced each year to keep the facility at the forefront of science.

Scientific Challenges*:*

Correlated Electron Systems: The effects of strong electron-electron interactions give rise to a remarkable range of anomalous behavior in condensed matter systems, producing phenomena as varied as metal-insulator transitions, colossal magnetoresistance, and high temperature superconductivity in heavy fermion metals, insulators and magnets. In particular, high-temperature superconductivity is a singularly spectacular example of the cooperative macroscopic phenomena such as the interplay of charge, spin, and lattice degrees of freedom that can arise from correlated electron behavior. Techniques such as inelastic x-ray scattering and neutron diffraction, among others, have enabled scientists to unravel the crystallographic and microscopic electronic structure of these materials, including stripes. This information will ultimately be used to answer questions such as what is the mechanism for superconductivity, how high can the temperature be for materials to remain superconducting, and will that temperature ever be room temperature.

Matter Under Extreme Conditions: Opportunities in high pressure research address a broad range of new scientific problems involving matter compressed to multimegabar pressures. Extreme pressures provide a fertile ground for the formation of new materials and novel physical phenomena as compression changes the chemical bonds and affinities of otherwise familiar elements and compounds. Highly collimated and intense synchrotron beams provide the ideal source for ultrafine and sensitive x-ray diffraction microprobes necessary to measure concentrated high stresses in a very small area. With the development of the SNS, innovative focusing optics, more sensitive detectors and emerging next-generation pressure cells, high pressure research at neutron sources can approach the routine pressure ranges available with diamond anvil cells at synchrotron x-ray sources. With the dramatic advances in techniques for preparing and investigating single crystals, studies of more complex materials become tractable. Similarly, scattering experiment performed in the presence of magnetic fields can be used to study materials during phase transitions (magnetic, structural, superconducting) thus allowing researchers to segregate magnetic field effects or to simulate effects normally observed via doping (for example).

In-situ Studies of Complex Materials: Recent advances in both sources and instrumentation have yielded gains in intensity on sample facilitating rapid experiments and in-situ configurations. Smaller samples can be probed with unprecedented resolution, accuracy, and sensitivity under various parametric conditions. In-situ synchrotron radiation techniques provide real-time observations of atomic arrangements with high spatial sensitivity and precision, which are important features in the development of novel processing techniques and in the search for new exotic materials. In-situ studies of complex materials including those undergoing time-dependent structural or magnetic phase transformations, disordered systems such as alloys and amorphous materials, organic thin films and self-assembled systems, and other condensed matter systems can be probed with a variety of scattering, reflectivity and spectroscopic techniques.

Funding Summary:

Dollars in Thousands

FY 2003	**FY 2004**	**FY 2005 Request**
37,821	41,877	42,058

Performer	**Funding Percentage**
DOE Laboratories	76%
Universities	24%

Major DOE laboratory performers include Ames, ANL, BNL, ORNL, LANL, SSRL.

This activity also provides support for the construction of seven instruments at the SNS including; High-Resolution Chopper Spectrometer (ARCS), Cold Neutron Chopper Spectrometer (CNCS), Ultra High Pressure Diffractometer (SNAP), High Resolution Thermal Chopper Spectrometer (SEQUOIA), Single Crystal Diffractometer (SCD), Disorder Materials Diffractometer (NOMAD) and the Hybrid Spectrometer (HYSPEC). Also under construction at DOE synchrotron radiation facilities are: APS; Inelastic Scattering Beamline, High Pressure Beamline, Powder Diffraction Beamline; NSLS; Microdiffraction beamline; ALS; Inelastic Scattering Beamline, AMO physics beamline upgrade; SSRL; Soft-X-ray Facility for Nanoscale Materials and Phenomena.

Projected Evolution:

Advances in neutron and x-ray scattering will continue to be driven by the scientific opportunities presented by improved source performance and instrumentation optimized to take advantage of that performance. The x-ray and neutron scattering activity will continue in fully developing the capabilities at the DOE facilities by providing instrumentation and research support. A continuing theme in the scattering program will be the integration and support of materials preparation (especially single crystals) as this is a core competency that is vital to US interests.

Research Activity: X-Ray and Neutron Scattering Facilities

Division: Scientific User Facilities
Primary Contact: Pedro A. Montano (pedro.montano@science.doe.gov; 301-903-2347)
Division Director: Pedro A. Montano

Portfolio Description:

This activity supports the operation of four synchrotron radiation light sources and three neutron scattering facilities. These are: the **Advanced Light Source** (ALS) at Lawrence Berkeley National Laboratory; the **Advanced Photon Source** (APS) at Argonne National Laboratory; the **National Synchrotron Light Source** (NSLS) at Brookhaven National Laboratory; the **Stanford Synchrotron Radiation Laboratory** (SSRL) at Stanford Linear Accelerator Center; the **High Intensity Flux Reactor** (HFIR) at Oak Ridge National Laboratory; the **Intense Pulsed Neutron Source** (IPNS) at Argonne National Laboratory; and the **Manuel Lujan Jr. Neutron Scattering Center** (Lujan Center) at Los Alamos National Laboratory.

Under construction is the **Spallation Neutron Source** (SNS) at Oak Ridge National Laboratory, which is a next-generation short-pulse spallation neutron source that will be significantly more powerful than the best spallation neutron source now in existence -- ISIS at the Rutherford Laboratory in England. On the drawing board is the **Linac Coherent Light Source** (LCLS) at Stanford Linear Accelerator Center, which is a free-electron laser that will provide laser-like radiation in the x-ray region of the spectrum that is 10 orders of magnitude greater in peak power and peak brightness than any existing coherent x-ray light source.

Unique Aspects:

The synchrotron radiation light sources and the neutron scattering facilities are the most advanced facilities of their kind in the world. Together, they serve more than 7,000 users annually from academia, national laboratories, and industry, a number that has more than tripled in the past decade and that can more than double again in the next decade as current facilities and those under construction are fully instrumented. These light sources and neutron scattering sources represent the largest collection of such facilities operated by a single organization in the world. Conception, design, construction, and operation of these facilities, which in current costs are in the hundreds of millions to in excess of a billion dollars, are among the core competencies of the BES program.

Relationship to Others:

This activity has very strong interactions with all BES programmatic research that utilizes synchrotron and neutron sources. This includes research in atomic physics, condensed matter and materials physics, chemical dynamics, catalysis, geosciences, high-pressure science, environmental sciences, engineering, biosciences, and much more. Interaction also exists with other parts of the Office of Science, notably BER, and the Department of Energy, notably DP, EE, and EM. There are frequent contacts with other agencies in order to better coordinate efforts in optimizing beamlines and instruments. This activity participates in a number of OSTP and NSTC interagency activities, e.g., OSTP Interagency Working Groups on macromolecular crystallography at the synchrotron light sources and on neutron sources and instrumentation. Finally, this activity is starting to establish more frequent contacts with international user facilities such as ESRF, SPring-8, ILL, ISIS, and others. The objective is to share experiences and to make optimal use of present facilities.

Significant Accomplishments:

The synchrotron radiation light sources. During the past two decades, BES has been the Nation’s major supporter of synchrotron x-ray light sources. BES support pioneered new storage ring lattices for improved beam stability and brightness; developed wiggler and undulator insertion devices that provide 10-12 orders of magnitude greater brightness than the best conventional x-ray sources; and discovered or developed such powerful experimental techniques as magnetic x-ray scattering, microbeam diffraction, x-ray microscopy, photoelectron spectroscopy and holography, inelastic x-ray scattering using nuclear resonances, extended x-ray absorption fine structure (EXAFS), and near-edge absorption fine structure (NEXAFS). The BES light sources are used by over 6,500 researchers annually from academia, government laboratories, and industry for state-of-the art studies in materials science, physical and chemical science, geoscience, environmental science, bioscience, medical science, and pharmaceutical science. Recent research at the light source facilities, supported by BES, by other agencies, by industry, and by private sponsors includes: high-resolution imaging of precision-fabricated thin films of copper, pointing the way toward much denser magnetic data storage for computers; imaging of contaminants in a polycrystalline silicon solar cell and their removal by heat treatment -- a step toward more efficient, less costly solar cells; development of a high-pressure "diamond anvil cell" enabling the creation of entirely new classes of materials such as biomaterials, semiconductor phases, and dense polymers; the solution of the structure of HIV (the AIDS virus) laying the groundwork for developing a vaccine; and the determination of the structure of a key (immunoglobulin-E) antibody receptor on immune system cells, opening the way to prevention of allergic reactions.

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

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, chemical attack, and excitation by photons, electrons, and other particles. A large number of experimental and theoretical tools are used to achieve these ends. In the last two decades, the experimental demands have motivated the development of centralized facilities, like the ones in existence for synchrotron radiation and neutron scattering. Such highly sophisticated and expensive tools are by nature centralized and staffed with specialists that provide to the user community expertise in order to optimize the scientific utilization of the facility. The development, construction and operation of these facilities are one of the most important missions and core competencies of BES. The scientific accomplishments of these facilities, as determined by triennial peer review, are reflected in the large number of publications appearing annually in the most important scientific journals, in the thousands.

Scientific Challenges:

The synchrotron radiation light sources. First, completion of SPEAR3 at SSRL will require upgrading the beamlines to make full utilization of the new more powerful radiation source. Second, the concepts of Participating Research Teams (PRTs) used at the NSLS and Collaborative Access Teams (CATs) used at the APS will be revisited; PRTs were extremely useful in the first decades of operation of NSLS as were CATs in the first years of operation of the APS. However, the larger, more diverse, and less experienced user base at all of the light sources may require new paradigms of operation to address new needs. Third, 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. Fourth, the promise of a coherent, short-wavelength x-ray source from the LCLS will require completely new instrument and experiment concepts.

The neutron scattering sources. First, the upgrades and new instrumentation at HFIR must be completed in a timely way to facilitate a robust user program. Second, the Lujan Center must show reliable, user-friendly operation with its robust suite of new and upgraded instruments.

Funding Summary:

Dollars in Thousands

	FY 2003	FY 2004	FY 2005 Request
	281,013	294,517	312,854
Advanced Light Source	42,844	43,205	42,200
Advanced Photon Source	90,894	93,410	97,400
National Synchrotron Light Source	36,950	38,325	38,400
Stanford Synchrotron Radiation Laboratory	25,903	30,305	28,100
High Flux Isotope Reactor	36,838	37,805	39,832
Intense Pulsed Neutron Source	16,714	16,655	17,222
Manuel Lujan, Jr. Neutron Scattering Center	9,914	10,110	10,300
Spallation Neutron Source	14,441	18,397	33,100
REDC	6,515	6,305	6,300
X-ray and Neutron Scattering Facilities	281,013	294,517	312,854

Projected Program Evolution:

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

One needs to foresee the instrumentation and scientific needs required by the future operation of the SNS at ORNL. The SNS will be for years to come the most important neutron spallation source in the world. It is important to be prepared for full utilization and judicious increases in the capabilities of SNS as recommended by all advisory committees to the Department.

Finally, the proposed 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 (230 femtoseconds with planned improvements that will further reduce the pulse length) enabling studies of fast chemical and physical processes. These characteristics open new realms of scientific applications in the chemical, material, and biological sciences including fundamental studies of the interaction of intense x-ray pulses with simple atomic systems, structural studies on single nanoscale particles and biomolecules, ultrafast dynamics in chemistry and solid-state physics, studies of nanoscale structure and dynamics in condensed matter, and use of the LCLS to create plasmas.

Research Activity: Materials Chemistry and Biomolecular Materials

Division: Materials Sciences and Engineering
Primary Contacts: Richard D. Kelley (Richard.Kelley@science.doe.gov; 301-903-6051)
Aravinda M. Kini (Aravinda.Kini@science.doe.gov; 301-903-3565)
Team Leader: William T. Oosterhuis
Division Director: Harriet Kung

Portfolio Description:

This activity supports basic, exploratory research on the design, synthesis, characterization, and properties of novel materials and structures. The general focus is on the chemical aspects of complex and collective phenomena that give rise to advanced materials. The portfolio emphasizes solid-state chemistry, surface and interfacial chemistry, and materials that underpin many energy-related areas such as fuel cells and batteries, catalysis, energy conversion and storage, friction and lubrication, light-weight and high-strength materials, membranes, luminescent materials, and materials aspects of environmental chemistry. It includes investigation of novel materials such as self-assembled structures, cluster and nanocrystal-based materials, quasicrystals, polymers, macromolecular assemblies and solids, superconductors, organic electronic and magnetic materials, porous materials, complex fluids, hybrid and composite materials and biomolecular materials. There is an increased emphasis on the synthesis of new materials with nanoscale structural control and taking advantage of unique material properties that originate at the nanoscale. Significant research opportunities also exist at the biology/materials science interface since the world of biology offers time-tested strategies and models for the design and synthesis of new materials – composites and molecular assemblies with unique properties and specifically designed functions. The program also supports the development of new experimental tools and techniques such as high-resolution magnetic resonance imaging (MRI) outside the magnet, x-ray and neutron reflectometry, time-resolved electron diffraction, optical and scanning probe microscopies for dynamic imaging, and surface force apparatus in combination with various spectroscopies.

Distinguishing Features:

To a large measure, the projects supported in this portfolio have a substantial emphasis on fundamental science and a significant "chemistry" component, which is invariably, coupled with physical and/or biological science components. Since new materials open up new possibilities and usher in new opportunities in energy-related technologies, there is considerable interest in the "discovery" of new materials, systems and properties. A sizeable portion of the scientific thrusts pursued in this portfolio are multi-investigator and multi-disciplinary in nature.
Investigators supported in this program are world leaders in solid state NMR and MRI, neutron reflectivity of soft matter, organic magnets, organic conductors and superconductors, biomolecular materials, polymer interfaces, nanoscience, organic-inorganic composite materials, basic science of tribology, and advanced inorganic materials including quasicrystals.
Several investigators in this program are pioneers of novel instrumentation/techniques such as high resolution MRI outside the magnet (Pines/LBNL), neutron reflectometers (Felcher/ANL and Russell/U. Mass), combinatorial materials chemistry for new materials discovery (Schultz/Scripps Research Institute), the surface force apparatus (Israelachvili/UC Santa Barbara and Steve Granick/UIUC), and spin-polarized metastable helium scattering (El-Batanouny/Boston University). The program has sought to identify and support high-risk, high-impact and often ground-breaking research, and will continue to do so.

Relationship to Others:

The Materials Chemistry program is a vital component of the materials sciences that interfaces chemistry, physics, biology, and engineering. This interfacing results in very active relationships.

- Within BES, there are jointly funded programs in the National Labs and Universities (about 10 currently), joint program reviews, joint contractor meetings and programmatic workshops.
- Within DOE, there is coordination through the Energy Materials Coordinating Committee (EMaCC) which involves representatives of SC, NNSA, FE, EM, NEST and EE&RE.
- Programs PI's are collocated and occasionally co-funded by EE&RE (batteries and fuel cells, green chemistry, solar energy conversion, hydrogen storage), FE (catalysis and advanced materials research), and NNSA-DP (nanoscience research).
- Within the federal agencies, the program coordinates through the Federal Interagency Chemistry Representatives (FICR) which meets annually; the Interagency Power Working Group, which meets annually to coordinate all federal electrochemical technology (e.g., battery and fuel cell R&D) activity; the

Interagency Polymer Working Group; and the NanoScience, Engineering, and Technology committee (NSET), which was initially formed to formulate the National Nanotechnology Initiative (NNI) and is currently a sub-committee of the National Science and Technology Council. This last committee meets monthly to coordinate the NNI.
- Very active interactions with NSF and NIH through joint workshops and joint funding of select activities as appropriate (two currently active).
- Industrial interactions: 15 active CRADAs at four DOE laboratories.

Significant Accomplishments:

This program is responsible for pioneering the combinatorial materials chemistry approach for the discovery of new materials (Schultz, 1995). It is also responsible for the discovery of the first organic magnet (Miller and Epstein, 1986), the highest-T_c organic superconductor (Williams et al. 1990), the first all-organic superconductor (Williams et al. 1996) and the first room temperature organic magnet (Miller and Epstein, 1991). The latter discovery created a new field of research, which has grown substantially since then, and has transformed organic magnets from a scientific curiosity to a thriving scientific activity, and is expected to have a huge impact on spintronics-based technologies. Recently, the first material that simultaneously exhibits bistability in three physical channels – electronic, magnetic and optical – was discovered (Haddon, 2002). A new approach involving the use of ordered intermetallic materials as fuel cell electrodes has been developed and it offers great promise for finding a non-platinum, direct fuel cell that uses organic liquids (methanol, ethanol etc.) as fuel (DiSalvo and Arbuna, 2003). A biomolecular route found in Nature has been harnessed to produce photovoltaic and semiconductor nanocrystals at low temperature and under environmentally benign conditions (Morse, 2003). A truly remarkable recent achievement is the generation of a bacterium with a 21amino acid genetic code, which can eventually lead to our ability to generate proteins with entirely new or enhanced biological functions (Schultz, 2003). It will also be possible to extend this technology beyond proteins to prepare the long sought after monodisperse versions of industrial polymers such as polyesters and polyimides.

The program also pioneered the development of several cutting-edge techniques for probing materials, e.g., neutron reflectivity for the study of interfaces, buried interfaces, and interfacial phenomena in magnetic materials, polymers, colloids, biomaterials, and other complex, multicomponent materials. Every neutron scattering facility in the world now has neutron reflectometers, which are in great demand. The program pioneered and developed the use of laser polarized xenon to significantly enhance NMR spectra and MRI images, which has revolutionized medical diagnostics technology. *Ex-situ* NMR or NMR without magnets is another technique developed in this program, which is expected to have an enormous impact on imaging in materials science, biology and medicine, and airport screening (humans and baggage) technologies.

Mission Relevance:

Materials Chemistry and Biomolecular Materials program provides support for fundamental research in surface and interfacial chemistry, nanoscience, polymeric and organic materials, solid state chemistry, and development of new tools and techniques to advance the field of materials sciences. Research in these areas is at the forefront of the synthesis, assembly, and understanding of materials. The research in this portfolio underpins many energy-related technological areas such as batteries and fuel cells, catalysis, energy conversion and storage, friction and lubrication, light-weight and high-strength materials, membranes, luminescent materials, and materials aspects of environmental chemistry.

Scientific Challenges:

The major challenge in this core research activity is identifying and supporting the research focused on synthesis and discovery of new materials with novel properties that can lead to entirely new energy-related technologies. Developing experimental strategies for the “atom-by-atom” synthesis of materials with unprecedented nanoscale (and sub-nanoscale) structural control is clearly an outstanding challenge. In this context, a detailed understanding of hierarchical and dynamic self-assembly processes ubiquitous in Nature can be an extremely valuable guide. Such a knowledge base can lead to low-temperature, energy-efficient synthesis routes to new materials and new manufacturing processes.

Another major challenge is the development of new experimental techniques and tools for the detection, analysis and manipulation of materials, their structures and their properties.

