Ten Years of Basic Energy Sciences Accomplishments

Provided below are vignettes of some significant Basic Energy Sciences (BES) program accomplishments from FY 1997 through FY 2006. These brief accounts appear in the BES sections of the President's FY 1999 through FY 2008 Budget Requests to Congress, respectively. The selected program highlights are representative of the broad range of studies supported in the BES program.

Selected FY 2006 Scientific Highlights/Accomplishments

Materials Sciences and Engineering Subprogram

- ***Nanofluidic transistor.*** Imagine a valve to precisely control the flow of liquids but with dimensions so tiny that only one molecule at a time can pass through it. Controlled flow of ions in a liquid was recently demonstrated through very small nanochannels barely large enough to pass large molecules. Named "nanofluidic transistors," the nanochannel assembly functions in a way similar to ordinary transistors where the flow of electrons can be regulated by applying a voltage. Demonstrations were carried out on a 35-nanometer channel constructed between two silicon dioxide plates; the channel was filled with water and potassium chloride salt. The flow of potassium ions could be completely stopped by applying an electric current across the channel. The regulation of the flow (or current) of charged molecules was also demonstrated. This exciting discovery now makes possible detection and separation of individual molecules in a fluid. Among the important implications of this discovery are advanced nanoscale chemical analysis with extreme sensitivity and the capability of sorting individual molecules.
- ***Unexpected spontaneous reversal of magnetization in nanoscaled structures.*** New and unexpected magnetic phenomena have been discovered in ultrathin bilayers of ferromagnetic and antiferromagnetic films. Ferromagnetic materials (e.g., iron) have a positive magnetization due to the alignment of the magnetic moments. Antiferromagnet materials (e.g., nickel oxide) have no net magnetization due to the anti-parallel alignment of the magnetic moments. In bulk magnetic materials, regions of aligned magnetic moments, termed magnetic domains, are expected to align with an external applied magnetic field. The magnetic strength is determined by the degree of alignment of the magnetic domains. In contrast to naturally occurring bulk magnetic materials, an ultrathin ferromagnetic layer in close contact with an antiferromagnetic layer will spontaneously align *opposite* to the applied magnetic field upon cooling. The close proximity of the two different layers also results in an increase in magnetic strength. The ability to control and detect the magnetic alignment in ultrathin magnetic materials could lead to new concepts in computer data storage design. The fundamental understanding of the unexpected phenomena may also influence future research and development of magnetic based biological and chemical sensors.
- ***Nano-electronic hydrodynamics and turbulence.*** Electrons moving across a nanometer-sized wire have been found to behave hydrodynamically, i.e., like a liquid flowing from one bucket to another through a small opening. This behavior is exactly contrary to expectations from a quantum mechanical prediction, and it has prompted theoretical predictions of new phenomena. Most striking is the prediction of possible turbulent electrical transport with eddy currents in nanoscale conductors that could seriously limit current flow. Such turbulent currents could then lead to extremely high electronic temperatures due to the "friction" of the electrons as they move against each other, resulting in potential premature failure at much reduced current flow. Experiments are being carried out to test these theoretical developments.
- ***Using bioinspired methods to synthesize and assemble materials.*** Biological systems are renowned for synthesizing inorganic materials under mild conditions and assembling them into exquisitely shaped structures with high precision and control. Recently, by emulating the underlying chemistry and approaches of biology, several inorganic materials have been synthesized under mild conditions (room temperature, neutral pH, etc.), with a potential for significant energy savings in their large-scale manufacture. Some of the materials synthesized include semiconducting titanium dioxide, gallium oxide, and zinc oxide for solar energy conversion; ferroelectric barium titanate nanoparticles for energy

storage; magnetite nanoparticles for ultra-high density magnetic information storage; and nanocrystalline palladium for hydrogen storage. Furthermore, by exploiting the ability of biological macromolecules (e.g., DNA, proteins, viruses) to self-assemble into large, well-defined structures and to nucleate the growth of inorganic materials, researchers have shown that complex electronic circuit elements and large ordered arrays of nanoparticles can be assembled with a precision that far exceeds the current top-down fabrication capabilities.