Funding Summary:

Dollars in Thousands

FY 2003	FY 2004	FY 2005 request
40,563	42,000	44,437

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Performers	Funding Percentage
DOE Laboratories	71%
Universities	27%
Other	2%

These are percentages of the operating research expenditures in this area; they do not contain laboratory capital equipment, infrastructure, or other non-operating components. Performers in FY2003 included 46 DOE Laboratory projects and 52 university grants. The 'Other' category includes a grant to a small company (Mission Support, Inc., in Utah) to develop new solid-state detectors for neutron scattering research and two projects supported jointly with the Division of Materials Research, NSF.

Projected Evolution:

In addition to maintaining a healthy core research activity, the program will further expand into nanoscience research, particularly at the nano-bio interface. It will seek to develop new multi-disciplinary approaches, with biology, chemistry, physics and computational science playing major roles, to model, design and synthesize new and novel materials. Some of the targeted areas that will receive support in the coming years include novel materials and innovative concepts that will impact solid state lighting, hydrogen production and storage, novel electrodes and membranes for improving the efficiency of fuel cells, and theory and modeling to aid new materials discovery. Also of particular interest is the development of new organic electronic materials with novel magnetic, conducting and optical properties. With the advent of advanced x-ray synchrotron and neutron facilities within the DOE complex, which are expected to provide new insights into the physics of advanced materials, e.g., superconductors, GMR and CMR materials, optical materials etc. there is a great demand for high-quality single crystals (and other forms) of such materials. Accordingly, there will be a new emphasis on single crystal growth of advanced materials, which will lead to better characterization, and consequently, better understanding of their properties. The program will also seek to facilitate multi-investigator, multi-disciplinary team research, to bring appropriate talents to bear on increasingly more complex and multi-functional materials. The program has sought to identify and support high-risk, high-impact and often ground-breaking research, and will continue to do so.

Research Activity: Structure and Composition of Materials

Division: Materials Sciences and Engineering
Primary Contact(s): Jane G. Zhu (jane.zhu@science.doe.gov; 301-903-3811)
Team Leader: Robert J. Gottschall
Division Director: Harriet Kung

Portfolio Description:

Structure and composition of materials includes research on the arrangement and identity of atoms and molecules in materials, specifically the development of quantitative characterization techniques, theories, and models describing how atoms and molecules are arranged and the mechanisms by which the arrangements are created and evolve. Increasingly important are the structure and composition of inhomogeneities including defects and the morphology of interfaces, surfaces, and precipitates. Advancing the state of the art of electron beam microcharacterization methods and instruments is an essential element in this portfolio. Four electron beam microcharacterization centers are operated at ANL, LBNL, ORNL, and the Frederick Seitz MRL at the University of Illinois.

Unique Aspects:

This activity is driven by the need for quantitative characterization and understanding of materials structure and its evolution over atomic to micron length scales. It is a major source of research in the U.S. that is focused on structure and defects in atomic configurations over all length scales and dimensionalities. The cornerstone is the operation of four complementary, network-interfaced Electron Beam Microcharacterization Centers. They develop instrumentation for characterizing the spatial organization of atoms from the Ångstrom to the micron scale, and make such equipment and the associated knowledge, methods, software, and other resources available to the broad scientific community. The portfolio includes characterization and analysis of materials by transmission and scanning transmission electron microscopy, atom-probe field ion microscopy, scanning probe microscopies, spin polarized low energy electron microscopy, electron beam holography, convergent beam electron diffraction and other state of the art methods. Recent unique advances within this CRA include: incorporation of a nanoindenter within a transmission electron microscope to observe the micromechanisms of deformation in real time; the determination that softening of lattice vibrations presages phase transformations, using a novel thermal diffuse scattering approach at a synchrotron light source; development of an understanding of how quantum dots can cause local substrate stresses which alter electronic band structure; and discovery of a new type of nanoscale crystalline "defect" structure at the intersection of a grain boundary and a surface.

Relationship to Others:

BES:
- Closely linked with activities under Core Research Activities on *Mechanical Behavior and Radiation Effects, Physical Behavior,* and *Synthesis and Processing*
- Linked with Computational Materials Sciences Center

Other Parts of DOE:
- Nuclear Energy Research Initiative
- Energy Materials Coordinating Committee

Interagency:
- Interagency Coordination and Communications Group for Metals
- Interagency Coordinating Committee on Structural Ceramics
- Nanoscale Science, Engineering, and Technology (NSET) subcommittee of the National Science and Technology Council (NSTC) – coordinating body for the National Nanoscience Initiative (NNI)

Significant Accomplishments:

This activity is responsible for the operation of four user centers for electron beam microcharacterization. They represent the Nation's only centralized facilities in electron beam scattering and related techniques that are available to outside users from the physical science community in academia, government laboratories, and industry. They have been the location of many world class scientific achievements in characterizing the structure and composition of materials. They represent the leading U.S. capabilities for structural and compositional characterization at atomic length scale, coupled with advances in detectability limits and precision of quantitative analytical measurement. The following breakthroughs have collectively enabled the highest spatial resolution and the lowest limit in elemental detectability to be accomplished in electron beam microcharacterization.

- Demonstrated the first spectroscopic imaging of single atoms within a bulk solid using an aberration-corrected scanning transmission electron microscope. The ability to collect electron energy loss spectra from an individual atom allows not only elemental identification, but also the determination of chemical valence and its bonding configuration or local electronic structure through analysis of the fine structure of the spectroscopic absorption edge. The advance is made possible by correction of lens aberrations to give a smaller, brighter beam, approximately 1 Ångstrom (0.1 nanometer) in diameter.
- Developed advanced computer processing methods for a through-focus series of electron microscope images to achieve an "information limit" that exceeds the resolution of the best-ever single optimal image. This method enabled the first imaging of the light non-metallic elements-carbon, nitrogen and oxygen.
- Developed a new interferometric electron beam technique to measure atomic displacements in crystals with unprecedented picometer accuracy.
- Developed and demonstrated new quantitative methods to image and measure the distribution of valence electrons in solids, which have made significant contributions to the understanding of electronic transport in high temperature superconductors.
- Conceived and constructed the first three-dimensional, energy compensated, position sensitive atom microprobe that permits compositional imaging and depth analysis with atomic resolution.
- Refined Atomic Location by Channeling Enhanced Microanalysis in an electron microscope to precisely define locations of various atomic elements and reveal an unprecedented level of information in a variety of technologically important alloys.
- Pioneered the application of electron beam holography to image and measure the grain-boundary potentials in vital ceramics such as superconductors, ferroelectrics, and dielectrics by exploiting the sensitivity of highly coherent electron waves to local electric fields.
- Developed the highest spatial resolution and lowest elemental detectability limit *in-situ* electron energy loss spectroscopy.
- Developed a new electron microscopy technique known as "fluctuation microscopy" that shows atomic arrangements in amorphous and glassy materials better than any alternative method.
- Incorporated a controlled nanoindentation apparatus within a transmission electron microscope for the first time, permitting the simultaneous atomic-scale observation and mechanical testing of nanoscale sample regions.

Other achievements under this activity include

- Developed the "Embedded Atom Method" that revolutionized the field of computational materials science by permitting large-scale simulations of atomic structure and evolution. It is currently being used by more than 100 groups worldwide and has resulted in over 1100 published works with over 2700 citations to the original work.
- Developed the "Constrained Local Moment" model for electron spin dynamics that won the Gordon Bell Award of the IEEE, presented at the High Performance Networking and Computing Conference, for the fastest real application. These calculations represented major progress towards a first principles understanding of finite temperature and non-equilibrium magnetic structure.
- Developed a new X-ray synchrotron method for directly measuring the ways atoms vibrate in a solid.

Mission Relevance:

The fundamental properties of all materials depend upon their structural arrangements and compositional distributions. Performance improvements for environmentally acceptable energy generation, transmission, storage, and conversion technologies likewise depend upon these characteristics of advanced materials. This dependency occurs because the spatial and chemical inhomogeneities in materials (e.g. dislocations, grain boundaries, magnetic domain walls, precipitates, etc.) determine and control critical behaviors such as fracture toughness, ease of fabrication by deformation processing, charge transport and storage capacity, superconducting parameters, magnetic behavior, and corrosion susceptibility.

Funding Summary:

Dollars in Thousands

FY 2003	FY 2004	FY 2005 Request
28,915	32,954	32,183

Performer	Funding Percentage
DOE Laboratories	68%
Universities	31%
Other	1%

These are percentages of the operating research expenditures in this area; they do not contain laboratory capital equipment, infrastructure, or other non-operating components.

Projected Evolution:

In the near term, program evolution builds upon recent accomplishments that span a wide range of areas including advances in microcharacterization science, the characterization of nanostructured materials, and detailed models of magnetic and structural phenomena. Electron scattering approaches supported by this program have higher spatial resolution than most other materials characterization techniques and are thus nearly unique in their ability to characterize discrete nanoscale and nanostructured regions within the interiors of samples. Characterization of semiconducting, magnetic, and ferroelectric materials benefits greatly from these abilities and from other research supported in this CRA. Concurrently, new frontiers in characterizing and understanding the microstructure and microchemistry of materials are being opened with the creation of novel characterization techniques.

The keystone of this activity is the set of capabilities to investigate structure and composition that is embodied in the four electron beam microcharacterization centers. Significant upgrading of equipment suites, acquisition of new capabilities, and commitment to adequate staffing levels will be required in the coming years to maintain these facilities as world-class user centers.

In the mid to long term, development of advanced characterization techniques is planned. The focus will be on aberration-corrected electron microscope designs, which will provide an array of opportunities for groundbreaking science. These include the possibilities of atomic-scale tomography, single-atom spectroscopic detection and identification, and increased experiment volumes within the microscope and consequently greater in-situ analysis capabilities (under perturbing parameters such as temperature, irradiation, stress, magnetic field, chemical environment).

Finally, sophisticated and highly integrated synthesis, characterization, and modeling efforts will lead to development of unique new analysis tools and breakthroughs in materials. We see opportunities to understand how nature produces model materials with desired structures and to utilize this understanding for the biomimetic synthesis of desired atomic arrangements and organizations. Further opportunities are likely to be discovered in self-assembled nanostructured materials, interfacial control, magnetic materials, and computational and modeling approaches to understanding atomic arrangements. At the same time, we anticipate that significant advances will be made in the detailed understanding of the mechanisms by which grain boundaries and interfaces in metals, ceramics, semiconductors, and polymers influence the properties and behavior of these materials. Implementing nanostructural control over these mechanisms will revolutionize the fundamental principles of materials design.

Research Activity: Mechanical Behavior and Radiation Effects

Division: Materials Sciences and Engineering
Primary Contact(s): Yok Chen (yok.chen@science.doe.gov; 301-903-4174)
Team Leader: Robert J. Gottschall
Division Director: Harriet Kung

Portfolio Description:

This activity focuses on understanding the mechanical behavior of materials under static, dynamic, uniaxial and multiaxial stresses and the effects of radiation on materials properties and behavior over a broad range of temperatures and times. The objective is to understand the defect-behavior relationship at an atomic level, and to develop unified models for mechanical behavior across broad ranges of length, temperature and time. In the area of mechanical behavior, the research aims to advance understanding of deformation and fracture and to develop predictive models for the design of materials having desired mechanical behavior. In the area of radiation effects, the research aims to advance understanding the mechanisms of radiation damage and amorphization (transition from crystalline to a non-crystalline phase), predict and learn how to suppress radiation damage, develop radiation-tolerant materials, and modify surfaces by ion implantation.

Unique Aspects:

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. The compelling need for understanding deformation mechanisms is related to the fact that virtually all structural metals utilized in energy systems are fabricated to desired forms and shapes by deformation processes. The compelling need in radiation effects - for valid predictive models to forecast the long-term degradation of reactor components and radioactive waste hosts - is expected to become increasingly critical over the next decade. Radiation tolerance of structural metals and insulating ceramics is also a matter of great concern for fusion energy systems.

Relationship to Others:

Other parts of DOE:
- Nuclear Energy Research Initiative (NERI)
- Energy Materials Coordinating Committee (EMaCC)
- Advanced Computational Materials Science for Nuclear Materials
- Close interaction with Engineering Physics

Interagency:
- MatTec Communications Group on Metals
- MatTec Communications Group on Structural Ceramics
- MatTec Communications Group on Nondestructive Evaluation
- Interagency Working Group on Nanotechnology

Significant Accomplishments:

Atomic Scale Revelations of Brittle Fracture: A molecular dynamics study has revealed for the first time how fracture processes at the atomic scale affect bulk behavior, such as dynamic fracture toughness and crack propagation rate. Using an interatomic potential derived from the modified embedded atom method, atomistic calculations showed that at low crack propagation rates, silicon fractures via perfect cleavage on atomic planes, but at higher crack propagation rates, atomic lattice defects, uneven crack surfaces and phonon vibrations are produced leading to an increase in the energy consumed during fracture. This increased energy consumption reduces the energy that would otherwise be available to drive cracks to even higher propagation rates and limits the maximum crack propagation rate to significantly less than the theoretical maximum crack propagation rate. The results demonstrate that molecular dynamics can be used to accurately reproduce bulk experimental results, while simultaneously capturing the atomic level details of the fracture process. The added significance of this method is that it can be easily extended to other materials and incorporated into models of large dynamic systems.

Silicon Carbide: Going Where Silicon-based Technology Cannot Go: Major breakthroughs in understanding atomic defects and nanostructures in silicon carbide enable this semiconductor material to be used in a new generation of devices for severe environments where silicon-based devices cannot operate. This new understanding can be used to overcome materials degradation problems that hinder advanced device development. Atomistic computational methods have determined critical defect formation and diffusion properties and accurately predicted evolution of nanostructures, phase transformations, and changes in volume and mechanical properties. The excellent agreement between computational predictions and experimental measurements provides the scientific confidence to use the computational methods to predict properties and behavior under extreme conditions that cannot be tested in the laboratory and to use defect engineering to minimize degradation, enhance materials reliability, and design materials that allow the remarkable physical properties and biocompatibility of silicon carbide to be fully utilized for energy-saving devices, advanced optoelectronics, improved sensors, medical devices, advanced-energy components, and chemically-challenging environments.

Mechanical Properties Affected by Magnetic Interaction - A New Fundamental Principle: Quantum effects involving magnetic interaction have been discovered to be responsible for unexpected solid solution hardening/softening in intermetallic alloys, thus resulting in their superior mechanical properties. This new phenomenon was discovered by careful coordination between theory and experiments: first-principle quantum-mechanical calculations coupled with polarized neutron diffraction and electron energy-loss spectroscopy (EELS). Experimental studies have revealed unusual interatomic spacing and resultant solid solution softening in nickel-aluminum alloys induced by iron, manganese and chromium solute atoms, which cannot be explained by the current hardening theories. Quantum mechanical calculations revealed the development of a large electron-spin polarization when these solute atoms substitute for aluminum in nickel-aluminum alloys. The spin polarization results in a large magnetic moment that dilates the lattice parameter and strongly affects mechanical properties of nickel-aluminum alloys. The calculated values are unambiguously supported by EELS and polarized neutron diffraction. These studies have led to the discovery of a new concept in the design of strong and tough intermetallic and metallic alloys for advanced heat engines and energy conversion systems. This new principle is expected to appear in textbooks illustrating cross-fertilization between two disciplines which have had no connection.

Mission Relevance:

The scientific results of this activity contribute to the DOE mission in the areas of fossil energy, fusion energy, nuclear energy, transportation systems, industrial technologies, defense programs, radioactive waste storage, energy efficiency, and environmental management. In an age when economics require life extension of materials, and environmental and safety concerns demand reliability, the ability to predict performance from a fundamental basis is a priority. Furthermore, high energy-conversion efficiency requires materials that maintain their structural integrity at high operating temperatures. It is also necessary to understand the deformation behavior of structural metals so as to fabricate them to desired forms and shapes. This activity seeks to understand the mechanical behavior of materials. It also relates to nuclear technologies including fusion, radioactive waste storage and extending the reliability and safe lifetime of nuclear facilities. For example, a recent study to understand environmental cracking of metallic alloys on the atomic scale has strong implications in pressurized water reactors.

Scientific Challenges:

There are two grand challenges: (a) Understanding the mechanism of amorphization at the atomic scale when oxides are irradiated with neutrons or positive ions. Amorphization degrades a material and adversely affects its physical and chemical properties. By understanding the mechanism and the parameters contributing to radiation tolerance, it will be possible to predict or engineer materials that are less susceptible to amorphization by radiation damage. (b) A unified model covering all length scales that can successfully explain deformation and fracture. Dislocation theory is typically valid for length scales less than 0.1 micron. Continuum elasticity and constitutive equations derived from it are typically limited to macroscopic length scales greater than 10 microns. These models do not converge in the interval often referred to as “mesoscale” between these limits. It is often possible, however, to control or "tune" microstructural features in this mesoscale regime by suitable adjustment of synthesis and processing parameters. Thus a unified model is sought that will quantitatively describe mechanical behavior (including strength, deformation parameters, and fracture toughness) over all length scales. A unified predictive model that is valid in the mesoscale regime could be used to design microstructures that could then be achieved via appropriate selection of synthesis and processing parameters and thus lead to optimized materials properties and behavior. Other challenges are: (a) Many metals and metallic alloys, including common steels, undergo a profound ductile-to-brittle transition over a small temperature interval, without detectable structural or chemical change. The understanding of the origins of this transition remains elusive and represents an on-going challenge. (b) Investigating and understanding nanoscale materials, their response to mechanical stress and radiation damage, will reveal previously inaccessible realms of materials behavior as well as paving the way to novel applications.

Funding Summary:

Dollars in Thousands

FY 2003	FY 2004	FY 2005 Request
13,323	13,600	13,600

Performer	Funding Percentage
DOE Laboratories	
Universities	

These are percentages of the operating research expenditures in this area; they do not contain laboratory capital equipment, infrastructure, or other non-operating components.

Projected Evolution:

In mechanics, three new directions are envisioned: (a) Research opportunities that can be realized by the application of mechanics fundamentals to the general area of self-assembly, directed self-assembly, and fluidics. These areas will constitute an increasingly significant part of the technology that mass-produces devices that harvest energy, sense trace amounts of matter, and manipulate information. (b) Roles of mechanics in biological, bio-inspired, and bio-hybrid material systems. Mechanics plays a fundamental role in understanding the biological functions at all scales. We are just beginning to utilize biology and biological techniques to develop new materials and devices that will have broad impacts on engineering. We need to understand how the hierarchical nano- and micro-structure of biological of soft materials controls the deformation and fracturing modes and behaviors of the biological systems and import this understanding to the behavior of hard alloys and ceramics that are used in the hostile environment of energy systems. (c) New challenging issues in inelastic deformation and fracturing of materials that have emerged as a result of the development of nano-devices, bio-polymers, and hybrid systems. With the emerging importance of nanoscale structures with high surface-to-volume ratios, many of the old unresolved topics, such as fragmentation and shear instabilities, need to be revisited from a multi-disciplinary perspective, taking advantage of more powerful parallel computational platforms and new experimental tools.

The accessibility of major users' facilities using neutrons and photons encourages a new dimension for the studies of mechanical behavior of materials. The advantages of using neutrons and photons, as opposed to the more traditional electrons, such as in transmission electron microscopy, are several: (a) in-situ and non-destructive experiments on bulk samples; (b) time-resolved studies; (c) three dimensional profiles; and (d) state-of-the-art neutron and photons facilities, which were not available only a few years back.

In the long term, we anticipate continued efforts to develop a unified model covering all length scales that will provide significant insights into deformation and fracture. Concurrent advances in microstructural characterization will be exploited to understand the ductile-to-brittle transition and permit this understanding to be exploited for the design of embrittlement-resistant materials. The origins of radiation tolerance will continue to be pursued including exploitation of parameters, which feed into the phenomena of radiation tolerance, such as structure, stoichiometry, and ionic (or atomic) size. Advanced computer simulations for modeling radiation-induced degradation developed during this time will also be essential to progress. During this time, the mesoscale and nanoscale modeling efforts will be extended to include nanostructured materials.

With long timescale computational capability now a reality, the study of radiation damage in solids has reached a new frontier: computational science will play a pre-eminent role in predicting radiation-damage evolution in materials. Future endeavors on advanced computational materials science for nuclear materials will examine the expected future contributions of high-end computing and computational materials science methods to structural materials performance issues relevant to use in future fusion and Generation-IV fission reactors. Research programs will address the need to predict material behavior under exposure conditions (irradiation, temperature, and mechanical loading) that represent a significant extrapolation beyond our existing knowledge base.

Research Activity: Physical Behavior of Materials

Division: Materials Sciences and Engineering
Primary Contact: Yok Chen (Yok.Chen@science.doe.gov; 301 - 903-4174)
Team Leader: Robert J. Gottschall
Division Director: Harriet Kung

Portfolio Description:

Physical behavior refers to the physical response of a material, including the electronic, chemical, magnetic and other properties, to an applied stimulus. This activity aims to characterize, understand, predict, and control the physical behavior of materials by developing the scientific basis underpinning such behavior, and furthermore, establishing rigorous physical models for predicting the response of materials. The form of stimuli ranges from temperature, electrical and magnetic fields, chemical and electrochemical environment, and proximity effects of surfaces or interfaces. Basic research topics supported include characterization of physical properties with an emphasis on the development of new experimental tools and instrumentations, and multi-scale modeling of materials behaviors. Specific areas of research include: electrochemistry and corrosion, high-temperature materials performance, electron transport behavior, superconductivity, fuel cells, semiconductors/photovoltaics, self-assembly of nanostructures/nanomaterials, and catalysis and magnetic properties of nanoclusters.

Unique Aspects:

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

Relationship to Others:

BES:

- Closely linked with activities under Core Research Activities on *Engineering Physics, Structure and Composition*, *Mechanical Behavior and Radiation Effects, Synthesis and Processing Sciences*, *X-ray and Neutron Scattering, and Condensed Matter Physics*
- Linked with Center of Excellence for Synthesis and Processing of Advanced Materials
- Linked with Computational Materials Sciences Network

Other Parts of DOE:

- Solid State Lighting/Building Technologies Program, Office of Energy Efficiency and Renewable Energy
- Nuclear Energy Research Initiative
- Energy Materials Coordinating Committee
- Hydrogen Coordinating Committee

Interagency:

- Interagency Coordination Group on Metals
- Interagency Coordination Group on Structural Ceramics
- Interagency Coordination Group on Nondestructive Evaluation
- Interagency Working Group on Nanotechnology
- OSTP Interagency Coordination Group on Hydrogen

Significant Accomplishments:

This activity has had broad and significant impact in many classes of materials and phenomena. In magnetic materials, continuous fundamental studies of bulk alloys and nanoclusters have led to the following breakthroughs:

- Discovery of the extraordinary giant magnetocaloric phenomena, which has led to the demonstration of high-efficiency refrigeration that does not require the use of any refrigerant. This technology completely eliminates ozone depleting chemicals (e.g., Freon) used by conventional refrigeration, and has the potential to develop into a global market.

- Development of ferromagnetic bulk metallic glasses with dramatic reductions in hysteretic energy loss, which has the potential of leading to $30 billion dollars per year in savings in improved energy efficient motors and transformers.
- The prediction and validation of extremely large magnetic moments in nanoclusters, which has the potential of leading to higher density nanomagnetic storage devices.

In semiconductors, major research accomplishments in silicon-based and other compound semiconductors are:

- Biocompatible semiconductor lasers have been developed for the rapid detection and analysis of chemical agents, such as anthrax spores. The device was based on recent advances in the surface chemistry of semiconductors and the concept of quantum squeezing of light emitted through a spore flowing at high speed in the laser's microcavity. This field-deployable biolaser should be able to identify different types of spores (e.g., anthrax) within a large population of harmless spores rapidly and effectively.
- Research in wide band-gap semiconductors has led to a succession of world records for energy conversion efficiency in solar photovoltaics, and been recognized by the 2001 John Bardeen Award from the American Physical Society.
- A new dielectric technology for capacitors, based on high dielectric constant ceramic perovskites oxides, has been developed. The new technology overcomes the conventional silicon dioxides thickness limitation of two to three nanometers (three to five atomic layers), and thus offers promise of further extending Moore's Law, which predicts the doubling of the performance/cost ratio for silicon-based devices every eighteen months. This breakthrough promises smaller, faster field effect transistors leading to faster and more versatile computers.
- A tenfold increase in the electrical conductivity of the semiconductor gallium arsenide was achieved and is now attracting market interest for application in electronic devices, diode lasers, reading compact discs and ultra-high speed transistors.
- A new milestone towards light-emitting silicon was achieved through the identification of oxygen atoms as the mediator of silicon energy states. The result suggests possible ways to enhance light emitting efficiency of silicon, and hence easier and cheaper ways to integrate optoelectronic components with silicon-based technology.

Other major accomplishments supported by this activity are:

- A "direct" visualization of the three-dimensional rearrangements of atoms in a crystal lattice triggered by a magnetic field was realized by an *in-situ* x-ray diffraction technique. The observation sheds light on the mechanism governing the magnetocaloric effect and paves the way to designing advanced materials for improved environmentally-friendly cooling technologies.
- Two-dimensional (2D) photonic band gap crystals in the visible wavelength have been fabricated based on the self-assembled periodic arrays of aligned carbon nanotubes. These aligned periodic carbon nanotubes are unique as they exhibit a "tunable" photonic bandgap not previously observed in the visible region and demonstrate the feasibility of fabricating large areas of 2D photonic crystals without sophisticated electron lithography procedures. These photonic crystals may find wide applications in optical signal processing and switching.
- A synergistic approach of combined photoelectron spectroscopy and quantum chemical calculations has provided crucial insights on the origin of the loss of nobility and the catalytic properties of nanoscale gold particles.
- An innovative visualization tool has provided new insights in the corrosion behavior of aluminum and its alloys. The results show that the "noise" from electrical signals is dominated by the pit growth processes as opposed to the initiation and re-passivation of protective oxides speculated previously and observed in stainless steels.
- Strong coupling and giant magnetic moments were predicted in manganese atom clusters in the presence of nitrogen. The predictions are consistent with recent experimental results and the finding will aid the design of new magnetic materials and novel spintronic devices.
- Novel zinc oxide nanostructures, including hierarchical structures with different symmetries, nanobridges, and nanowalls have been synthesized by an innovative vapor transport and condensation technique. The results demonstrate the feasibility of joining two different nano-components into a hierarchical structure. The nano-composites exhibited superior electrical and thermal conductivities.
- Russian doll models for the stabilization of silicon cage structures found that unfavorable energetics in the stretching of silicon to silicon bonds were responsible for previous failed attempts to synthesize the 60-atom silicon structure.

- A new epitaxial liquid-assisted growth method, which involves a fluoride compound in precursor films, has been developed to grow thick films of superconducting YBCO. The study yielded an understanding of the complex and unconventional growth process, which involves reactions of precursor films to form the desired compounds in several sequential steps. The understanding can be extended to other technologically important oxides that are of critical importance in solid-state electronic devices.
- Nanocrystals of semiconductor cadmium selenide were demonstrated to successfully remove excess carbon dioxide from the atmosphere. The technology could potentially convert unwanted carbon dioxide into useful organic molecules with major environmental benefits.
- Experimental studies of interfacial forces have resulted in an atomic understanding of interfacial adhesion and the ability to tune frictional forces at the atomic level. The development of instrumentation that enabled this work was recognized by an R&D 100 award.
- Pioneering work in rare earth alloys, recognized by another R&D 100 Award, has led to high performance phosphors that are now marketed in television tubes, and cheaper and more powerful permanent magnets, including the development of a new market and the spawning of a private sector company that markets it.
- A new wetting model was constructed and validated by recent AFM observations of the interfacial structures between molten metals and ceramic surfaces. The model takes into account diffusion of the solid substrate under the molten metal and successfully explains why the contact angle differs for droplets that are growing versus those that are evaporating. Understanding the behavior at these metal-ceramic interfaces is critical to improving various industrial processes including soldering, brazing, coating, and composite processing.
- An innovative approach enabled the first direct observation on how water behaves near a hydrophobic surface. Measurements made by the surface force apparatus revealed the thrashing and rippling behavior of water near hydrophobic surfaces. These insights open doors to understanding a wide range of biological dynamic processes from protein folding and enzyme reactivity.
- A new study confirms the theoretical analysis that molecules of hydrogen, oxygen, and even water can travel across conducting membranes in opposite directions from what would normally be expected from chemical potential gradients. The new analysis shows that the behavior is a result of the simultaneous, coupled transport of multiple conducting species. The understanding of membrane transport is important in the development of advanced materials for energy storage such as fuel cells.

Mission Relevance:

Research in this activity underpins the mission of DOE in many ways by developing the basic science necessary to improve reliability of materials in mechanical and electrical applications, for example energy storage and the extension of safe and reliable lifetimes of all energy-conversion technologies. With increased demands being placed on materials in real-world environments (extreme temperatures, strong magnetic fields, hostile chemical environments, etc.), understanding how their behavior is linked to their surroundings and treatment history is critical. Research in mission-relevant topics in this activity include corrosion (4.2% of GNP), photovoltaics, fast-ion conducting electrolytes for batteries and fuel cells, novel magnetic materials for low magnetic loss ($30 billion/year) and high-density storage, and magnetocaloric materials for high-efficiency refrigeration.

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 CRA 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.

Funding Summary:

Dollars in Thousands

FY 2003	FY 2004	FY 2005 Request
20,262	20,500	22,450

Performer	Funding Percentage
DOE Laboratories	77%
Universities	23%

These are percentages of the operating research expenditures in this area; they do not contain laboratory capital equipment, infrastructure, or other non-operating components.

Projected Evolution:

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

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

Finally, in order to understand the complex phenomena that are linked to both a material and its local environment, a long-term investment is needed. During this funding period, we anticipate supporting programs that apply advances in both experimental techniques and computational methodologies to understand the macroscopic behavior of materials by studying materials at all length scales and multiple time scales. In particular, bridging models covering the *mesoscale* (covering phenomena in the range of 0.1 to 10 microns) will be developed. This is vital to linking disparate length scales and creating a scientifically rigorous understanding of materials performance and behavior. It is also vital to link the time scales that correspond to fast reactions and relaxation processes in materials.

Research Activity: Synthesis and Processing Science

Division: Materials Sciences and Engineering
Primary Contact(s): Jane Zhu (Jane.Zhu@science.doe.gov; 301-903-3811)
Team Leader: Robert Gottschall
Division Director: Harriet Kung

Portfolio Description:

Synthesis and Processing Science addresses the fundamental understanding necessary to extend from design and synthesis to the preparation of materials with desired structure, properties, or behavior. This includes the assembly of atoms or molecules to form materials, the manipulation and control of the structure at all levels from the atomic to the macroscopic scale, and the development of processes to produce materials for specific applications. The goal of basic research in this area ranges from the creation of new materials and the improvement of the properties of known materials, to the understanding of such phenomena as adhesion, diffusion, crystal growth, sintering, and phase transition, and ultimately to the development of novel diagnostic, modeling and processing approaches. This activity also includes development of *in situ* measurement techniques and capabilities for quantitative characterizations to understand the growth processes at atomic or nanometer length scales.

Unique Aspects:

- The Materials Preparation Center (MPC) at the Ames Laboratory is operated for the purposes of understanding and further developing innovative and superior processes and for providing small quantities of unique, research-grade materials that are not otherwise available to academic, governmental, and industrial research communities.
- Through the Center of Excellence for the Synthesis and Processing of Advanced Materials (CSP), coordinated, collaborative research partnerships related to synthesis and processing of advanced materials are promoted between DOE national laboratories, universities, and the private sector.
- Advanced growth techniques and *in situ* diagnostics have been developed for the synthesis of improved thin-film structures of advanced materials.
- Non-equilibrium processing methods are studied using advanced modeling techniques and experimental methods, including innovative real-time, *in-situ* techniques enabled by synchrotron radiation.

Relationship to Others:

This program is intimately related to the other research activities in the Division of Materials Sciences and Engineering as the synthesis and processing of materials is a critically important area of materials research and development.

Through materials supplied by the Ames MPC, linkage is provided to other federal offices, the academic community, the industrial community and international research institutions. During FY2003, the MPC supplied a variety of specialized material products to 117 different clients (157 orders) at 92 academic, national and industrial laboratories worldwide. The MPC continued to provide Sn-Ti alloy to Oxford Superconducting Technology for the fabrication of Sn-Ti/Nb superconductors. Working with the Jet Propulsion Laboratory (JPL), MPC continued its effort related to the preparation of $LaNi_{4.8}Sn_{0.2}$ cryocooler metal hydride sorbent alloy for the Planck space vehicle. One amorphous metal alloy project was continued FY2003, in which aluminum based metal powders were prepared for the DARPA's Structural Amorphous Materials program in conjunction with Pratt & Whitney. An additional project was initiated in late FY 2003 with the U.S. Army's Aberdeen Proving Grounds on a hafnium based kinetic energy penetrator program. MPC's unique high pressure gas atomization system played a major role in its involvement in these programs.

Additional linkages within the Department of Energy are provided through the Energy Materials Coordinating Committee and its subcommittees. Interagency coordination is provided by participation in the MatTec Communications Group on Metals, the MatTec Communications Group on Structural Ceramics, and the National Nanotechnology Initiative.

Significant Accomplishments:

This program has changed the way people understand and think about the preparation of materials. Experimental, theoretical and computational tools are developed and applied to advance the scientific understanding of complicated thermodynamic and kinetic phenomena underlying processes ranging from self-assembly to far-from-equilibrium reactions that take place in welding. In the epitaxial growth area, a new technique has been developed to deposit ultrathin metallic layers on oxide, which will help next-generation computers boot up instantly by making entire memories immediately available for use. The thin metal layer achieves epitaxial crystallinity after the deposition of only a few atomic layers. This process should be applicable to a wide range of metals on metal oxides. Significant progresses have been made in the growth of single crystalline thin films of ferroelectric and ferromagnetic oxides using the molecular-beam epitaxy technique. New candidate ferromagnetic semiconductors have recently been grown by doping transition-metal oxides with magnetic impurities, which are nontraditional but strongly magnetic and thermally robust diluted magnetic semiconductors. Recent breakthroughs in the synthesis of complex oxides have brought the field to an entirely new level, in which complex artificial oxide structures can be realized with an atomic-level precision comparable to that well known for semiconductor heterostructures. Not only can the necessary high-quality ferroelectric films be now grown, but ferroelectrics can be combined with other functional oxides, such as high-temperature superconductors and magnetic oxides, to create multifunctional materials and devices. The shrinking of the relevant lengths to the nanoscale produces new physical phenomena.

New techniques, developed to measure local electromagnetic properties, now permit a fundamental understanding of the mechanism by which solid-solid interfaces and crystalline defects control the behavior of nanostructured as well as macroscopic materials. For the first-time, suppression in dielectric-constant has been observed directly at grain boundaries, contradicting traditional assumptions generally made about grain-boundary behavior, utilizing scanning impedance microscopy and nano-impedance spectroscopy. In the welding area, a coupled thermodynamic and kinetic model was developed to describe stability of the principal phases in stainless steels. This knowledge has led to the modification of the standard diagram used to choose welding electrode compositions for stainless steels. Additional modeling work utilizing massively parallel computers has permitted the linkage of macro- and microscopic scale phenomena during the melting and solidification of a weld. This permits simulation and visualization of weld microstructure as a function of processing conditions, e.g. during the melting, addition of new compounds, and resolidification that occurs during welding. Experimentally, tracking of real-time phase transformations that occur during weld solidification was made possible using synchrotron radiation and provided invaluable data to support scientific modeling and simulation leading to better electrode design. Recognitions include the recipients of the Sparaagen Award and the Warren F. Savage Award from the American Welding Society.

Specific achievements include:

- Investigations of self-assembled heteroepitaxial semiconductor quantum dots using real-time stress sensing and light scattering showed how elastic repulsion determines evolution of dot arrays. Repulsion promotes spatial ordering, accelerates ripening kinetics, and enhances quantum dot phase transition.
- In the self-assembly area, developing scientific understanding of surfactant interactions with ceramic compounds and other materials, including biological tissues, has permitted the growth of ordered porous ceramic structures with hierarchical architecture spanning from the nano- to the macro-scale.
- A rapid, efficient self-assembly process for making nanophase composites that mimic the complex construction of seashells was developed resulting in a strong and tough (crack resistant on impact loading) material.
- Ceramic substrates were synthesized with tailored and regularly ordered nanoscale pores of controlled shapes and sizes. These substrates were found to remove deadly heavy metals such as mercury, lead and silver from contaminated water.
- A breakthrough in the fundamental understanding of the processing of ceramic aerogels led to a new, non-toxic, low temperature, and low-pressure process to produce films in an environmentally benign manner. This discovery overcame the sixty-year barrier to the large-scale commercial utilization of these films, won the prestigious Iler Award of the American Chemical Society and was cited as an important discovery by the Wall Street Journal.
- The Materials Preparation Center has completed over 3700 requests for specialized materials preparation and characterization services since its establishment. In addition to the previously mentioned accomplishments, MPC has enabled the following technologies:
    - ♦ Lead free solder
    - ♦ Magnetocaloric gadolinium-silicon-germanium alloys
    - ♦ Recyclable lightweight automotive composite materials

  - Terfenol-D which is a mangetostrictive alloy containing terbium, dysprosium, and iron that was developed at the Center and led to the spin-off of a new private sector company which now markets this material
- Quasicrystal coatings produced by plasma-arc spray that have superior wear resistance and thermal insulation behavior coupled with reduced surface friction for potential thermal barrier wear resistant coating applications in aircraft-engine components.
- A uniform three-dimensional coating process known as "Plasma Ion Immersion Processing" was improved so as to fabricate hard coatings, such as diamond-like carbon, that exhibit low sliding friction and superior wear resistance. This process is cost-effective and achieves a high rate of implantation over a very large surface area with uniform thickness and coating quality over complex three-dimensional geometries.
- A nanophase molecular template method was developed to synthesize films that exploit the dielectric properties of air to achieve ultra-low dielectric constants for the next generation of microelectronic devices and computers.
- Developed a unified, fundamental understanding of the multifaceted behavior of H in Mg-doped, p-type GaN that, in several respects, goes beyond what has previously been achieved for H in compound semiconductors. These studies represent a new level of quantitative understanding of hydrogen behavior within compound semiconductors.
- Investigation of the dynamics of self-assembled supramolecular organic oligomers, polymers, and metal chelate systems has revealed methods to control both intra- and intermolecular interactions leading to systems with tunable optical properties.