- ***Unveiling the superconductor mystery.*** Understanding the phenomena of superconductivity and its mechanism has been among the most challenging issues facing the condensed matter and materials physics communities. The mystery of superconductivity is being tackled by a concerted effort, coupling synthesis and characterization with theory, modeling, and simulation. The recent discovery of superconductivity in actinide- and boron-containing materials indicates superconductivity may exist in many material systems yet to be discovered. The search for new materials is augmented by sophisticated techniques to modify the electronic properties of known superconducting materials, both chemically and electrically. Advances in new characterization tools, including proximal probes, have made possible the discovery of new phenomena, including competing phases within the superconducting phase. First principles calculations assisted by generalized density functional theory enabled accurate predictions of the electronic structure of superconducting materials. When coupled to an electron pairing mechanism, numerical models are being developed to predict the superconducting transition temperature as a first step towards a priori design of new superconductors.

- **Chemical Sciences, Geosciences, and Energy Biosciences Subprogram**

  Measuring the ultrafast motion within a molecule using its own electrons. Modern ultrafast lasers make it possible, in principle, to follow in real time the motions of the atoms that comprise a molecule. However, optical lasers are only indirect probes of atomic motion. This problem will be alleviated with the advent of the world's first x-ray free-electron laser, the Linac Coherent Light Source (LCLS), since x-rays allow direct tracking of atomic positions. Until the LCLS is available, optical laser pulses can be used in clever ways to track atomic motion in molecules. In one recently demonstrated example, the molecule's own electrons are used as the probe of atomic motion in a highly excited molecule. The electric field from an intense, optical laser pulse initially pulls electrons away from the molecule and then accelerates them back toward it. The highly energetic electrons scatter from the molecule. Rather than measure the scattered electrons, as might be done in an electron diffraction experiment, the new method exploits another phenomenon that is particularly sensitive to atomic motion. When the electrons re-collide with the molecule, they emit x-ray radiation in a process known as high-harmonic generation (HHG), and it is these x-rays that are detected. The wavelength of the re-colliding electrons is comparable to distances between atoms in a molecule; thus, the HHG x-rays emitted are highly sensitive to atomic motion within the molecule. This new method shows great promise as a way of imaging energetic molecules undergoing ultrafast structural transformations, including the fundamental action of all of chemistry, and the making and breaking of chemical bonds.

- ***Sunlight-driven transformation of carbon dioxide into methanol.*** The first step in the chemical transformation of carbon dioxide into a transportable fuel such as methanol involves the interaction of light with a catalyst in a process known as photocatalysis. It has long been known that the photocatalytic formation of methanol from carbon dioxide can be initiated by high-energy ultraviolet radiation. Recent work has demonstrated that the critical first reaction that splits carbon dioxide into carbon monoxide and a free oxygen atom can also be triggered with visible light. This advance makes it feasible to consider harnessing sunlight to drive the photocatalytic production of methanol from carbon dioxide. The key to the new advance is to perform the initial photocatalytic reaction on the walls of the nanometer-sized channels of a porous silica solid through the excitation by visible light of a bimetallic catalyst. The energy from the absorption of light causes an electron to transfer from one metal in the catalyst to the other and subsequently activates the gaseous carbon dioxide to eliminate an oxygen atom to yield the carbon monoxide product. Various combinations of metals are now being explored with the goal of designing a complete and sustainable system to produce methanol.

- ***Catalytic synthesis of alternative fuels and chemicals.*** Current manufacturing technologies for fuels and chemicals are often inefficient. The need to dramatically improve efficiency in fuel and chemical production is motivating the search for new chemical pathways using new catalysts tailored to guide chemical reactions with precision toward a selected product without wasteful sub-products. Recent approaches enlist different catalysts to cooperate in parallel to transform molecular intermediates. Sometimes referred to as tandem catalysis, this approach can potentially yield ultrahigh selectivity. An example is the venerable Fisher-Tropsch production of diesel fuel from carbon monoxide and hydrogen. Model catalysts for this polymerization reaction are typically unselective and yield a mixture of hydrocarbons or alcohols with carbon-chain lengths varying over a wide range. For minimum energy consumption and maximum yield, the ideal process should provide a very narrow carbon-chain range. Two recent advances may rejuvenate the Fisher-Tropsch process: the discovery of efficient metathesis catalysts, which led to the Nobel Prize in Chemistry for 2006, and the selective activation of carbon-hydrogen bonds. Two catalysts are necessary to carry out these two very different functions simultaneously on the same growing polymers. The carbon-hydrogen activation catalyst limits the yield of low-end hydrocarbons, and the metathesis polymerization catalyst simultaneously controls the high-end hydrocarbons. This can potentially lead to an ideal diesel-oil without the need for energy-intensive separations. This new tandem catalysis application is being followed intensely by researchers worldwide for its potential to revolutionize the science of alternative fuels and chemicals synthesis.