Mission Relevance:
This research supports the Department of Energy’s overarching goals for improved energy efficiency, protection of the environment, and the advancement of scientific knowledge. Specific relevant applications include discovery of new materials for efficient energy production and use; hard and wear resistant surfaces to reduce friction and wear; high-rate, superplastic forming of light-weight, metallic alloys for fuel efficient vehicles and other structures needed in land and air transportation applications; high-temperature structural ceramics and ceramic matrix composites for high-speed cutting tools, bearings, engines and turbines (to enable fuel efficiency and low-pollutant emissions); ordered intermetallic alloys for harsh applications (requiring heat, load, wear and corrosion resistance), including engines and turbines (also to enable fuel efficiency and low pollutant emissions); response of magnetic materials to applied static and cyclical stress; plasma, laser, and charged particle beam surface modification to increase corrosion and wear resistance; and welding and joining, including dissimilar and non-metallic materials.

Scientific Challenges:
Understanding the physics and chemistry of the synthesis and processing, as well as the thermodynamics and kinetics of reaction, of nanoscale materials and structures and the elements of the processing environment are critical to the preparation of larger components. There are significant experimental, theoretical and computational challenges in understanding what is occurring so that the benefits of nanoscale phenomena can be realized in larger scale components. Major scientific challenges also remain in the fabrication and the fundamental understanding in the non-trivial assemblies of inorganic, organic, composite, and biomimetic materials. There is a need for creative and innovative methods to investigate complex systems, such as composite materials with multifunctionality.

Future efforts are required to synthesize new materials for the advancement of science and technologies, to gain the fundamental understandings for better control of materials manipulation and properties, and to solve materials problems, such as adhesion and stability under thermal and environmental stress. Although there is steady progress in the synthesis and processing of materials, there still exists a serious deficit in the ability to produce (new) materials with desired properties and microstructures by rational design and synthesis. Experimental methods and theoretical models need to be developed to achieve mesoscopic structures via various methods, such as self-organized and directed growth. Scientific challenges also lie in new composite materials with various matrices, and in ecologically-benign materials.

Funding Summary:

Dollars in Thousands

FY 2003	FY 2004	FY 2005 Request
11,839	12,000	12,975

Performer	Funding Percentage
DOE Laboratories	60%
Universities	40%

These are percentages of the operating research expenditures in this area; they do not contain laboratory capital equipment, infrastructure, or other non-operating components.

Projected Evolution:

- Increased emphasis on understanding the opportunities and challenges presented by nanoscale materials and by the processing of larger components containing nanoscale materials and structures.
- Further progresses will be made in the growth and understanding of epitaxial heterostructures of ferromagnetic, ferroelectric and/or superconducting compounds using the molecular-beam epitaxy technique.
- Science-based understanding of advanced synthesis and processing methods such as self-assembly, molecular- and supramolecular-directed nanostructure formation, and novel deposition methods will be investigated. This understanding will be applied to attain new structures, compositions, and materials behavior, to fabricate materials with new functionalities, and to reduce the energy and environmental impact of processing.
- Processing research will be extended to include new ceramic, intermetallic, semiconducting, organic, composite, and biomimetic materials and material structures, including nanocrystalline materials, films, coatings, and crystals. Analytical techniques and modeling will be developed and applied to determine and predict the relationship of synthesis and processing parameters towards structure, purity, deformability, residual stresses, toughness, adhesion, and electronic, optical and magnetic properties.
- Processing capabilities of the Materials Preparation Center will be expanded to include intelligent process control and modeling and to provide new innovative synthesis and processing techniques. Plans include the use of a plasma-heated skull-melting furnace with capabilities to cast or atomize materials, and microstructure-sensitive processing to provide real-time monitoring and correlation with process models.
- An understanding of interfacial interactions at the molecular level will be developed, and their influence on molecular conformation and ordering will be shown for evolving nanostructures. An understanding of how short and long-range molecular forces mitigate the formation of ordered amorphous structures will be extended to develop an understanding of how biological systems control the formation of ordered assemblages of crystalline nanoparticles.

Research Activity: Engineering Physics

Division: Materials Sciences and Engineering
Primary Contact(s): Timothy Fitzsimmons (Tim.Fitzsimmons@science.doe.gov; 301-903-9830)
Team Leader: Robert J. Gottschall
Division Director: Harriet Kung

Portfolio Description:

Engineering Physics advances scientific understanding underlying the dynamic interactions of single and multicomponent solid and fluid systems. Research considers the behavior and interactions of fluids including organic, biological and complex fluids with each other and with solid systems; the transport of energy on and within these systems; and the development of means to advance the characterization of these systems. Issues under consideration frequently span several orders of magnitude in length and time scales and range from atomic interactions to macroscopic behavior and subpicosecond chemical events to fatigue events that may take years to reach completion. Accordingly they present a considerable challenge to theory, computational simulation and experiment. Questions of ongoing interest include understanding and predicting the behavior of (1) nanoscale structures and systems, including those with biological components; (2) dynamics of fluids, especially multi-component and complex fluids, but also including heat transfer, solidification and granular materials; and, (3) interactions of phonons with interfaces, secondary phases or with micro and nanoscale defects in solids. Opportunities of current and future interest include transport issues related to hydrogen storage and production, nano-motor design, thermal transport in nano-fluids.

Unique Aspects:

Engineering Physics has a unique role to play in National Nanotechnology and Hydrogen Initiatives to further the understanding of nano- and meso-structures, devices and systems; molecular machines; transport behavior to and within consolidated nano-particulate material; and the dynamic behavior of multiphase, complex and biologically inspired materials. This activity has and maintains a leadership role in the fundamental understanding of multiphase fluid flow, heat transfer, and in the fundamental behavior of granular materials.

Relationship to Others:

Interacts with the community through: (1) workshops such as the Workshop on Multiphase Fluid Flow, May, 2002 and the upcoming Symposium on Computational Approaches to Disperse Multiphase Flows, in October, 2004; (2) program presentations to the American Society of Mechanical Engineers, the American Society for Engineering Education and other groups.

Interacts with other agencies and interagency working groups such as: (1) NSF – Exploring potential joint interests in fluid flow and heat transfer (2) NSTC Interagency Working Group on Nanotechnology and (3) Interagency Coordinating Committee on Non-Destructive Evaluation.

Interfaces and coordinates with the Synthesis and Processing, Physical Behavior, Mechanical Behavior and Radiation Effects, and Condensed Matter Theory Core Research Activities. Work in droplets and sprays supports work in combustion which is funded in a number of other programs in the Department of Energy.

Collaborates with the Mathematical, Informational and Computational Sciences Division on work of mutual interest.

Significant Accomplishments:

- Development of a nanosized *biological* motor for use in MEMS and NEMS devices
- Creation of the first *synthetic* nanosized electric motor
- Research on nanomotion from biomolecular interactions has led to the development of instruments for detecting and identifying molecules
- Adding small quantities of carbon nanotubes to a fluid dramatically increases its ability to conduct heat, however, theory predicts an even larger increase in conductivity. Experiments and simulations point to poor thermal coupling between the nanotubes and the fluid with implications for designing advanced heat transfer systems.
- Thermal conductivity of single crystal silicon nanowires has been discovered to be two orders of magnitude lower than the bulk thermal conductivity of silicon, a highly desirable property for thermoelectric applications. Simultaneously, the results reveal their limitation for electronics and photonics applications.

- Record heat flux dissipation achieved with micro-channel two-phase flow (27,600 W/cm^2).
- Oil and gas companies are using results of research for more efficient transport and exploration of crude oil and natural gas. The Syncrude pipeline, which yields a 97% saving in energy to transport the crude, would not have been built without these developments.

Mission Relevance:

Improved understanding of dynamic behavior at the nano- and micro-scale will advance sensing and control capabilities, lead to accurate predictions of materials and systems behavior, and enable larger-scale applications of devices with nano-scale components. Together these advances will further lead to higher process efficiency and lower energy consumption. Improving the knowledge base on multi-component fluid dynamics and heat transfer will have a major impact on energy consumption because these phenomena are an integral part of every industrial process. Potential impacts include improved efficiency of fossil and nuclear based power generating systems.

Scientific Challenges:

How can we accurately model the transport of hydrogen and heat through nanoscale materials, and nanoporous and mesoporous structures? What are the explanations for anomalous thermal behavior of nanofluids and nanowires? Where do the continuum approximations break down in multicomponent systems containing fluids? Can we adequately describe, simulate and engineer macroscale systems to take advantage of nanoscale behavior? Challenges include understanding: 1) the potential of chemical and biological systems to construct complex, nanostructured materials under ambient conditions; 2) the role of interfaces and structure on the behavior of simple and complex fluids; 3) how more realistic sized groupings of drops and bubbles interact with each other and with their environment; 4) the mechanics and energetics of molecular mechanical devices; 5) simple and complex systems driven far from thermodynamic equilibrium; and 6) the interactions of phonons with defects and interfaces.

Funding Summary:

Dollars in Thousands

FY 2003	FY 2004	FY 2005 Request
15,297	14,038	13,500

The program provides funding for 51 university grants, 13 programs at national laboratories, and 1 program in industry. Funding demographics is shown below:

Performer	Funding Percentage
DOE Laboratories	46%
Universities	52%
Other	2%

These are percentages of the operating research expenditures in this area; they do not contain laboratory capital equipment, infrastructure, or other non-operating components.

Projected Evolution:

The program will continue to refine its core of excellence in nanotechnology and microsystems, multi-component and complex fluid dynamics, granular materials, heat transfer, and other select areas such as phonon behavior. The program will increasingly pursue understanding of the dynamics of the solid-liquid interface, of multicomponent fluids at the micro- and nano-scale, and the interface and dynamics of organic and biological materials with fluids and solids.

Core Research Activity: Experimental Program to Stimulate Competitive Research
Division: Materials Sciences and Engineering
Primary Contact(s): Matesh N. Varma (matesh.varma@science.doe.gov; 301-903-3209)
Team Leader: William Oosterhuis
Division Director: Harriet Kung

Portfolio Description:

Basic research spanning the entire range of programmatic activities supported by the Office of Science in states that have historically received relatively less Federal research funding. The DOE designated EPSCoR states are Alabama, Alaska, Arkansas, Delaware, Hawaii, Idaho, Kansas, Kentucky, Louisiana, Maine, Mississippi, Montana, Nebraska, Nevada, New Mexico, North Dakota, Oklahoma, South Carolina, South Dakota, Tennessee, Vermont, West Virginia, and Wyoming, and the Commonwealth of Puerto Rico and US Virgin Islands. BES manages EPSCoR for the Department.

Unique Aspects:

The program objective is accomplished by sponsoring two types of grants: 1) Implementation Grants, and 2) Laboratory-State partnership Grants. Implementation grants are for a maximum period of six years with an initial grant period of three years. Maximum funding for these grants is $750,000 per year. One-to-one state matching funds are required. The Laboratory-State partnership grants are for a period of one to three years. Maximum funding for these grants is $150,000 per year. Exactly 10% state matching funds are required. DOE/EPSCoR has placed a high priority on integrating the scientific manpower development component with the research component of the program. In addition, it is promoting strong research collaboration and training of students at the DOE national laboratories where unique and world-class facilities are supported by the Department. This program is science-driven and supports the most meritorious proposals based on peer and merit review. Workshops and discussions are regularly held with representative scientists from EPSCoR states to acquaint them with the facilities and personnel at the DOE laboratories.

Relationship to Others:

The core activity interfaces with all other program core activities within the Office of Basic Energy Sciences. In addition, it is responsive to programmatic needs of other program offices within the department.

Significant Accomplishments:

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

- **Basic Energy Sciences**: 1)Researchers at the university of Alabama have experimentally established the remarkable tolerance of ilmenite-hematite (IH) materials to neutron and proton radiations. The IH of all compositions retain their semiconducting and magnetic properties even after being exposed to these radiations for an extend time. A simple two terminal "varistor" devices using both ceramic and film structures was constructed and demonstrated that they retain their characteristics almost unaltered after irradiation. This can lead to development of IH based devices suited for applications in space and in radiation environments. 2) Micro-optics group in Montana has developed and demonstrated fast focus control using a deformable mirror. This deformable mirror can change its shape in response to a control voltage, thus changing the focus in an optical instrument. Because the mirror is small this shape change can happen in a few microseconds. Optical Coherence Tomography (OCT), uses backscattered light from a laser beam to image tissues in the body. Focus control for an OCT system requires the ability to change focus cyclically at the line scan rate, typically 8 to 16 kHz, faster than is possible using traditional mechanical focus adjustment. This focus control is easily accomplished with the newly developed mirrors, and will enable much higher resolution OCT imaging in the future.
- **Biological and Environmental Research**: Abasic sites are the most common DNA damages and are replication-blocking lethal and mutagenic lesions. Scientists working on this project have successfully crystallized for the first time a replicative DNA polymerase in complex with DNA that has just incorporated a nucleotide opposite an abasic site. This structure is unique in that multiple protein conformations have been captured within a single crystal that represent steps along the switching pathway between the DNA polymerizing and editing modes of the protein. The results show that when a nucleotide is incorporated opposite

an abasic site, the DNA geometry becomes distorted, the DNA fails to translocate and switches to the editing mode, thus accounting for the ability of an abasic site to block replication

- **High Energy Physics**: The unification of forces in four space-time dimensions helps us to understand the three apparently different gauge interactions, strong, weak and electromagnetic, in terms of a single gauge interaction. Such a grand unification has been tested experimentally and works very well. However, there are Yukawa interactions, responsible for giving masses to all fermions, which are completely unrelated to the gauge interactions. In the context of higher dimensions, the Higgs fields can be extra dimensional components of the gauge fields, and the Yukawa interactions are just part of the gauge interactions in higher dimensions. The gauge symmetry is broken by compactifying the extra dimensions on an orbifold. In this project a theory is proposed which achieves such a true unification. The theory is based on two extra space-like dimensions with super symmetry. This theory gives rise to unification of the gauge and Yukawa couplings, in remarkable agreement with the current data. The theory also makes predictions which can be tested in the upcoming Large Hadron Collider. This work has achieved for the first time, the true unification of all the elementary particle and forces in the framework of local quantum field theory.

- **Renewable Energy and Efficiency**: The researchers at Jackson State University are working to improve the amount of ethanol that can be produced from Southern Pines. Acid hydrolysis is being developed for conversion of biomass into a liquid process stream (hydrolyzate) that can be either directly fermented into ethanol or further processed by enzymatic conversion into a then more fermentable stream used to make ethanol. Southern Pine acid hydrolyzate containing sugars and inhibitors, such as furans and phenolics, was treated with a weak anion resin and laccase immobilized on kaolinite. Fermentation of the sugars in the treated hydrolyzate resulted in significantly higher ethanol production levels than those achieved with the untreated hydrolyzate.

- **Defense Programs**: Optical sensors based on Faraday rotation were developed for monitoring electric and magnetic fields. These sensors are being developed for use in improved operation of the electron beam accelerators and imaging systems that are used in DOE stockpile stewardship program.

Mission Relevance:

The principal objective of the DOE/EPSCoR program is to enhance the abilities of the designated states to conduct nationally competitive energy-related research and to develop science and engineering manpower to meet current and future needs in energy related areas. Most of the research clusters that have graduated from the DOE EPSCoR program after six years of funding have found alternate funding for continuing the research activity. This demonstrates that the research clusters funded by EPSCoR are becoming competitive. In addition, EPSCoR grants are supporting graduate students, undergraduates and postdoctoral fellows, and encouraging them to be trained in world-class research at DOE national laboratories. The work supported by the EPSCoR program impacts all DOE mission areas including research in materials science, chemical science, biological and environmental science, high energy and nuclear physics, fusion energy science, advanced computer science, fossil energy science, and energy efficiency and renewable energy science.

Scientific Challenges:

Initially only nine states were awarded implantation awards, which left many of the designated states without any DOE EPSCoR funding. To accommodate participation from a larger number of states in the program and to leverage the state-of-the-art unique capabilities of the national laboratories, a State-Laboratory partnership program was initiated in FY98. As a result of this program, approximately 28 partnership awards were approved in FY98 and FY99. In FY00 and FY01 twenty additional State-Laboratory partnership awards were funded in response to solicitation number 99-21. In FY03 another solicitation was issued and in response to this solicitation ten State-Laboratory partnership awards were made in FY04, and an additional four are expected to be made in FY05. This component of the program has successfully increased the number of states receiving funds from DOE EPSCoR program. The program continues to meet the challenge of providing a balance between the implementation awards and the Laboratory-State partnership awards.

Funding Summary: BY EPSCoR STATES

(Dollars in Thousands)

	FY 2003	FY 2004	FY 2005 Estimate
Alabama	946	987	735
Alaska	0	0	0
Arkansas	205	140	146
Delaware*	-	-	0
Hawaii**	0	0	0
Idaho	100	98	102
Kansas	881	547	695
Kentucky	1224	107	224
Louisiana	287	272	284
Maine	0	0	0
Mississippi	685	398	667
Montana	580	515	375
Nebraska	1,155	0	120
Nevada	1,146	0	0
New Mexico**	0	135	135
North Dakota	137	410	406
Oklahoma	339	275	135
Puerto Rico	435	375	375
South Carolina	781	454	316
South Dakota	0	125	125
Tennessee*	-	-	0
Vermont	1,064	877	709
US Virgin Islands*	-	-	0
West Virginia	1,405	248	291
Wyoming	130	130	270
Technical Support	222	80	60
Other***	0	1,500	1,503
Total	11,722	7,673	7,673

* Delaware, Tennessee, and US Virgin Islands became eligible for funding in FY 2004.
**Hawaii and New Mexico became eligible for funding in FY 2002.
***Uncommitted funds in FY 2004 and FY 2005 will be competed among all EPSCoR states.

SBIR contribution is not included in the Funding Summary Total above.