- ***Carrier multiplication: a possible revolutionary step toward highly efficient solar cells.*** In a normal solar cell, a single photon from the sun is converted into a single carrier of electrical current (an electron-hole pair) in a bulk crystal material called a semiconductor. This process is inherently inefficient because much of the energy of the solar photon is wasted as excess heat in the semiconductor. Recent experiments on the interaction of photons with nanocrystalline samples of semiconductors have demonstrated a remarkable effect, known as carrier multiplication, in which a single photon creates multiple charge carriers. Recent work has demonstrated that as many as seven charge carriers can be created with a single photon and that the process is universal, i.e., it occurs in all types of nanocrystalline semiconductors. These new results suggest that nanoscale confinement plays an important role in the carrier multiplication mechanism, which is now thought to be an instantaneous excitation of multiple electrons by a single photon. Critical issues must be addressed before an operational solar cell based on carrier multiplication can be created, such as separating and harvesting the charge carriers to create electrical current. However, present estimates of the conversion efficiency for a solar cell based on carrier multiplication are as high as 50 percent, which is about twice that of the best solar cell in current operation. Doubling solar cell conversion efficiency would represent a revolutionary advance in our ability to harness renewable energy from the sun.

- ***Visualizing chemistry: the promise of advanced chemical imaging.*** The emerging possibility of "chemical imaging" is transforming the way scientists follow the chemical transformation of molecules on surfaces, within cells, or immersed in other complex environments. Chemical imaging is the term given to a set of experimental techniques that use photon beams, electron beams, or proximal electromechanical probes to track molecules in two- or three-dimensional space and real time, while keeping track of chemical identity and even molecular structure. In the ideal limit, chemical imaging means nanometer spatial resolution, femtosecond temporal resolution, and "fingerprint" recognition of the molecular mass and structure. As a recent example, researchers are using focused laser beams (space and time information) coupled with mass spectrometry (chemical identification), to track specific metabolites in functioning cells. Multiplexing the mass information allows the simultaneous mapping of several species. Understanding the metabolic transformation of important biomolecules in cells is the first step toward influencing them in service of improved biochemical processes. Other examples include the use of chemical imaging to examine single-site catalysts as they influence reactions on surfaces and light-harvesting "antenna molecules" that are key participants in photochemical charge-transfer processes.

Selected FY 2006 Facility Accomplishments

- **The Advanced Light Source (ALS) at LBNL**

  Experiments begin on new femtosecond X-ray beamline. Experiments using ultrafast soft x-rays began in FY 2006 on Beamline 6.0.1.2. High-resolution x-ray spectroscopy and diffraction at photon energies from 150–1800 eV are now possible using the new, high-brightness, in-vacuum-undulator beamline, which increases the flux by a factor of 1000 relative to its predecessor. Beamline 6.0.1, a complementary hard x-ray beamline using the same insertion device and extending the photon energy available to users from 2.2–10 keV, was also installed, and its commissioning was begun. In the first measurements, soft x-ray pulses of 200-femtosecond duration were used to study phase transitions in vanadium oxide.

- **The Advanced Photon Source (APS) at ANL**

  Record nanofocusing with an innovative lens design. A new device, the Multilayer Laue Lens, developed at Argonne National Laboratory jointly between the APS and the Center for Nanoscale Materials, has set a world's record for line size resolution produced with a hard x-ray beam. The wafer from which the device was made won a 2005 R&D 100 award, given to the world's top 100 scientific and technological innovations. Enhancements to the device have now increased its ability to focus the x-rays with an energy level of 19.5 keV to less than 20 nanometers. Using the lens, researchers will be able to visualize three-dimensional electronic circuit boards to find circuit errors, map impurities in biological or environmental samples at the nanometer scale, or analyze samples inside high-pressure or high-temperature cells because hard x-rays, unlike soft x-rays, are able to penetrate container walls. This device has potential for a multitude of uses, including possible incorporation at the nanoprobe beamline at APS associated with the Center for Nanoscale Materials facility.