SBIR	321	222	222

Research Activity: Nanoscience Centers

Division: Scientific User Facilities

Primary Contact(s): Kristin A. Bennett (Kristin.Bennett@science.doe.gov; 301-903-4269)
Altaf (Tof) Carim (carim@science.doe.gov; 301- 903-4895)

Division Director: Pedro Montano

Portfolio Description:

This activity supports construction and the subsequent operation of Nanoscale Science Research Centers (NSRCs) at DOE laboratories that already host one or more of the BES major user facilities. Nanotechnology is the creation and use of materials, devices, and systems through the control of matter at the nanometer-length scale, at the level of atoms, molecules, and supramolecular structures. Nanoscience and nanotechnology will fundamentally change the way materials and devices will be produced in the future and subsequently revolutionize the production of virtually every human-made object. Nano-science will explore and develop the rules and tools needed to fully exploit the benefits of nanotechnology. Each NSRC will combine state-of-the-art equipment for materials nano-fabrication with advanced tools for nano characterization. The NSRCs will become a cornerstone of the Nation's nanotechnology revolution, covering the full spectrum of nano-materials and providing an invaluable resource for universities and industries.

Unique Aspects:

Nanoscale Science Research Centers were recommended by the NSTC Interagency Working Group on Nanoscale Science, Engineering, and Technology (IWGN) as part of DOE's contribution to the National Nanotechnology Initiative (NNI). The NNI proposed significant increases in this Nation's investment in nanotechnology in order to ensure a competitive position in this rapidly developing field of science and technology. European nations and Japan are already heavily committed to this field of research, which promises to revolutionize technology in the 21st century. The most recent example is the planned construction of a large center for Micro and Nanotechnology near Grenoble at a projected cost of about $300M. Grenoble is a major research center in Europe where the European Synchrotron Radiation Facility (ESRF) and the Institut Laue-Langevin (ILL) neutron source are localized. The importance of collocation of NSRCs with facilities for x-ray and neutron scattering was also recognized by the IWGN. Hence, the Basic Energy Sciences program will play a major role in the NNI through the establishment of NSRCs affiliated with major BES scientific user facilities already sited at the DOE national laboratories, particularly the synchrotron radiation light sources, the neutron scattering facilities, and the electron beam microcharacterization facilities..

NSRCs will provide unique scientific and engineering capabilities not available in any of the parallel programs sponsored by other government agencies. For example, the National Science Foundation will sponsor research programs in nanoscience at universities, but such programs will be limited in scope and size and will not be comparable to the large-scale facilities in Europe or Japan. Three NSRCs are being planned by BES to cover the diverse aspects of nanoscience and to leverage existing DOE facilities. These centers were selected after an intense peer-review process. The proposed centers will be located at Lawrence Berkeley National Laboratory, Oak Ridge National Laboratory and Los Alamos National Laboratory / Sandia National Laboratories.

Each Center will combine state-of-the-art equipment for materials nanofabrication with advanced tools for nano characterization. The purposes of NSRCs are as follows:

- Advance the fundamental understanding and control of materials at the nanoscale regime.
- Provide an environment to support research of a scope, complexity, and disciplinary breadth not possible under traditional individual investigator or small group efforts.
- Provide the foundation for the development of nanotechnologies important to the Department of Energy.
- Provide state-of-the-art equipment to in-house laboratory, university and industry researchers and optimize the use 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 Others:

This activity will have strong interaction with all BES programmatic research performed at national laboratories and academic institutions. A significant fraction of the research will use the collocated synchrotron radiation light sources and the neutron scattering facilities. BES continues as a member of the NSTC Interagency Working Group on Nanotechnology to coordinate activities across the government. In addition, individual NSRCs have strong working relationships with academia, industry, state-sponsored nanoscience activities, and one another.

Significant Accomplishments:

This activity is presently in Project Engineering Design stages.

Mission Relevance:

The mission of the Office of Science is "To advance basic research and the instruments of science that are the foundations for DOE's applied missions, a base for U.S. technology innovation, and a source of remarkable insights into our physical and biological world and the nature of matter and energy." The Nanoscale Science Research Centers provide a unique opportunity for a major advance in carrying out that mission.

Scientific Challenges:

Scientific Challenges: Preparing for the challenges of this new millennium requires strategic investments that will help our nation develop a balanced R&D nanotechnology infrastructure, advance critical research areas, and nurture the scientific and technical workforce of the new century. The nanotechnology research and development is a top priority for the future. In response, DOE has taken the initiative of constructing three NanoScience Centers at LBNL, ORNL and SNL/LANL with the following project goals: (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 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 scientific challenges, all of which involve the collocation of disparate disciplines in order to fabricate and assemble nanosized components. One of the must 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 will 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 this interface.

Construction Challenges: The major challenges are associated with the schedule of design and construction required in order to achieve successful completion of the project. To be most timely, the NSRCs should be completed by FY06.

Funding Summary:

Dollars in Thousands

	FY 2003	**FY 2004**	**FY 2005 Request**
Construction – Other Project Costs	100	400	600
Project Engineering and Design	11,850	2,982	2,012
Center for Nanoscale Materials, ANL	0	10,000	12,000
Center for Nanophase Materials Sciences, ORNL	23,701	19,882	17,811
The Molecular Foundry, LBNL	0	34,794	32,085
Center for Integrated Nanotechnologies, SNL/LANL	4,444	29,674	30,897
Center for Functional Nanomaterials, BNL	0	0	18,465
TOTAL	40,095	97,732	113,870

Projected Program Evolution:

The initial stages of this program are associated with the design and construction of the Nanocenters at three National Laboratories: LBNL, ORNL and SNL/LANL. In addition, it is necessary to develop a well balanced and fair user program for this new type of National Laboratories facility. Scientific utilization and programmatic integration in the National Laboratories is prerequisite for successful operation in the near future of these Nanoscale Science Research Centers.

Research Activity: Atomic, Molecular, and Optical Science

Division: Chemical Sciences, Geosciences, and Biosciences
Primary Contact(s): Michael P. Casassa (E-Mail: Michael.Casassa@science.doe.gov; 301 903-0448)
Team Leader: Eric Rohlfing
Division Director: Walter Stevens

Portfolio Description:

The AMOS activity supports experimental and theoretical studies of the fundamental properties of atoms, ions, and small molecules and the interactions between electrons, photons, and ions in collisions with atoms, molecules, and surfaces. Research is aimed at the most complete quantum mechanical description of such properties and interactions. Topics of interest include: interactions of intense electromagnetic fields, induced by highly charged ions or lasers, with atoms and molecules; coherent control of quantum mechanical processes; development and application of novel x-ray light sources in advance of next generation light sources; theory and experiment on ultracold collisions and quantum condensates.

Unique Aspects:

The underpinning aspect of the AMOS activity gives it a unique relationship with BES activities that utilize photon, electron, neutron, and heavy ion probes at the BES user facilities. The relationship will continue to be exploited, particularly with respect to forefront research into the generation and application of ultrashort, intense x-ray pulses. The AMOS program is a major supporter of synchrotron-based AMOS studies in the U.S., which includes ultrashort x-ray pulse science and high-resolution spectroscopy at the ALS and APS. The AMOS program continues its role as the principal U.S. supporter of research into the properties and interactions of highly charged atomic ions, which is of direct consequence to fusion plasmas.

Relationship to Others:

The AMOS activity co-funds with BES Condensed Matter Physics an ultrafast x-ray beamline at the ALS. The program has contributed substantially to ongoing and planned experiments concerning x-ray characterization and AMO science at the Sub-Picosecond Photon Source (SPPS) and Linac Coherent Light Source (LCLS) at SLAC. Fundamental insight and data obtained in the AMOS activity are relevant to Fusion Energy Science programs in atomic data for fusion modeling and basic plasma physics. This synergy is particularly noticeable at the Multicharged Ion Research Facility (MIRF) at ORNL, which is co-funded by BES and FES. There is overlap in the interactions of intense laser fields with high-energy plasmas relevant to defense programs in DOE. A close working relationship exists with the NSF Atomic, Molecular, Optical and Plasma Physics Program, and these two programs co-fund the NAS/NRC Committee on Atomic, Molecular and Optical Science (CAMOS). In FY2003, the AMOS Program provided partial support for three Gordon Conferences: Quantum Control of Light and Matter; Photoions, Photoionization and Photodetachment; and Atomic Physics. The program had active participation in the Conference on Super Intense Laser Atom Physics (SILAP) that involved an international community of scientists who are interested in the interaction of intense laser fields with matter.

Significant Accomplishments:

During the past five years, the AMOS activity has been a major U.S. supporter of experimental and theoretical studies of the fundamental properties of atoms, ions and small molecules and of collisional interactions between atoms, ions, molecules and surfaces. This has lead to the acquisition of a vast database on the properties of atoms, ions and small molecules. This information is now being used to manipulate the quantum behavior of these species. It has also lead to the development and application of powerful new methods for momentum imaging of collision fragments that have seen wide application in atomic, molecular, and chemical physics. More recently, the initiative on Novel X-Ray Light Sources has lead to the further development and scientific application of ultrafast x-ray sources using table-top lasers and 3rd generation synchrotrons (ALS and APS). Quasi phase matching of high-harmonic generation (HHG) for soft x-ray production has been demonstrated and fundamental interactions of intense and controllable laser fields with atoms and small molecules leading to ionization and fragmentation have been examined. New projects in 2003 focused on electron-driven processes in gaseous and condensed phases, the production and utilization of ultracold molecules and multidimensional spectroscopy for characterization of the optical properties of nanoscale materials. Some of the program's highlighted work and awards from the year include: Professors Margaret Murnane and Henry Kapteyn and co-workers at the University of Colorado used a waveguide to limit plasma-induced defocusing and generate HHG in argon at photon energies up to 250 eV, significantly extending its range. Dr. Victor Klimov and co-workers at Los Alamos National Laboratory showed that a novel synthesis can produce thin films composed of lead selenide nanocrystals in a titania matrix that exhibit amplified spontaneous emission in the near-IR. Dr. Debbie Jin of JILA/University of Colorado became a 2003 McArthur fellow for her recent work to advance atomic cooling to the study of quantum degeneracy in Bose-Fermi mixtures. Prof. Herschel Rabitz, Princeton University was awarded the Willis E. Lamb Medal for Laser Science and Quantum Optics at the 33rd Winter Colloquium on the Physics of Quantum Electronics for inventing the learning algorithm approach to the coherent control of quantum phenomena. In 2003 four AMOS PIs were named Fellows of the American Physical Society; currently ~70% of the PIs in the program are APS Fellows.

Mission Relevance:

AMO Science underpins a wide spectrum of BES research activities and lays the foundation for enhanced future utilization of BES light sources, electron beam microcharacterization centers, and neutron scattering facilities. The knowledge and techniques acquired through the AMOS program have potential impact in the development of new probes of matter in the gas and condensed phases using photons, electrons, and ions; on our understanding of nanostructured materials; and on our ability to model low- and high-temperature plasmas. AMOS contributes at the most fundamental level to the science-based optimization of current energy sources and the development of new ones.

Scientific Challenges:

AMO science is currently undergoing a transition from a field in which the fundamental interactions of atoms and molecules are probed to one in which they are *controlled*. The enormous database of knowledge acquired over the last several decades and the powerful technical innovations in laser technology are the two forces driving this transition. AMOS practitioners can now shape the quantum mechanical wavefunctions of atoms and small molecules using controllable laser fields, trap and cool atoms (and soon molecules) to temperatures near absolute zero where condensation into a single quantum state occurs, create coherent matter waves by manipulating quantum condensates, create novel surface structures using highly charged ion beams, and coherently drive electrons in atoms so that they generate high-harmonic radiation in the soft x-ray region. Ultrafast science is now moving into the x-ray regime with enormous potential for following the motion of atoms on the time scale of chemical reactions.

Funding Summary:

Dollars in Thousands

FY 2003	FY 2004	FY 2005 Request
13,379	13,401	13,401

Performer	Funding Percentage
DOE Laboratories	39 %
Universities	60 %
Other	1 %

These are percentages of the operating research expenditures in this area; they do not contain laboratory capital equipment, infrastructure, or other non-operating components.

The activity provides funding for 49 university grants supporting about 60 students and partially supporting about 59 faculty and senior staff. It also funds 3 programs at national laboratories supporting about 19 senior staff and 5 students and postdocs. Programs at the laboratories are multi-investigator efforts focusing on problems that require extensive participation by experienced scientists. These programs usually underscore the user facilities at the SC laboratories, including the Multicharged Ion Research Facility (MIRF) at ORNL, the ALS at LBNL and the APS at ANL. A new program at LANL on optical properties of semiconductor quantum dots, which was funded under NSET in FY2002, is strongly affiliated with the nascent Center for Integrated Nanotechnologies at LANL/SNL. The activity supports the J. R. MacDonald Laboratory at Kansas State University: a multi-investigator program devoted to the experimental and theoretical study of intense-field physics produced either by ultrafast lasers and collisions with highly charged ions.

Projected Evolution:

Coherent control of nonlinear optical processes and tailoring quantum mechanical wavefunctions with lasers will grow in importance. Such control will be vital to the ultimate realization of laser-controlled chemistry and to our ability to store and read information in quantum systems.

The development and application of novel x-ray light sources using existing synchrotrons or table-top lasers will continue. Topics of interest include the development of high-harmonic generation or its variants as useable soft x-ray sources, development and characterization of femtosecond pulses of x-rays at existing synchrotrons and new accelerator-based sources, and applications in the chemical and materials sciences.

AMO science plays a strong role in nanoscale science efforts. Opportunities include the development of AMO theory for artificial quantum structures in materials, the utilization of light force trapping and cooling to create ultracold samples of atoms and molecules including quantum condensates, the use of nonlinear spectroscopies to characterize the optical properties of nanoscale materials and the manipulation of condensates to create coherent matter waves. Quantum condensates of bosons and fermions represent novel nanostructures whose properties (superfluidity, Cooper pairing, etc.) increasingly blur the boundary between atomic and condensed matter physics.

Fundamental studies of highly charged ions and their interactions with atoms, molecules, and surfaces will continue to further develop the knowledge base important to fusion plasmas. A new thrust area related to this effort will be to utilize the experimental and theoretical tools of AMOS in the study of low-energy electron-molecule interactions in the gas and condensed phases. Such interactions play vital roles in determining the subsequent chemistry in low-temperature plasma processing, which is used extensively in the semiconductor industry and in radiation environments such as mixed-waste storage tanks.

Research Activity: Chemical Physics Research

Division:	Chemical Sciences, Geosciences, and Biosciences
Primary Contacts:	Frank P. Tully (Frank.Tully@science.doe.gov ; 301-903-5998)
	Richard L. Hilderbrandt (Richard.Hilderbrandt@science.doe.gov; 301-903-0035)
Team Leader:	Eric A. Rohlfing
Division Director:	Walter J. Stevens

Portfolio Description:

This activity supports experimental and theoretical investigations into the molecular origins of gas-phase chemistry and chemistry at surfaces. Gas-phase chemistry emphasizes the dynamics and rates of chemical reactions at energies characteristic of combustion with the aim of developing validated theories and computational tools for predicting chemical reaction rates for use in combustion models and experimental tools for validating these models. The study of chemistry at well characterized surfaces and the reactions of metal and metal-oxide clusters lead to the development of theories on the molecular origins of surface-mediated catalysis. Because of the relevance of gas-phase chemistry to combustion, the program manager for chemical physics is also responsible for oversight of the operation of the Combustion Research Facility.

Unique Aspects:

The Department of Energy is the largest supporter of basic research in combustion in the federal government. This program is the principal supporter of high-temperature chemical kinetics and gas-phase chemical physics in the Nation. This program is strongly coupled to the Combustion Research Facility (CRF), Sandia National Laboratories. The facility, through collocation of BES-, DOE Technology Office-, and industry-supported programs, is an effective force for integration of basic and applied research. The latter includes internal combustion engines, coal and biomass combustion, industrial burners for process heat, and high-temperature materials processing and manufacturing. The CRF houses the Nation’s foremost fundamental research program on laser-based optical diagnostics for the measurement of chemical and fluid-mechanical parameters. Similarly, chemical physics research supported at PNNL is emerging as a premier program in the application of fundamental molecular research to the environmental management and restoration problems of the Department.

Relationship to Others:

Combustion research is also conducted under various research programs within EE and FE. Linkages with this program vary in formality. In addition, combustion-related chemical physics research is conducted by AFOSR, ONR, ARO, NASA, NIST, and NSF. The AFOSR and NASA programs support research in propulsion. NASA and NIST programs investigate fire propagation. ONR and ARO research focuses on organic waste remediation. NSF supports basic research. Surface science is supported through several Federal programs, both applied and basic.

Significant Accomplishments:

Within the last ten years, theories and computer codes for the calculation of chemical properties and, in particular, chemical reaction rates have achieved a high degree of accuracy and reliability for systems of a few atoms. The theoretical developments have been inspired and validated by nearly a quarter of a century of molecular beam, spectroscopy, dynamics and kinetics research on the detailed measurement of reactions as functions of collision energy and internal energies of reactants and products. Research in the DOE chemical physics program has played a prominent role in this development. Professor Y. T. Lee, one of three recipients of the 1986 Nobel Prize in Chemistry for molecular-beam chemical dynamics research, was supported by the Chemical Physics program for his entire U.S. research career. Continuing laser-based experimental research and computationally intensive theoretical work provide the fundamental basis for developing a predictive capability for chemically reacting flows.

Mission Relevance:

Nearly 85% of the Nation’s energy supply has its origins in combustion and this situation is likely to persist for the foreseeable future. Although an ancient technology, the complexity of combustion–the interaction of fluid dynamics with hundreds of chemical reactions involving dozens of unstable chemical intermediates–has provided an impressive challenge to predictive modeling of combustion processes. The chemical physics program supports the development of theories and computational algorithms to predict the rates of chemical reactions at temperatures characteristic of combustion. It supports the development and application of experimental techniques for characterizing gas-phase reactions in sufficient detail to develop, test, and validate predictive models of chemical reaction rates. Predicted and measured reaction rates will be used in models for the design of new combustion devices with maximum energy efficiency and minimum, undesired environmental consequences.

The research supported by the chemical physics program for the molecular characterization of chemical dynamics at surfaces is aimed at developing predictive theories for surface-mediated chemistry such as is encountered in industrial catalysis or environmental processes. Surface-mediated catalysis reduces the energy demands of industrial chemical processes by bypassing energy barriers to chemical reaction. Surface-mediated catalysis is used to remove pollutants from combustion emissions. At the molecular level, surface-mediated catalysis is not well understood. New catalysts are few; improvements come principally from modification of known catalytic materials. There is no body of organized knowledge such as exists for the field of organic chemistry that can be used to find new catalysts for new or existing processes. The knowledge gained from this research program will guide in the development of a predictive capability for surface chemistry.

Scientific Challenges:

The calculation of the electronic structures of open shell systems such as radical reaction intermediates and excited electronic states cannot currently be done with chemical accuracy. This capability is absolutely essential for the calculation of rates of reactions of significance to combustion.

The calculation of the electronic properties of molecules with chemical accuracy scales as the seventh power of the number of electrons. Calculations for molecules with five or more atoms are beyond current and projected computational accuracy. Approximations of proven, reliable accuracy are needed.

Spectra of molecules in high energy states characteristic of combustion are extraordinarily complex and as yet do not yield useful information about the imminent chemical fate of the observed molecule.

The interaction of fluid dynamics with chemistry on the nanoscale is not sufficiently well characterized to provide parameterization of subgrid models.

Molecular dynamics experiments are extraordinarily difficult and yield large amounts of detailed state-to-state reactive and non-reactive data. How can all of these data be made useful?

No equivalent of the Woodward-Hoffmann rules, that have been as useful as predictive tools in organic chemistry, exists for surface chemistry.

Funding Summary:

Dollars in Thousands

	FY 2003	**FY 2004 Request**	**FY 2005 Request**
Chemical Physics Research	32,097	30,334	31,617
Combustion Research Facility	5,935	5,967	6,169
Chemical Physics Research Total	38,032	36,301	37,786

These funds provide support for ~130 PIs along with their graduate students and postdoctoral associates. Programs at the laboratories are multi-investigator efforts on problems that require extensive participation by experienced scientists.

Performer	**Funding Percentage**
DOE Laboratories	72 %
Universities	27 %
Other	1 %

These are percentages of the operating research expenditures in this area; they do not contain laboratory capital equipment, infrastructure, or other non-operating components.

Projected Evolution:

The focus of the chemical physics program is the development of a molecular-level understanding of gas-phase and surface-mediated chemical reactivity of importance to combustion and catalysis. The desired predictive capability spans the microscopic to macroscopic domains – we require the ability to compute the results of individual gas-gas and gas-surface interactions as well as their complex, collective behavior in real-world devices. Currently, we are placing an increased emphasis on theories and computational approaches for structure and dynamics of open shell systems and large molecules and on the interaction of chemistry with fluid dynamics. In surface chemistry, we continue to emphasize the development of a structural basis for gas/surface interactions, encouraging more coupled experimental and theoretical research efforts. Expanding into the future, we plan to initiate efforts on the detailed chemical physics of energy transfer in large molecules, the molecular origins of condensed phase behavior, and the nature and effects of weak interactions including hydrogen bonding. These molecular phenomena impact numerous DOE and national needs.

Research Activity: Photochemistry and Radiation Research
Division: Chemical Sciences, Geosciences, and Biosciences
Primary Contact: Mary E. Gress (mary.gress@science.doe.gov; 301-903-5827)
Team Leader: Eric A. Rohlfing
Division Director: Walter J. Stevens

Portfolio Description:

The activity supports fundamental molecular level research on interactions of radiation with matter in the condensed phase.

The photochemistry research effort emphasizes fundamental processes aimed at the capture and conversion of solar energy. Biomimetic models (photochemical and photoelectrochemical) seek to mimic the key aspects of photosynthesis – antenna, reaction center, catalytic cycles, and product separation. The research encompasses organic and inorganic photochemistry, photoinduced electron and energy transfer, photoelectrochemistry, biophysical aspects of photosynthesis, and molecular assemblies for artificial photosynthesis.

The radiation sciences effort supports fundamental studies on chemical effects produced by the absorption of energy from ionizing radiation. The radiation chemistry research encompasses heavy ion radiolysis, models for track structure and radiation damage, characterization of reactive intermediates, radiation yields, and radiation-induced chemistry at interfaces. Accelerator-based electron pulse radiolysis methods are employed in studies of highly reactive transient intermediates, and kinetics and mechanisms of chemical reactions in the liquid phase and at liquid/solid interfaces.

Unique Aspects:

This activity is the dominant supporter (85%) of solar photochemistry in the U.S. and the sole supporter of radiation chemistry. Specialized electron pulse radiolysis facilities at Notre Dame, ANL, and BNL serve the academic research community, industrial users, and other national laboratories. A new laser-driven electron accelerator at BNL features a 7 picosecond pulse width and the capability for synchronized electron pulse-laser pump-laser probe experiments.

Relationship to Others:

The solar photochemistry research effort interfaces with activities in BES, including: Energy Biosciences activities in biochemical aspects of photosynthesis; Chemical Physics in theoretical calculations of excited states and computational modeling; Catalysis and Chemical Transformations on electron transfer reactions in homogeneous and microheterogeneous solutions, and advanced catalytic materials; and Materials Sciences fundamental photovoltaics research. The research is relevant to EE activities in the Office of Solar Energy Technologies on photovoltaics, and in the Office of Hydrogen and Superconductivity Technologies on hydrogen production.

The radiation sciences activity interfaces in BES with Catalysis and Chemical Transformations in reaction kinetics in homogeneous solutions, and Materials Sciences in radiolytic damage to glasses and radiation-induced corrosion of structural materials. There are also important interfaces with EM activities in waste remediation and NE activities on nuclear reactors, and nuclear processing and storage. Radiolytic processes in solution, particularly heavy ion radiolysis, are of interest to the NIH regarding radiation damage to biological systems in medical diagnosis and therapy.

Significant Accomplishments:

Stratospheric ozone depletion by chlorofluorocarbons was predicted by F. Sherwood Rowland of UC, Irvine, in 1974. Professor Rowland's research, solely supported by this activity, involved the chemistry of "hot" chlorine atoms produced by nuclear recoil and complementary photolytic reactions. Rowland was awarded the Nobel Prize in 1995. Radiotracers for nuclear medicine were pioneered by Alfred Wolf at BNL. The "special pair" model for electron donor chlorophyll molecules in photosynthesis was introduced by Joseph Katz and James Norris of ANL. Photosynthetic molecular models for light to chemical energy conversion were developed by Michael Wasielewski of ANL and by Professors Gust, Moore, and Moore of Arizona State University. The "inverted region" in Marcus electron transfer theory was verified in pulse radiolysis experiments by John Miller at ANL.

Mission Relevance:

Solar photochemical energy conversion is a long-range option for meeting the world's future energy needs. An alternative to solid-state semiconductor photovoltaic cells, the attraction of solar photochemical and photoelectrochemical conversion is that fuels, chemicals, and electricity may be produced with minimal environmental pollution and with closed renewable energy cycles. A strong interface with EE solar conversion programs exists at NREL, involving shared research, analytical and fabrication facilities, and a jointly shared project on dye-sensitized solar cells.

Radiation chemistry methods are of importance in solving problems in environmental waste management and remediation, nuclear energy production, and medical diagnosis and radiation therapy. Fundamental studies on radiation-induced processes complement collocated NERI and EMSP projects.

Scientific Challenges:

In solar photoconversion, knowledge gained in charge separation and long-distance electron transfer needs to be applied in a meaningful way to activation of small molecules (CO_2, N_2, and H_2O) via photocatalytic cycles. The major scientific challenge for photoelectrochemical energy conversion is that small band gap semiconductors capable of absorbing solar photons are susceptible to oxidative degradation, whereas wide band gap semiconductors, which are resistant to oxidative degradation in aqueous media, absorb too little of the solar spectrum. Ongoing research activities include multibandgap, multilayer cascade-type semiconductors, photosensitized nanoparticles, and surface coatings that protect against photocorrosion. Experimental and theoretical studies on photosynthetic pigment-protein antenna complexes should lead to advances in design of efficient and robust artificial light-collecting molecular assemblies. Computational chemistry methods incorporating recent advances in calculation of excited states should be developed and applied in design of photocatalysts and molecular dynamics simulations in artificial photosynthesis. Fundamental studies on photochemical reaction pathways offer opportunities for less energy intensive and more environmentally benign processing of specialty chemicals and high volume industrial intermediates.

A recent workshop "Research Needs and Opportunities in Radiation Chemistry" has identified new directions, connections, and impacts of radiation chemistry. A common theme is the need to explore radiolytic processes that occur across solid-liquid and solid-gas interfaces, where surface chemistry can be activated and changed by radiolysis. Solid-liquid interfaces abound in nuclear reactors and high level radioactive wastes. Colloidal particles participate in gas production, gas retention, and in organic degradation of high level wastes. In regard to environmental remediation, radiation chemistry is one of the most promising advanced oxidation processes for degradation of organic pollutants. 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. A proposed subpicosecond electron accelerator at ANL would enable investigation of the primary events in radiation chemistry, now virtually unknown except for theoretical models, wherein fundamental processes link physics to the chemistry of radiolysis.

Funding Summary:

Dollars in Thousands

FY 2003	FY 2004	FY 2005 Request
24,853	28,502	29,477

Performer	Funding Percentage
DOE Laboratories	67 %
Universities	33 %

These are percentages of the operating research expenditures in this area; they do not contain laboratory capital equipment, infrastructure, or other non-operating components.

The program provides funding for 49 university grants supporting about 46 graduate students, 51 postdoctoral research associates, and partially supporting about 56 faculty. There are nine programs at DOE laboratories supporting 45 senior staff and 46 graduate students and postdocs. Programs at the laboratories are multi-investigator efforts on problems that require extensive participation by experienced scientists. In photochemistry, major research groups are supported in inorganic photochemistry and electron transfer at BNL; in photoelectrochemistry at NREL and NDRL; and in photosynthesis at Ames, ANL, and LBNL. Many of the research efforts at the DOE laboratories involve strong collaborative interfaces with university and industrial communities. The radiation chemistry effort is centered at specialized electron pulse radiolysis facilities at Notre Dame, ANL, and BNL. The Notre Dame Radiation Laboratory serves as the primary radiation research user facility, hosting approximately 40 users/year from academia and industry.

Projected Evolution:

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

Electron pulse radiolysis methods will investigate reaction dynamics, structure, and energetics of short-lived transient intermediates in the condensed phase. Radical ion excited states will be studied in novel synchronized electron pulse-laser pump-laser probe experiments. Fundamental studies on reactivity of nitrogen oxides in aqueous solution are pertinent to understanding radiolytic degradation of nuclear tank waste. Studies of solvent effects on free radical reaction rates in supercritical fluids are relevant to next-generation supercritical water-cooled nuclear power plants. Subpicosecond electron pulse radiolysis is being developed at ANL based on a table top terawatt laser system. Electron pulses are produced by focusing terawatt laser pulses into a supersonic helium gas jet. The approach is different from the laser-driven photocathode method employed at pulse radiolysis facilities at BNL, Osaka, and Paris; where the time resolution is 7 ps, 0.2 ps, and 2 ps, respectively. Electron pulse radiolysis studies on the previously unexplored femtosecond time scale are proposed on solvation and thermalization of electrons in water; the dynamics of solvation and prethermalized species; solvation in confined media such as mesoporous silica and micelles; and charge injection into metal oxides. In the more distant future, the ability with the terawatt ultrafast high field facility to generate simultaneously subpicosecond electrons and x-rays will be exploited for detection of structural changes upon electron injection.

Research Activity:	**Catalysis and Chemical Transformations**
Division:	Chemical Sciences, Geosciences, and Biosciences
Primary Contacts:	Raul Miranda (Raul.Miranda@science.doe.gov; 301-903-8014) John Gordon (John.Gordon@science.doe.gov; 301-903-2153)
Team Leader:	John C. Miller
Division Director:	Walter J. Stevens

Portfolio Description:
The long-term goal of this activity is to develop a predictive science of chemical catalysis and reactivity. Its specific objective is to develop mechanistic understanding of chemical reactions that pertain to energy production, storage, and conservation; environmental remediation and pollution prevention; renewable and fossil resource processing; and novel materials synthesis. The research portfolio addresses catalytic reactions in solution and on gas-solid or liquid-solid interfaces (e.g., alcohol carbonylation catalyzed by organometallic complexes, and hydrocarbon reforming catalyzed by supported noble metals). This activity funds also the study of molecular processes and structure-activity relationships in chemical systems of large complexity, such as reactions that model petroleum or coal fractions processing, hydrogen production and storage, automobile exhaust conversion, fuel cell conversion, specialty chemical synthesis, polymer synthesis, nanomaterials synthesis, and others. As outcome of the investigation of the catalysis of chemical transformations, fundamental advances are being made in inorganic, organometallic, porous, and nano material synthesis; surface and physical chemistry; organic chemistry and chemical technology.

Unique Aspects:
This activity funds the largest fraction of basic research in catalysis in the Federal Government. It covers heterogeneous, homogeneous, and bio catalysis under a single umbrella. The integration promotes synergism among disciplines and innovation in fundamental approaches as well as applications. In terms of instrumentation, this program has helped with the establishment of surface science and inorganic synthesis laboratories at universities and encourages the use of large-scale facilities at National Laboratories. Principal investigators are increasingly utilizing synchrotron, neutron and electron sources and computational tools to significantly advance catalysis research.

Relationship to Others:
Funding for surface science and inorganic synthesis is coordinated with the programs of Materials Chemistry and Chemical Physics in the BES division. Support for the applied aspects of catalysis of oil and coal processing and environmental remediation is provided by FE and EE. At the NSF, heterogeneous and bio catalysis are funded within its Engineering Directorate while homogeneous catalysis is funded within the Math and Physical Sciences Directorate (Organometallic and Inorganic Chemistry program). Also at the NSF, the surface science and materials aspects of catalysis are spread among three divisions (Chemistry, Materials, and Chemical and Transport Systems). At other agencies, the NIH funds the health-related applications of homogeneous, enzymatic, and bio catalysis, the EPA funds the application of catalysis to environmental remediation, and the ONR and ARO support the application of catalysis to military purposes.

Significant Accomplishments:
The science and practice of catalysis over the last several decades have led to many achievements of fundamental interest. A significant contribution has been made to the current molecular-level understanding of catalytic cracking of hydrocarbons in zeolites, reforming of hydrocarbons over supported bimetallic alloys, and desulphurization of heteroaromatics over supported metal sulfides. Reactions of importance in environmental chemistry, such as NO decomposition, have been studied in detail over model single crystal metals and supported metals. Results of those investigations have dramatically improved the knowledge of catalyst structure-reactivity relationships. This activity has also led to fundamental advances in the catalysts required for the selective oxidation of hydrocarbons for the manufacturing of monomers and fine chemicals. During the past decade, one of the most significant accomplishments in homogeneous catalysis was the development of novel single-site metallocene catalysts for polymerization of alkenes. The control of polymer tacticity resulted in property enhancement and a largely expanded utilization of polyalkene plastics, from extending the shelf life of food we buy to enhancing the efficiency of the cars we drive. Other very significant achievements were the catalytic synthesis of organic acids by alcohol carbonylation

and the generation of important monomers by olefin metathesis. More recently, methane selective oxidation was achieved both homogeneously and heterogeneously. For their achievements, researchers in this program have been widely honored by scientific societies, as they have received three-quarters of the awards in Organometallic Chemistry given by the ACS, and all but one of the fundamental catalysis awards given to US academics by the North American Catalysis Society.

Mission Relevance:
The fuel and chemical industry is a primary producer and consumer of energy. Catalysis plays an essential role in both energy production and energy conservation, as over 90% of all chemical processes are catalytic. Energy conservation and environmentally benign processing are both benefits of the high selectivity and activity achievable through catalysis. The economic impact of catalysis is outstanding, as the chemical industry is responsible for a significant fraction of the GDP (over $900B in 2002) and is one of the few sectors that historically have had a positive balance of trade for the US (over $20B in 2002). This program contributes the basic knowledge that relates catalytic structure to chemical functionality and to reaction mechanism. As the demand for greener processing increases, and as the use of more refractory feedstocks or the need for novel materials rises, the motivation to discover new chemical routes and hence new catalysts will also increase. Consequently, the phenomenological knowledge that must be reduced to a comprehensive set of scientific principles will continue to augment. This research funded under this activity is producing the fundamental concepts that are needed to carry out predictive catalyst design.

Scientific Challenges:
The grand challenge for this area of research is the *a priori* molecular-level design and synthesis of catalysts with controlled reactivity and durability. Such knowledge is of relevance for the production of catalysts that convert natural resources into energy or desired products in an energetically efficient and environmentally benign manner. That challenge can be met by coordinating fundamental research on chemical synthesis, structural characterization, mechanistic studies and theoretical interpretation.

The current challenge in inorganic synthesis is the atomistic and molecular control of structure, shape, and functionality, all of which can be facilitated by the development of libraries of modular ligands. For the particular case of biomimetic catalyst development, synthesis and use of versatile ligands must be promoted. Likewise, air- and water-resistant complexes must receive priority. The control of macromolecular structure continues to be a challenge. Secondary structures that produce shape-selective reaction environments must be attained by the use of, for example, dendrimers, polypeptides, zeolites, and imprinted media.

In solid state synthesis, the current frontier is to produce catalytic materials with nanoscale control of composition, homogeneity, shape, and structure. A challenge is to design molecular precursors and convert them into solid-state structures with desired chemical functionalities that are durable under reaction conditions. Traditional routes of surface chemistry, aqueous-solution chemistry, and high-temperature chemistry need to be complemented by softer routes. For example, coordination chemistry may be used to build nanoparticles that are surface-functionalized with metal compounds. Organic or biological strategies may then be used to arrange the particles into preconceived patterns. These arrangements will provide molecular recognition properties (for example, size, shape, chirality, hydrophobicity, etc.)

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

The study of reaction mechanisms will be promoted by the synergistic use of theory, simulation and experimentation. In particular, identification and structural characterization of the transition states still remains a challenge for most reactions. Classical labeling, trapping and molecular probe experiments must be complemented with time-resolved *in-situ* vibrational spectroscopy in order to acquire information on bonding dynamics.

The development of chemo-, regio-, and stereo-selective reactions is of primary importance to the advancement of the science of catalysis, since those reactions present the highest demands on catalysts. Conformers at equilibrium are usually separated by barriers of less than 3 kcal/mol. While high selectivity has been obtained with homogeneous catalysts in selected instances, heterogeneous catalysts require substantially more study, possibly with help from biomimetics.

Catalysis of bond cleavage and reformation has, for the most part, been restricted to hydrocarbons (CC, CH bonds), halogenated compounds (CX bonds), and nitrogen and sulfur containing compounds (CS, CN bonds). Moreover, past and current research has also addressed the selective addition of oxygen, hydroxyl, or nitrogen to hydrocarbon and aromatics. For homogeneous catalysis, the challenge is to carry out these selective reactions under solvent-less conditions or with green solvents such as supercritical CO_2, while maintaining stability. For heterogeneous catalysis, the challenge is to work at low temperature and pressure conditions with high activity and selectivity. For both types of catalysis, a major challenge is to obtain selective conversion for reactants such as short-chain saturated hydrocarbons and other refractory molecules. Likewise, new challenges for all types of catalysts have arisen in activating molecules and materials derived from biorenewable resources.

Besides hydrocarbon chemistry, a newer challenge is the elucidation of the catalytic mechanisms for the synthesis of molecular and nanomaterials. For example, the catalytic synthesis of carbon nanotubes is currently being optimized utilizing purely Edisonian approaches. Chirality control has remained elusive because of lack of understanding of the structure-determining steps. As another example, the nucleation and subsequent growth of silicon nanowires from silane or its derivatives on molten gold nanoparticles proceeds through catalytic pathways that are completely unknown. Finally, the synthesis of compound semiconductors and more complex nanomaterials constitute an excellent challenge for the development of catalytic science and its application to a new area.