- **The National Synchrotron Light Source (NSLS) at BNL**

  Novel undulator design developed and installed. A custom-designed, cryogenic-ready, in-vacuum, miniature-gap hybrid undulator has been installed in the X25 straight section of the NSLS x-ray ring. The new radiation source, the first of its kind, will be an order of magnitude brighter than the original wiggler. By cooling the magnet array, this insertion device can have a higher magnetic field and a higher radiation resistance, resulting in a larger photon energy tuning range. Consequently, unlike previous miniature-gap undulators in use at the NSLS, this new undulator will be continuously tunable from 2 to 20 keV by employing all harmonics up through the 9th. This upgrade will provide significant benefits to the macromolecular crystallography program at the NSLS. This technology will be useful to all medium-energy storage rings in the world.

- **The Stanford Synchrotron Radiation Laboratory (SSRL) at SLAC**

  Operation at high current of 500 mA. The SPEAR3 accelerator reached its design current of 500 mA for the first time during a special run last year. Under similar test conditions, a selected beam line (BL 6) was subsequently operated successfully at 500 mA to test the performance of newly designed optical components, including the liquid-nitrogen-cooled double crystal monochromator. The success of this test paves the way for commissioning the other beam lines. The SPEAR3 accelerator received permission to operate routinely at 500 mA following an extensive accelerator readiness review. Authorization for operating beam lines for users at 500 mA is expected during the FY 2007 user run, when selected time periods will be allocated to commission, characterize, and operate beam lines at high current. SSRL is planning to operate full time with high current in FY 2008.

- **The Spallation Neutron Source (SNS) at ORNL**

  Commissioning and initial instrument results. Construction and commissioning of the Spallation Neutron Source, an accelerator-based neutron source that will provide the most intense pulsed neutron beams in the world for scientific research and industrial development, was completed, and the facility began operations in late FY 2006. The backscattering spectrometer that is part of the initial suite of instruments has unprecedented dynamic range and an energy resolution of better than 3×10^{-6} electron volts. Initial operation of this hardware involved test measurements of excitations in picoline (a hydrocarbon), which confirmed the performance of the instrument.

Selected FY 2005 Scientific Highlights/Accomplishments

Materials Sciences and Engineering Subprogram

- ***Synchrotron X-Rays Demonstrate Nanoscale Ferroelectricity.*** Films only a few atoms thick have been made that retain the controllable electric polarization needed for next generation nanoscale devices. Such ultrathin ferroelectric films have the potential to revolutionize future electronics, sensors, and actuators. Previous studies suggested that, as devices are miniaturized, they lose their ferroelectric character. These studies showed that ferroelectricity persists in films only 6 atoms thick. This landmark success was achieved using a unique instrument to observe thin film growth with high intensity x-rays from the Advanced Photon Source. X-rays reveal in real time the film structure as it grows, atomic layer by atomic layer. The in-situ x-ray techniques developed for this study can now be used to understand the synthesis and environmental interactions of other complex materials, thus addressing a wide range of energy-related challenges.

- ***A Superconductor that Tolerates Magnetic Fields.*** One of the biggest obstacles to the practical use of superconductors is the motion of magnetic flux due to an electric current in a superconductor. This motion of magnetic flux reduced the superconducting properties. A large research effort has gone into finding ways to prevent energy loss occurring from the movement of magnetic flux in copper oxide high temperature superconductors. It has been found that the magnetic flux in certain magnesium diboride films is intrinsically motionless, or "frozen," in applied magnetic fields up to 14 Tesla. Such a complete apathy to an applied magnetic field has never been seen before in any other superconductor. While the theoretical explanation for this behavior has eluded scientists, the experimental finding has drawn a lot of attention. This behavior may make it possible to fabricate superconducting wire that can carry very large electric currents.
- ***Using Electron Spin, not Electron Charge, to Carry Information.*** Today's computers are based on resistive circuitry using the movement of charged electrons. The resistance generates heat, and the removal of this heat is a fundamental limiting factor in creating the next generation of ultra small and ultra fast circuit elements. In a remarkable discovery, theorists have determined that in certain materials a spin current can be created with the application of a suitably oriented electric field, with no dissipation of energy. The spin current could potentially be used to carry out the same logic operations with no energy loss. This has been verified recently with experiments on gallium arsenide. This discovery may lead to computers with much greater capabilities including speed and capacity due to smaller circuit elements and with a significant reduction in energy loss.
- ***Plutonium Helps Understand Superconductivity's Mysteries.*** Magnetic resonance studies of the fundamental mechanism responsible for superconductivity in $PuCoGa_5$ reveal strong similarities to the high-T_c copper oxide materials. These results confirm earlier theories that this unique family of plutonium superconductors is nearly magnetic. This is a new class of superconducting materials and forms a conceptual bridge between two families of magnetically mediated superconductors, the heavy fermion metals and the copper oxides. The discovery of additional classes of superconducting materials enhances our ability to understand the mechanisms responsible for high temperature superconductivity.
- ***Ultrafast Studies of Nanocrystals.*** The fastest phase transition between nanocrystal structures ever recorded has been observed by ultrafast laser techniques. The reversible structural change in nanocrystals of vanadium dioxide switches the material from a semiconductor to a metallic phase, increasing the electrical conductivity by a factor of 100-10,000 depending on nanoparticle size. Correspondingly large changes from optical transparency to high reflectivity occur at the same time. Lasers with pulses as short as one ten-trillionth of a second were used to track the phase change in vanadium dioxide nanoparticles. This discovery may be key to possible applications requiring extremely rapid switching from transparent to reflective states. These include protective overlayers for sensitive infrared detectors, nonlinear optical switches, fiber-optic pressure sensors, and electrically or optically triggered transistors that could switch hundreds of times faster than conventional silicon devices.
- ***First Direct Observations of Quasiparticles.*** Quasiparticles provide a convenient simplification to describe the behavior of electrons in a superconductor. A quasiparticle can be thought of as a single particle moving through a system, surrounded by a cloud of other particles either pushed away or dragged along by its motion. Prior investigations of their dynamics have been indirect. Through the use of a new optical technique it was possible to perform the first direct study of the dynamics of quasiparticles in a superconductor. It was discovered that the quasiparticles can propagate remarkably far, several hundreds of nanometers. Knowledge of the dynamics of quasiparticles, specifically their

rates of diffusion, scattering, trapping, and recombination, is critical for the both the applications and fundamental understanding of superconductivity.

- ***Confining Electrons in New Two-dimensional Materials.*** Transition metal oxides, like semiconductors, are materials that confine electrons to a plane. It may now be possible to construct near-perfect layered materials of two perovskite structured materials. It has been shown through computational models that a single layer of $LaTiO_3$ in $SrTiO_3$ will serve as an electron donor and positive charge layer to retain those electrons in a thin layer as a two-dimensional electron gas (2DEG). Electrons behaving like a 2DEG appear to be an exotic phenomenon, but they are not. Many semiconductor electronic devices operate by creating just such a gas by an applied electric field inducing a thin conducting region at an interface—the field effect transistor being the prime example. Such thin electron layers have become a valuable tool for scientists studying the ways in which electrons organize their collective behavior. By expanding the materials available to create 2DEGs, new, more diverse opportunities have been created to expand our knowledge of electronic behavior that in turn can produce new applications.
- ***Inexpensive Route to Solar Cells Using Nanomaterials.*** New and novel semiconductor nanocrystal-polymer solar cells with surprisingly high efficiencies have been fabricated. In a solar cell, the conversion of light energy to electrical current occurs at the nanometer scale. Thus the development of methods for controlling materials on this scale creates new opportunities for more advanced solar cells. These advances are required because, although solar cells based on silicon and gallium arsenide have achieved high efficiencies and have found a variety of markets, more widespread applications remain limited by their high cost of production. These new cells are formed in an inherently inexpensive process from a colloidal solution of semiconductor nanocrystals in a semiconducting polymer. The unique features of nanosized objects are exploited to optimize the cell performance by controlling the shape of the nanocrystals. The performance of the new cells already rivals that of the best polymer-based devices. While the power conversion efficiency is still below that of current amorphous silicon and single crystal devices, there are opportunities to increase performance further by adding additional nanocrystal components to capture more of the solar spectrum. Furthermore, the same methods can be extended to address other optoelectronic applications, such as photodetectors and light emitting diodes.
- ***Predicting Magnetism in Nanomaterials.*** As recording media and sensors become smaller and ever-denser, it is increasingly important to control magnetism in nanostructures. But the physical properties of magnetic nanostructures are linked in complex ways and are difficult to predict, much less control. In this work, the magnetic properties of a cobalt nano-wire next to a platinum surface step were predicted from first-principles. The results are in perfect agreement with experiment and show the importance of a proper quantum mechanical description of the interplay of different magnetic phenomena. This work, based on newly developed quantum mechanical models implemented on high-performance computers, shows that accurate predictions can be made for a nanostructure comprised of a few hundred atoms. With continued theoretical development and more powerful computers, this paves the way toward prediction and control of more complex and useful magnetic structures.
- ***Explaining Materials Deformation Mechanisms from Atomic-scale Measurements.*** Using the world's most advanced electron microscope, the first direct observations of atomic details in complex crystalline dislocation cores revealed the atomic mechanisms underlying the deformation of intermetallic compounds with complex crystal structures. It was discovered that the diffusion of chromium atoms into and out of the crystal dislocation cores hinders dislocation motion in Laves-phase Cr_2Hf, a model intermetallic compound, thus providing a clue as to the origin of the brittleness and poor low temperature ductility of these intermetallic alloys. The poor low-temperature ductility of these intermetallic alloys has prevented their fabrication and use for decades. Some of the most attractive high-strength alloys for advanced high-temperature fission and fossil energy conversion applications possess similar complicated atomic configurations and lack the low-temperature ductility required for their fabricated by conventional cold deformation processes without crack formation. This discovery provides new atomistic insight into the behavior of crystal dislocations in complex intermetallic compounds necessary to design new fabricable alloys with the required strength at high service temperatures.