Funding Summary:

Dollars in Thousands

FY 2003	FY 2004	FY 2005 Request
33,854	34,453	36,402

Performer	Funding Percentage
DOE Laboratories	58 %
Universities	38 %
Other	4 %

These are percentages of the operating research expenditures in this area; they do not contain laboratory capital equipment, infrastructure, or other non-operating components.

The laboratory programs are multi-investigator efforts and make use of specialized facilities at LBNL, BNL, ORNL, NREL, ANL and Ames, usually involving collaborators from universities.

Projected Evolution:

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

Better understanding of the reactivity of matter will result from more complete integration of experiment and theory, reproducible synthesis of catalysts, and thorough characterization of catalysts and reactions. An effort is needed to promote scientific cooperation among groups with complementary expertise in synthesis, structural characterization, intermediate and transition state characterization, dynamics simulation, and kinetics determination. National laboratories or university centers may serve as focal points for knowledge integration.

Following from the specific scientific challenges outlined above, it has become apparent that the convergence of heterogeneous, homogeneous, and biocatalysis must be promoted. Ideas and approaches motivated by biological reaction systems will be used to derive new biomimetic homo- or heterogeneous analogues. For example, two such particular ideas are the use of long-range or secondary structure to affect not just selectivity but also activity of inorganic catalysts, and the use of tunable structural flexibility to affect reaction pathways and hence selectivity.

New single investigator efforts are expected to be focused on the challenges mentioned. The following examples illustrate the areas where mechanistic understanding and new methodology are needed. (a) Synthesis of hybrid organometallic-heterogeneous catalysts from molecular precursors such as organometallic or cluster compounds or organic-inorganic host-guest complexes. (b) Synthesis of mixed metal inorganic compounds and derived high-temperature catalysts consisting of crystalline nanoporous structures with precisely positioned chemical functions. (c) Selective functionalization of saturated hydrocarbons or stereoselective functionalization of complex molecules by heterogeneous catalysis. (d) Characterization of kinetically relevant intermediates and catalyst dynamics with high spatial and time-resolution and *in situ* spectroscopy, microscopy and diffraction, and in particular, with synchrotron and neutron-based techniques and advanced computational techniques. (e) Environmentally benign transformations using solvent-less homogeneous catalysis, low-temperature heterogeneous reactions, and tandem or programmable catalysis, i.e., precise matching of functionalities among dissimilar catalysts.

Research Activity: Separations and Analysis

Division: Chemical Sciences, Geosciences, and Biosciences
Primary Contact: William Millman (William.Millman@science.doe.gov; 301-903-5805)
Team Leader: John C. Miller
Division Director: Walter J. Stevens

Portfolio Description:

This activity addresses the scientific principles that underlie energy-relevant chemical separations and analytical methods, capitalizing on the synergistic relationship between these two areas of chemistry.

The portfolio for separations science emphasizes, but is not limited to, the separation of radionuclides and other metal ions, and seeks molecular-level understanding to support advances in both large-scale and analytical-scale separations. Molecular-level understanding is also sought for separation methods that have the potential to significantly impact energy use, such as membrane-based processes. Supercritical fluid solvents are being explored with potential benefit to "green chemistry". The use and impact of nanoscale and supramolecular structures on various separations processes are of growing interest.

The analytical research portfolio has historically emphasized mass spectrometry and seeks to elucidate the chemical and physical principles that underlie ionization and excitation processes and modern approaches to mass discrimination. A more recent sector of the portfolio seeks to understand and use the interaction of electromagnetic radiation with matter in phenomena such as molecular fluorescence, laser ablation and surface-enhanced Raman scattering. Hyphenated laser-mass spectrometry techniques such as MALDI –MS, laser ablation ICP-MS and laser ionization ion mobility-MS are being explored. The extension of these ultrasensitive techniques to single-molecule detection and observation is being explored. Research to understand chromatography at the molecular level reflects the synergy between separations and analytical sciences. This activity also contributes to the maintenance of the scientific infrastructure required to meet as-yet-undefined challenges in separations and analysis.

Unique Aspects:

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

Relationship to Others:

The activity is closely coupled to the Department's stewardship responsibility for actinide and fission product chemistry and to its clean-up mission. It emphasizes the separation and analysis of actinide and fission product elements and their decay products. Some overlap and coordination with the BES Heavy Element Chemistry Program is natural. Similarly, elements of the analysis science portfolio benefit from cooperation with the BES Chemical Physics and Atomic and Molecular Science Programs. The basic nature of the research has led to advances in technologies ranging from those that support nuclear non-proliferation efforts to those underpinning aspects of the Human Genome Project.

Significant Accomplishments:

This activity is responsible for such notable contributions as the concept of host-guest complexation, for which Professor Donald Cram (UCLA) shared the 1987 Nobel Prize in Chemistry; the use of the inductively coupled plasma (ICP) for emission and mass spectrometry; and, more recently, the concept of bifunctionality in ion-exchange resins and solvent extraction. A Presidential Green Chemistry Award in 1997 was shared by researchers supported by this activity for their contributions to the understanding of processes in supercritical carbon dioxide that enabled the introduction of a chloro-fluorocarbon-free process for the dry-cleaning industry. This new commercial process relies on fundamental understanding developed with the support of this activity. The 2002 Nobel Prize in Chemistry recognized the fields of electrospray mass spectrometry and matrix-assisted laser desorption/ionization (MALDI) mass spectrometry. Basic research in both techniques is carried out in the program.

Mission Relevance:

The success of the Manhattan Project was, in large part, due to our ability to develop industrial-scale processes for separating plutonium from irradiated fuel. Thus began the intense interest of the Department of Energy and its predecessor agencies in the science that underlies separation processes. The missions of the Department have evolved, and it must now face the legacy of accumulated wastes from the cold war era. Knowledge of molecular-level processes is required to characterize and treat these extremely complex mixtures and to understand and predict the fate of associated contaminants in the environment. In addition, separation science and technology have huge economic and energy impacts. For example, distillation processes in the petroleum, chemical, and natural gas industries annually consume the equivalent of 315 million barrels of oil (~5.4% of total petroleum consumption). It is further estimated that separations processes account for more than 5% of total national energy consumption. Separations are essential to nearly all operations in the processing industries and are necessary for many analytical procedures.

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

Scientific Challenges:

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

Funding Summary:

Dollars in Thousands

FY 2003	FY 2004	FY 2005 Request
14,547	13,517	16,441

Performer	Funding Percentage
DOE Laboratories	58 %
Universities	42 %

These are percentages of the operating research expenditures in this area; they do not contain laboratory capital equipment, infrastructure, or other non-operating components.

This activity provides funding for about 45 university grants supporting, at any given time, on the order of 50-60 students and 20-25 postdocs. In addition, 13 programs at national laboratories support numerous senior staff, and additional students and postdocs. Programs at the laboratories are typically multi-investigator efforts on problems that require extensive collaboration by experienced scientists. These programs act as the focal point for specific research efforts vital to the DOE mission. This BES activity supports research programs at ORNL, ANL, and PNNL, with smaller efforts at Ames, LBNL and INEEL. Many of the research efforts at the national laboratories involve collaborations with the university and industrial communities.

Projected Evolution:

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

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

An expanded activity would support work to understand the self-assembly process by investigating energetics and rate-controlling steps; increased effort in characterization of the aqueous-oxide interface, as well as general liquid-solid and liquid-liquid interfaces; analysis of scattering and NMR data to characterize amorphous media; enhanced effort in molecular modeling to support ligand design; field-enhanced spectroscopy; expanded university effort in manpower-intensive organic and inorganic synthesis; provide support to enhance collaboration between universities and national laboratories; and maintenance and upgrade of national laboratory infrastructure. The activity will evolve to meet the challenges in self-assembly, characterization of interfaces, single-molecule detection, and gas-phase ion chemistry. A synthesis of results of analytical research to enable collection of basic data, ligand design to control possible reactions, as well as modeling and computational science, will be required to enable the prediction of macroscopic behavior from known molecular properties.

Research Activity: Heavy Element Chemistry

Division: Chemical Sciences, Geosciences, and Biosciences
Primary Contact(s): Lester Morss (Lester.Morss@science.doe.gov); 301-903-9311
Team Leader: John C. Miller
Division Director: Walter Stevens

Portfolio Description:

This activity addresses the scientific principles that form the basis for the understanding of the chemical behavior of actinide, transactinide, and fission product elements and their compounds. Areas of interest are coordination chemistry and reaction kinetics of actinides in aqueous and non-aqueous solutions; gas-phase and solid-state chemical bonding; measurements of chemical, thermodynamic, and magnetic properties; synthesis of actinide-containing materials; chemical properties of the heaviest actinide and transactinide elements; and theoretical methods for the prediction of heavy element electronic properties, molecular structure, and reactivity.

The actinide elements form a unique chemical series in the periodic table due to the filling of the 5f electron subshell. Their nuclear properties, and the resulting use of uranium and plutonium isotopes as energy sources and in weapons, cause some actinide isotopes to be essential industrial materials. This activity supports efforts to develop a fundamental understanding of chemical bonding and reactivity of the actinides and transactinides, and to determine the similarities and differences between the actinides and the 4f (lanthanide) series or the 3d, 4d, and 5d transition metal series. There is a close and synergistic relationship between the heavy element chemistry program and the separations science program. The heavy element chemistry program contributes to the maintenance of the scientific infrastructure required to meet future challenges in heavy element chemistry and to provide unique facilities for the education of students.

Unique Aspects:

This activity represents the only source of funding for basic research in the actinides, transactinides, and fission products in the United States. Its major emphasis is on understanding the underlying chemical and physical principles of the actinide and fission product materials. The activity is primarily based at the national laboratories because of the special facilities needed in order to handle these radioactive materials safely.

Relationship to Other Programs:

This activity provides the fundamental understanding of the properties of the actinides, transactinides, and fission product elements that are necessary for the Department of Energy missions in nuclear energy, stewardship responsibilities for defense programs, and environmental clean-up. The heavy element chemistry program conducts unclassified basic research on all the actinide and transactinide elements, while the applied programs generally limit their investigations to the chemical and material properties of specific elements and systems of strategic, economic, or programmatic interest. This activity also has close ties to the DOE BES separations and analysis activities, which have a major focus on the separation of actinides and fission products from other elements.

Significant Accomplishments:

The heavy element chemistry activity had its genesis in the Manhattan project. It continues today as the nation's only basic research program supporting the exploration of the physical and chemical properties of the transuranium elements and their compounds. The early goal was to determine the basic inorganic chemistry and physical properties of the new elements and their compounds and to discover new elements. The chemical properties of the transuranium elements, especially plutonium, originally were determined from microscale experiments. The processes for the separation of plutonium from uranium and fission products on an industrial scale were developed and scaled up from these results. The completion of the High Flux Isotope Reactor (HFIR) at ORNL in the 1960's provided a stable supply of curium and heavier elements that continues to the present. The inorganic chemistry of the elements through einsteinium (Es, atomic number 99) has been determined with small but weighable quantities of the elements. For the elements heavier than Es in the periodic table, tracer techniques and one-atom-at-a-time chemistry have been developed and carried out through element 108 to determine chemical properties.

Taken together, the results from this activity have repeatedly confirmed the Seaborg hypothesis that the actinides are best represented in the periodic table as a 5f element series placed under the 4f (lanthanide) series. Interpretations of spectroscopic results have provided estimates of thermodynamic quantities such as oxidation-reduction potentials and enthalpies of sublimation. Specific electronic transitions determined in this activity have proven useful in developing processes for laser isotope separation of uranium and plutonium. Structural systematics of the actinide metals, oxides, and halides as a function of atomic number have been determined. Magnetic measurements have shown that the light actinide metals have delocalized 5f orbitals (*i.e.*, the 5f electrons form bands), but that the f electrons become localized at americium, element 95. Thus, the magnetic behavior of the first part of the actinide series resembles that of the d-orbital transition metals but the heavier actinides exhibit behavior similar to the rare earth metals.

Mission Relevance:

Knowledge of the chemistry of the actinide and fission product elements is necessary for the successful conduct of many of DOE's missions. In the defense area, understanding the chemistry and material properties of specific actinides was key to the development of our nuclear deterrent, and now plays a major role in the stewardship of the nuclear stockpile. This program conducts the broadly based unclassified research on actinides that provides the scientific basis for framing the narrower issues facing the DOE's defense programs. In the area of nuclear energy, this activity provides the fundamental understanding of actinide and fission product chemistry that underpins the development of advanced nuclear fuels, as well as the predictions of how spent nuclear fuels degrade and radionuclides are transported under repository conditions. Driven by the necessity to identify possible important species in highly basic solutions found in the waste tanks at the Hanford and Savannah River sites, this activity has had a renewed emphasis on the chemistry of the lighter transuranium elements and fission products. Knowledge of the molecular speciation of actinide and fission products materials under tank conditions is necessary to treat these complex mixtures. Molecular speciation information is also needed to predict the fate of actinide and fission product elements accidentally released to the environment. Finally, the analytical methods developed as part of the basic research funded under this activity have broad application across all the applied missions of DOE that deal with nuclear materials.

Scientific Challenges:

The role of the 5f electrons in bond formation remains the fundamental unanswered question in actinide chemistry, and hence provides the central focus for this program. The 5f orbitals participate in the band structure of materials that contain the light actinide metals and some of their alloys. Whether the 5f orbitals participate significantly in molecular compounds is still unclear. Molecular-level information on the geometry and energetics of bonding can now be obtained from experiments carried out at the Nation's synchrotron light sources, and from multi-photon laser excitation studies. These new tools are enabling studies of actinides in the gas phase, as small clusters and at interfaces such as between solutions and mineral surfaces or other well-defined solids. However, actinide and fission product samples have to be treated with special consideration because of their radioactivity, which has limited the types of experiments that can be safely conducted. For example, in the soft x-ray regime new sample preparation techniques need to be developed so that micro-quantities of well-characterized actinide samples can be measured using high vacuum techniques, or in "wet" cells to study actinide chemistry at liquid-solid interfaces.

Sophisticated quantum mechanical calculations that treat spin-orbit interactions accurately will need further development so that they can be used for predicting the properties of molecules that contain actinides. Development and validation of such computer codes will provide a means for obtaining fundamental information about actinide species that are difficult to study experimentally, will predict the electronic spectra of important species, and will correlate the optical spectra with actinide molecular structure. Ultimately, experimentally validated theoretical calculations will be the key to understanding the role of the 5f electrons.

Funding Summary:

Dollars in Thousands

FY 2003	FY 2004	FY 2005 Request
9,974	9,375	9,375

Performer	Funding Percentage
DOE Laboratories	75 %
Universities	15 %
Other	10 %

These are percentages of the operating research expenditures in this area; they do not contain laboratory capital equipment, infrastructure, or other non-operating components.

This activity supports research in heavy element chemistry at universities and encourages collaborations between university and laboratory projects in this area. Graduate and postdoctoral students are trained in this area and provide personnel for the technological challenges associated with the heavy elements. Twenty-four undergraduate students, chosen competitively from universities and colleges throughout the United States, are taught actinide chemistry and radiochemistry each summer in two programs at BNL and San Jose State University

Projected Evolution:

Kinetic, thermodynamic, and electrostatic effects in separations processes and in synthetic reactions involving the actinides are not well understood. Modern tools brought about by technological innovations can now be brought to bear on these topics. Heavy Element Chemistry research pursues advances in gas-phase chemistry that explore new reactivity patterns, high-pressure studies of actinide alloys, and spectroscopic investigations of new actinide materials. Other areas where new advances are expected are the design, synthesis and effectiveness of preorganized chelating agents for the separations of particular actinide ions; characterization of important actinide and fission product species in separations processes for a more fundamental understanding of why particular separations processes work; effects of temperature on actinide solution structure/property relationships; photophysics and photochemistry of actinide ions in their excited states; actinide organometallic chemistry; and theoretical work on actinide molecular clusters and compounds.

More sophisticated quantum mechanical calculations of actinide compounds and actinide species in aqueous solution are being undertaken. New facilities for safely handling radioactive materials at the synchrotron sources will permit more widespread use of techniques such as XANES, EXAFS, and x-ray scattering on radioactive samples, thus providing more detailed information on actinide speciation in solutions and in crystalline and amorphous solids. These data will complement data from other techniques, and can be used to validate and extend the quantum mechanical calculations.

Improved modeling of actinide transport requires understanding of the processes describing sorption on surfaces. Surface complexation models exist, but experimental validation of these models has not been readily available. Technological advances now allow molecular characterization of actinide surface species to be explored. An enhanced program of characterizing and modeling the nature of the interactions of actinides with well-characterized liquid-solid interfaces, including mineral surfaces under environmentally relevant conditions, is needed.

The magnetic and electronic properties of actinide intermetallic systems are not understood. These effects depend on the hybridization of the 5f electrons with conduction electrons. The strength of such hybridization is a direct function of the local metal bond environment around the actinide ion and much work needs to be done, especially on transuranium compounds. Work in this area should provide a much better understanding of the changes in the types of bonding exhibited by the light *versus* the heavy actinides.

Increased emphasis will be placed on encouraging academic investigators to enter this field and to address outstanding questions in heavy element chemistry. Because most academic institutions do not have the facilities necessary to safely handle radioactive materials, it is anticipated that most academic investigators will conduct their experimental work in collaboration with one or more national laboratory. Increased academic involvement is essential for training the next generation of scientists with experience in handling radioactive materials.

Finally, the actinide facilities in the national laboratories are aging. In order to continue to carry out forefront research, infrastructure problems at these laboratories must be addressed.

Research Activity: Chemical Energy and Chemical Engineering

Division: Chemical Sciences, Geosciences, and Biosciences
Primary Contact(s): Paul H. Maupin (Paul.Maupin@science.doe.gov; 301-903-4355)
Team Leader: John C. Miller
Division Director: Walter Stevens

Portfolio Description:

This activity supports fundamental research in two major research areas: Electrochemistry and Thermophysical Properties. The electrochemistry area addresses the chemical and physical transformations underlying chemical energy storage and conversion and their relationships to limitations in the performance of electrochemical systems. Research activities center on the physics and chemistry of interactions at interfaces between anode, cathode, and electrolytes. The program covers a broad spectrum of fundamental studies of composite electrode structures, failure and degradation of active electrochemical systems, and thin film electrodes, electrolytes, and interfaces to provide fundamental knowledge that will lead to improvements in operating characteristics for electrochemical systems. The program also addresses aspects traditionally of interest to that portion of the chemical engineering community interested in modeling and predicting the thermophysical properties of systems that underpin engineering design activities. This includes studies of thermodynamic behavior, mixing, and physical and chemical rate processes in these systems. Particular attention is given to linked experimental and theoretical aspects of phase equilibria in simple and complex fluids including supercritical phenomena. Also included are fundamental studies of theoretical approaches for understanding thermophysical and thermochemical properties, molecular simulation, and the generation of new equations of states. Emphasis is given to improving and/or developing the scientific basis for engineering generalizations and their unifying theories.