- ***Discovery of Mechanism of Surface Mass Transport.*** Researchers have discovered that trace concentrations of sulfur can enhance the rate of mass transport on copper surfaces by many orders of magnitude and have established the atomic scale mechanism by which this enhancement occurs. This discovery was enabled by low-energy electron microscopy measurements of the motion of singe-atom-high steps on copper exposed to calibrated doses of sulfur. By comparing observations of the motion of these steps with theoretical predictions based on calculations of the electronic structure of the surface, this research established that surface mass transport is catalyzed by the formation of a large number of mobile copper sulfide clusters. Such highly mobile clusters are believed to be a common feature of impure surfaces. The enhanced mass transport allows the formation of much flatter and more defect free surfaces. This discovery provides insight to many previous puzzling observations of anomalous surface mass transport. It is an important advance towards the capability to control the nanoscale morphology of surfaces, a critical necessity for nanoscale applications.
- ***Superior Iron-based Alloys and Steels.*** Fundamental laws of alloying coupled with advanced microanalytical characterization led to the discovery that yttrium containing iron-based alloys substantially enhance the stability of the amorphous (non-crystalline) state. Two technical implications are: (1) large bulk physical dimensions of this class of amorphous alloys can be made and (2) this understanding provides a new direction for designing bulk amorphous metals for structural and functional applications. Bulk tool steel was fabricated that was twice as hard as conventional tool steel. These achievements are milestones in the science of amorphous metals and the design of functional complex metallic alloys. Even more important, this research has demonstrated that microalloying is a new approach for designing bulk amorphous alloys. Their unique atomic configurations and the absence of a crystalline lattice allow bulk amorphous metals to outperform their crystalline counterparts by exhibiting superior magnetic and mechanical properties and corrosion resistance coupled with high thermal stability.
- ***Fracture Resistance Mechanism in Ceramics.*** Structural ceramics are complex structures of micron-sized matrix grains separated by a nanoscale intergranular film. For many years it has been observed that certain additives, specifically rare-earth atoms, influence the ceramic's fracture resistance. But detailed information about how this effect is achieved and how it can be controlled had been inaccessible with current diagnostic capabilities. Now, new scanning transmission electron microscopy (STEM) and associated chemical analysis techniques have revealed the local atomic structure and bonding characteristics of the grain boundaries with close to atomic resolution. Applied to silicon nitride ceramics containing a range of rare-earth additives, these methods together have revealed how each atom bonds at a specific location depending on atom radius, electronic configuration and the presence of oxygen; this variation in bonding sites can be directly related to the fracture resistance or toughness of the ceramic.
- ***Better Protective Coatings.*** Previously unattainable insight into stress development and failure mechanisms in thermally grown surface oxides on metal alloys has been obtained by a new in-situ synchrotron x-ray technique. This technique enabled, for the first time, the uncoupling and isolation of mechanical stress contributions from oxide growth, phase transformations, and creep deformation processes. For pure thermally-grown alumina, steady state oxidation creates compressive stresses. However, when certain "reactive elements" are added to the alloy, it is found that tensile stresses develop instead. Maximizing the tensile offset can lead to dramatic improvement in performance of a protective oxide. A 10 percent shift in the tensile direction can translate to a 40 percent improvement in operating lifetime. Better control of early stage oxidation leads to thinner, and thus longer lifetime protective oxides by speeding the transformation to a stable oxide structure. These results underpin future alloy development for high-temperature nuclear and fossil energy generation technologies and more fuel efficient jet engine applications where operating lifetime has great economic value.
- ***New Composite Materials that Respond to Magnetic Fields.*** Magnetic-field-structured composites are a novel class of material in which magnetic particles, dispersed in a polymerizable medium, are organized into chains and other structures by magnetic fields while the polymer solidifies. These chains of particles can be electrically conductive, and this electrical conductivity can be extremely sensitive to temperature, pressure, and chemical vapors that penetrate and swell the polymer. In the present work it was demonstrated that even modest magnetic fields produced by simple copper coils cause these materials to contract significantly, like artificial muscles. This contraction was found to be

accompanied by an enormous, 50,000-fold increase in electrical conductivity. This is by far the largest "magnetoresistance" effect ever observed in such modest magnetic fields and paves the way to using magnetic fields to control heat and current transport in micro and nano machines, and to tailoring the sensing response of these materials.

- ***The "Giant Proximity Effect."*** The reproducible confirmation of the existence of a Giant Proximity Effect (GPE) has challenged experimentalists for over a decade. In the traditional Proximity Effect (PE), a very thin layer of normal metal, when placed between two thicker superconductor slices, behaves like a superconductor. That is, superconducting or paired electrons retain phase coherence even while separated by the normal metal gap. In the newly discovered GPE, the normal-metal barrier layer is as much as 100 times thicker than in the PE case, a result that stands outside of any present theories. In addition to challenging the theoretical community and providing new clues to the causes of high-temperature superconductivity, this result may lead to new advances in superconducting circuitry as it is relatively easy to prepare reproducible thick barriers which will improve device uniformity and yield.
- ***World's Smallest Nanomotor.*** The smallest synthetic motor—a 300 nanometer gold rotor on a carbon nanotube shaft—has been demonstrated. This "nanomotor" continues the dramatic advances in the miniaturization of electromechanical devices and is a key step in the realization of practical synthetic nanometer-scale electromechanical systems (NEMS). In initial testing, the rotor rotated on its nanotube shaft for thousands of cycles with no apparent wear or degradation in performance. This is attributed to the unique low-friction characteristics of the carbon nanotube shaft. The new motor design has significant potential for NEMS applications. It should be possible to fabricate arrays of orientationally-ordered nanotube-based actuators on substrates by using alignment techniques.
- ***Magnetohydrodynamic Turbulence in Liquid Metals.*** Application of a strong magnetic field can completely change flow characteristics of an electrically conducting fluid. The transformation may occur in processes ranging from the generation of sunspots to crystal growth. One particular aspect of this phenomenon, the damping of flow variations along the magnetic field lines and the corresponding development of elongated or even two-dimensional flow structures, affect nearly all aspects of turbulent flow behavior, including heat transfer and mixing. In a series of high resolution numerical experiments it has been shown that the anisotropy of flow (or directionality of flow) patterns is a robust universal feature determined primarily by the strength of the magnetic field, conductivity, and kinetic energy. Furthermore, the elongation of flow patterns is approximately the same for flow structures of different size. This property can be effectively employed for accurate modeling of magnetohydrodynamic turbulence. The results of the work are relevant to technological applications, such as continuous casting of steel, crystal growth, and development of lithium breeding blankets for fusion reactors.
- ***Nanoparticle Catalysts.*** Methods were developed for depositing and stabilizing nanometer-sized platinum group metals, including palladium and rhodium, on surfaces of carbon nanotubes in supercritical fluid carbon dioxide. Uniformly distributed monometallic and bimetallic nanoparticles with narrow size distributions are formed on the surfaces of the carbon nanotubes. The carbon nanotube-supported palladium and rhodium nanoparticles demonstrated improved performance over commercial carbon-based palladium and rhodium catalysts for hydrogenation of olefins and aromatic compounds. These new nanoscale catalysts are currently being tested as electrocatalysts for low temperature polymer electrode fuel cells applications.