Unique Aspects:

This activity is the only federal program that supports fundamental electrochemical research as an interdisciplinary program incorporating the disciplines of physics, chemistry, materials science (metallurgy, ceramics, and polymer science), and chemical engineering targeted at understanding the underlying molecular phenomena in electrochemical energy storage and conversion processes and for electrochemical methods useful in analytical chemistry.

Relationship to Others:

Coordination of fundamental and applied research efforts in electrochemistry across the government is accomplished by participation in the Interagency Power Working Group where the program manager is the vice chair of The Chemical Working Group. Close coordination with the Battery and Fuel Cell programs in EE-Office of Transportation Technologies is accomplished through joint program meetings, workshops, and strategy sessions. Coordination in the Chemical Engineering area is primarily with the Chemical Industry Team in the Office of Industrial Technologies in EE through participation in the Chemical Industry Vision 2020 planning activity and the development of joint SBIR topics. A similar relationship with the Fuels program in FE has led to joint SBIR topic development. Additional interaction with the Chemical and Transport Systems division in the Engineering Directorate at NSF is accomplished through direct contact.

Significant Accomplishments:

Lithium and lithium ion batteries: The most significant accomplishment in electrochemistry research that was supported by the office was a spin off from early research on the electrochemistry of reactive metals in polar aprotic solvents by the late Charles Tobias of LBNL. It is widely acknowledged that this research (circa 1964) led to the first lithium battery. The same electrolyte solvent systems are still used today in the current generation of rechargeable lithium and lithium ion batteries. Replacements for Chlorofluorocarbons (CFC's): Research in thermophysical properties led to the development of an equation of state used in identifying replacements for CFC's that were responsible for destroying the ozone in the stratosphere. Hydrogen bonding in water: Research in molecular simulation led to clearing up controversial neutron scattering results on the nature of hydrogen bonding in water under supercritical conditions. Thin film rechargeable lithium batteries: Research in solid state electrolytes led to a new generation of thin film rechargeable lithium batteries that are about the thickness of saran wrap. Room temperature molten salt electrolytes: Research in molten salt electrolytes led to new room temperature systems that are showing promise in reactive metal systems such as sodium and lithium. The structural origin of water's anomalous properties: A new formalism for the quantification of structural order in water, based on the introduction of two order parameters has been developed.

Mission Relevance:

Understanding the thermophysical behavior of molecules, mixtures, and solutions under a variety of conditions impacts a large range of energy relevant technologies. In aqueous systems the relevance ranges from steam properties, power production, nuclear reactor technology, geothermal processes, scaling, corrosion, gas hydrates, mineralization, and biochemical processes to industrial processes utilizing aqueous processing. In nonaqueous systems it includes, fuel and chemical processing and manufacturing, natural gas production and utilization, materials processing and synthesis, and green chemistry. In electrochemistry, understanding what controls electrode and electrolyte performance is key to future improvements in electrochemical components used in nuclear weapons, remote sensing for nonproliferation applications, electronic devices, telecommunications, satellites, solar and wind energy utilization, electric power production, and electric and hybrid vehicles, as well as advanced electroanalytical chemistry methods.

Scientific Challenges:

As yet, we do not have the theory, the computational or experimental ability to understand the role of interfaces in chemical and electrochemical processes. In the electrochemistry area the limited understanding of electrochemistry at the interface of dissimilar solids and phases and at buried interfaces is hindering progress in achieving high power and low cost systems needed in electric and hybrid vehicles, for effective use of wind and solar energy sources, and for distributed power generation by chemical fuel cells. In the chemical engineering area the challenge is a different type of interface, that is, the interface of theoretical and computational methods from the molecular and nanometer scale to the mesoscale where the collective properties of chemical systems impact energy intensive chemical process designs. Efforts to link atomic/molecular properties to colligative properties will continue to be a challenge. In complex liquids the problem is worse. We do not yet have a basic understanding of the liquid state that compares with either the solid or gaseous states.

Funding Summary:

Dollars in Thousands

FY 2003	FY 2004	FY 2005 Request
9,779	10,637	10,687

Performer	Funding Percentage
DOE Laboratories	49 %
Universities	48 %
Other	3 %

These are percentages of the operating research expenditures in this area; they do not contain laboratory capital equipment, infrastructure, or other non-operating components.

The program provides funding for 40 university grants supporting about 40 students and partially supporting about 45 faculty and senior staff and 7 programs at national laboratories supporting about 15 senior staff and 10 postdocs. Programs at the laboratories are multi-investigator efforts on problems that require extensive participation by experienced scientists. These programs usually underscore the user facilities at the SC laboratories or act as the focal point for specific research efforts vital to the DOE mission. This program supports research of this type in ANL, BNL, LBNL and ORNL. Many of the research efforts at national laboratories involve interfaces with the university and industrial communities and user facilities.

Projected Evolution:

Opportunities deal with the emergence of the ability to control electrode structures on the nanometer scale. Preliminary studies have shown that this has a great impact on the electrochemical efficiency of electrode processes and the rate at which they respond to electrochemical potentials. New funding would capitalize on this new frontier and explore the nature of electrochemical reactions in this new realm. In the thermophysical property focus area, a trend towards greater use of molecular level theory and molecular simulation is increasing the need for increased activities at the interface of computational quantum chemistry and process design in chemical engineering. New funding would address these issues as well and seek to provide a theoretical basis for the incorporation of nanoscale to mesoscale modeling capabilities of importance to the process industries.

Research Activity: Geosciences Research

Division: Chemical Sciences, Geosciences and Biosciences
Primary Contact: Nicholas B. Woodward (Nick.Woodward@science.doe.gov; 301-903-4061)
Team Leader: John C. Miller
Division Director: Walter Stevens

Portfolio Description:

Geochemistry research focuses on advanced investigations of mineral-fluid interactions and developing new methods and techniques for investigating them. It includes studies on rates and mechanisms of reaction, coupled reactive fluid flow, surface geochemistry and geochemical reactivity, and isotopic tracking of mineral-fluid interactions. Improved imaging and tracking of geochemical processes at the atomic (angstrom) to system (kilometer) scale is critical for progress in understanding geochemical systems. Geophysics research focuses on developing an improved understanding of rock, fluid, and fracture physical properties and developing new methods and techniques for investigating them. It includes studies on the surface determination of geologic structures and rock property distributions at depth, improved methods of collection, inversion, and analysis of seismic and electromagnetic data, and identification of geophysical signatures of natural and man-made heterogeneities such as fractures, and fluid flow pathways. All of these studies are focused on improving our resolution in understanding multi-phase heterogeneous natural systems, distributions of chemical, mechanical and physical properties and improved approaches to up-scaling of theoretical predictions and experimental measurements to field-scale systems. The improved resolution comes from improvements in scientific understanding of processes, improved analytical and experimental tools, and improved computational approaches to modeling and algorithm development.

Unique Aspects:

This activity has an agency-wide mandate to provide new knowledge as the foundation for targeted applications in energy and environmental quality. Earth science-related problems are recognized as key elements in seven DOE applied activities (FE - Oil program; FE - Gas program; FE - CO2 sequestration program; NN – Seismology program; EM Science program; RW – Yucca Mountain program; and the EE – Geothermal program). Unique strengths of the program lie in its emphasis on cutting-edge atomic-scale experimental, theoretical, and modeling studies in both geochemistry and geophysics built on the capabilities of DOE National Laboratory facilities and over a hundred university research projects.

Relationship to Others:

The Geosciences Program provides 20% ($20M) of the Nation's support for individual investigator-driven fundamental research (NSF + DOE =$100M) in solid Earth sciences. The BES Geochemistry activities match the size of the Individual Investigator programs in the NSF petrology and geochemistry areas and the BES Geophysics activities match the size of the Individual Investigator programs of the NSF geophysics and NSF hydrology areas, but BES focuses on a narrower range of fundamental issues critical to DOE's mission particularly in shallow Earth situations.

Significant Accomplishments:

The GSECARS beamline has been built and commissioned (in collaboration with NSF-EAR) as a center for high-resolution analytical geochemistry for the whole Earth sciences community, including multiple DOE applied program users. One of the program's research projects at APS was selected by that institution as one of its top five studies done in 2000. Geosciences research projects and a Geosciences workshop on Terrestrial Sequestration of CO_2 were the foundations for the DOE Carbon Sequestration Roadmap in the area of geological sequestration and remain the basis for identifying research opportunities in this area for the Office of Science and the Office of Fossil Energy. Geosciences investigators have published major review volumes on Synchrotron Science related to Geosciences, Molecular Modeling applied to Geosciences, Nanophases in the shallow Earth environment and on Biomineralization.

Importance/Mission Relevance:

The activity contributes to the solution of Earth science-related problems in multiple DOE mission areas by providing a foundation of scientific understanding for applications such as (but not limited to): the potential of seismic imaging for reservoir definition or explosion detection, reactive fluid flow studies to understand contaminant remediation, or geothermal energy production, and coupled hydrologic-thermal-mechanical-reactive transport modeling to predict repository performance. The applied activities all seek fundamental research results as the foundations for their directed research and development efforts, both from the national laboratories and from the university community. In particular, the Geosciences activity provides funding for long-term crosscutting research efforts at national laboratories, which are directly and immediately transferred to the applied programs when needed. The activity also supports the development of research capabilities and communities within both national laboratories and universities that provide manpower for applied programs. An example is the Environmental Management Science Program in OBER, which derives over 25% of its subsurface science investigators from projects initially supported by BES Geosciences. The Geosciences activity in BES provides the majority of individual investigator basic research funding for the federal government in areas with the greatest impact on unique DOE missions such as high-resolution Earth imaging and low-temperature, low-pressure geochemical processes in the subsurface.

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. New investigations are needed at the smallest scales studying electronic properties, geochemical reactivity, solute properties, and isotopic distributions in both inorganic and organic systems. Mineral-fluid-microbe systems are also new targets for systematic examination. Understanding pristine natural systems and DOE-specific sites requires improving our capabilities to make and understand high-resolution geochemical and geophysical measurements experimentally and in the field and to model them. Understanding mineral-fluid interactions are 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. 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. In addition, new research on high-pressure/high-temperature mineralogical systems will create new opportunities to study and manipulate fundamental mineral and mineral-fluid properties and interactions. Upgrading national laboratory and university investigator experimental, field instrumentation and computational capabilities with new instrumentation and facilities is a continuing challenge. Even with new improved analytical equipment, technical challenges will continue in mastering data-fusion approaches to multiple-technique measurements, such as combined x-ray and neutron analyses or combined seismic-electromagnetic measurements. Computational capabilities driven by the PC-cluster approach with new higher speed chips (1.8GHz and greater) will enable optimization of clusters for individual molecular dynamics, seismic, electromagnetic, geomechanical and hydrologic modeling techniques and provide unique support to experimental analysis.

Funding Summary:

Dollars in Thousands

FY 2003	FY 2004	FY 2005 Request
20,332	20,491	20,332

Performer	Funding Percentage
DOE Laboratories	44 %
Universities	56 %
Other	0 %

These are percentages of the operating research expenditures in this area; they do not contain laboratory capital equipment, infrastructure, or other non-operating components.

Projected Evolution:

In the near term, geosciences research continues its basic activity in fundamental geochemistry and geophysics, and research related to CO_2 sequestration. It continues a multi-laboratory project led by Oak Ridge on Chemical Interactions at the Metal Oxide Aqueous Solution Interface in collaboration with the NSF funded NIRT university-based program. Eight short courses have been held in the Geosciences Education Initiative series. The activity continues working with various groups on investigating uses of neutrons in Geosciences. The activity works with NSF-Earth Sciences to develop a collaborative approach on fundamental science projects to be conducted at the NSF Earthscope – Plate Boundary Observatory

In the mid-term, the activity initiates new research efforts Imaging of the Earth 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. University facilities program discussions begin. New high-pressure/high-temperature research activities begin to investigate how physical and chemical properties in the Earth vary with depth and Earth dynamics. The GSECARS at the APS reaches its full operational potential as a national user facility for the Geosciences Community.

In the longer term (3-5 years), collaboration begins with NSF-Earthscope, requiring both facilities support and increased funding for critical scientific investigations. The Neutrons for Geosciences begin enabling new approaches and new discoveries in the geosciences. There is an increased usage of neutrons within the geosciences – which similarly requires both facility support and funding for scientific investigations.

Research Activity: Energy Biosciences Research

Division: Chemical Sciences, Geosciences and Biosciences

Primary Contact(s): James E. Tavares (James.Tavares@science.doe.gov; 301-903-6190)
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Team Leader: James E. Tavares
Division Director: Walter J. Stevens

Portfolio Description:

The Energy Biosciences program supports fundamental research in the plant and microbial sciences. The mission of the program is to create a science base to inspire future energy-related biotechnologies. This includes:

- Mechanistic studies on solar energy capture by plants and microbes through photosynthesis;
- Research on the mechanisms and regulation of carbon fixation and carbon/energy storage;
- Examination of metabolic pathways for biological synthesis, degradation and molecular interconversions;
- Experimental activities focused on the regulation of plant growth and development;
- Studies on novel biosystems and their potential for material synthesis and catalysis; and
- Coordinate and collaborate with other DOE and federal funding programs to assure rapid scientific advances related to energy-related biotechnologies.

Unique Aspects:

The Energy Biosciences program is the sole federal program devoted to the fundamental science underlying the use of biological systems to produce and conserve energy.

- Prime provider of funding for molecular research on plants without a focus on traditional crops and agricultural bioprocesses.
- Major supporter of research on microbial systems that have broader emphases than model systems currently used in the biomedical community.
- Energy Biosciences occupies an unusual niche within DOE at the interface between the life sciences and physical sciences that can promote multi- and cross-disciplinary research activities to study biological systems.

Relationship to Others:

The program strives to support fundamental research that may influence the directions of the biotechnology-related programs in the Office of Energy Efficiency and Renewable Energy; Office of Fossil Energy; and the Office of Environmental Management. The program collaborates and coordinates its activities with NSF, USDA and NIH in areas of mutual interest where there are multiple benefits.

Significant Accomplishments:

The program has had a significant impact on the scientific disciplines supported. Among the longer term accomplishments are determining the biosynthetic pathway for biological methane production from CO_2 and molecular hydrogen; the elucidation of the biochemistry and genetic regulation of plant lipid synthesis; determining the carbohydrate chemistry and structure of plant cell walls; and providing a central role in developing *Arabidopsis thaliana* as a model plant experimental system. Scientists supported by the program have received numerous awards and prizes including the 1997 Nobel Prize to Dr. Paul Boyer for his work on ATP, the energy currency of living systems.

Mission Relevance:

The program focuses on plants and microbes as biological systems that capture solar energy through photosynthesis, store photosynthetically-fixed carbon into a variety of organic compounds including potential as fuels and chemical feedstocks, or can convert plant-derived or industrial waste materials into useful chemicals and fuels. The program strives for mechanistic understanding that will provide potential technical options to use whole plants and microbes or their components in energy-related processes. New commercial activities in ethanol production, pulp and paper manufacturing, and *in planta* production of oils are examples of technical options built on the foundations laid by the Energy Biosciences program.

A goal of the Department of Energy by the year 2050 is to dramatically increase the utilization of bioenergy resources. Renewable resources (agricultural, industrial and forestry wastes and specialty energy crops and trees) currently supply three percent of the nation's total current energy consumption. A major increase in bioenergy production is an extremely ambitious goal with anticipated societal benefits of enhanced national energy security, improved environmental protection involving carbon neutral processes, improved rural economic growth, and long-term sustainable global development. There is considerable bipartisan support for expanded use of sustainable and renewable energy resources and it is likely to remain a focal point of the Department's activities in the future. A major role of the Energy Biosciences program is to provide the fundamental knowledge base for achieving these goals.

Scientific Challenges:

Traditionally, mechanistic biology has been summarized and catalogued in relatively simple linear models. Analysis of both spatial and time-dependent dynamics and its subsequent integration in a coherent fashion represents a significant challenge, but also new opportunities. Understanding interactions that occur within the nanoscale range will be an area of increased emphasis. Another enormous scientific challenge facing all biology is to assimilate the vast amounts of genomic-sequence data and associate them with specific biochemical, physiological and developmental processes. Studies specific to energy-related organisms and processes must be rationally integrated with the broader biological efforts. Whole genome analysis of plants and microbes may reveal unknown genetic capacity with relevance to energy-related processes and potential biotechnological applications and thus represents another important challenge. The vast majority of metabolic studies have focused on hydrocarbons and the major nutrient elements nitrogen, sulfur and phosphorous. There are other elements that are metabolized extensively by microbes. Microbial mineral respiration offers unique challenges on the interface of several traditional disciplines.

Funding Summary:

Dollars in Thousands

	FY 2003	**FY 2004**	**FY 2005 Request**
Molecular Mechanisms	11,797	12,133	13,108
Metabolic Regulation of Energy Production	18,665	19,195	18,695
TOTAL Energy Biosciences Research	30,462	31,328	31,803

Performer	**Funding Percentage**
DOE Laboratories	9 %
Universities	90 %
Other	1 %

Funding numbers do not include awards for conferences or training activities.

The program is providing support for 238 specific activities in FY2003.

- 9.4% of the research funds are allocated to the National Laboratories and 90.6% of the funds are provided to academic, federal and other non-profit institutions.
- The research programs cooperate with many private companies; however, the only direct financial support provided to the industrial sector is through the SBIR/STTR program.
- The program provides substantial funding for two dedicated institutes, the Michigan State University/ Department of Energy Plant Research Laboratory and the Complex Carbohydrate Research Center at the University of Georgia.

Projected Evolution:

The plant sciences research supported at DOE has evolved considerably from the late nineteen forties where the emphases were on radiation damage and breeding to demonstrate the peaceful use of the atom. Recent advances in sequencing plant genomes (e.g. *Arabidopsis* and rice) provide new opportunities to leverage traditional strengths of the program in genomics and biochemistry against powerful capabilities in imaging and computation. This new focus on systems plant biology will be especially useful to identify global networks of genes involved in specialized plant processes in growth, development or metabolism.

Research opportunities in the microbial sciences are also evolving as technologies evolve and the large-scale genome projects in microbiology yield rapid identification of genetic material. Gene identification is critical if one wants the full set of tools needed to study the role of proteins and their mechanism of function in microbes, plants or any other life form. The rapidly developing information on microbial genes and the proteins they encode can provide insights on protein processing and assembly, pathway delineation and metabolic regulation. The research supported during the next five years is expected to reflect these new opportunities and a systems biology approach.

Research activities at the interface between biology and the physical sciences, earth sciences and engineering will continue to be explored based on the philosophy that the best interdisciplinary studies are true partnerships where all participating communities benefit.