Chemical Sciences, Geosciences, and Energy Biosciences Subprogram

- ***Timing the World's Shortest X-Ray Pulses.*** Light sources based on particle accelerators, such as the Linac Coherent Light Source (LCLS), will revolutionize x-ray science due to their unprecedented brightness and extremely short pulse duration. To take full advantage of x-ray pulses that last only a few femtoseconds (10^{-15} seconds), they must be timed relative to equally short pulses from an optical laser. Such measurements are vital to a wide range of LCLS experiments in which a sample is excited by an optical pulse and probed by an x-ray pulse. At the Stanford Linear Accelerator Center, ultrashort x-ray pulses were generated when 80-femtosecond electron pulses from an accelerator were sent through an undulator magnet; the x-ray and electron pulses were perfectly coincident in time. A crystal placed near the path of the electron beam experienced intense electric fields that altered the optical properties of the crystal, the electro-optic (EO) effect. An optical laser beam passing through the crystal sensed the EO effect, turning the time delay between the optical pulse and the electron/x-ray pulse into a spatial displacement on a detector. The current timing resolution of 60 femtoseconds could be improved to 5 femtoseconds, matching the projected performance of accelerator-based light sources into the foreseeable future.

- ***Molecular Fragmentation Observed in Unprecedented Detail.*** Researchers working at the Advanced Light Source have advanced our ability to observe the total destruction of a molecule to new levels of sophistication, challenging theoretical understanding and paving the way for research to be performed at next-generation light sources. When a hydrogen molecule is exposed to x-ray photons of the appropriate energy, the two electrons it possesses can be ejected at once, leaving behind two positively charged nuclei that rapidly explode. Thus, absorption of one x-ray photon causes the complete destruction of the molecule. Using modern techniques of three-dimensional imaging and ultrafast timing, the motions of all four particles from a single event can be related to one another. The results are surprising and challenge our current theoretical understanding of how x-rays interact with matter.

- ***Complete Ionization of Clusters in Intense VUV Laser Fields.*** BES-supported researchers have developed a theory that explains recently-observed ionization behavior of xenon clusters that were exposed to intense, coherent vacuum ultraviolet (VUV) pulses from a free-electron laser (FEL). Surprisingly, at intensities that produce only single ionization of an isolated xenon atom, the clusters irradiated by the FEL showed massive ionization in which every atom in the cluster was highly ionized, producing ions with charge states up to +8. This implies that each xenon atom in the cluster absorbed about 30 VUV photons. The key difference between clusters and isolated atoms is that energetic electron-ion collisions occur within the clusters and modify the single-photon absorption cross section, thus allowing a large number of photons to be absorbed. This process is called "inverse bremsstrahlung" and, when incorporated into a simple linear absorption model, clearly reproduces the experimental observations. Theories such as this will be needed to understand the behavior of matter when it is exposed to intense, coherent X-ray pulses from next-generation light sources such as the LCLS.

- ***The Roaming Atom: Straying from the Lowest-energy Reaction Pathway.*** A fundamental tenet of modern chemical reaction theory is the concept of the transition state, a transient molecular entity that lies on the most direct pathway from reactants to products and whose properties govern the rate of reaction. Recently, it was shown that in a simple chemical reaction, the decomposition of formaldehyde, a substantial fraction of the dissociating molecules avoid the region of the transition state entirely. These studies combine ion imaging experiments with theoretical trajectory calculations to reveal that the dissociation takes place via a mechanism in which one hydrogen atom begins to roam away from the molecule and nearly dissociates, then returns to react with the remaining hydrogen atom. Along with other recent findings on reactions such as $O + CH_3$, these results challenge conventional notions of chemical reactions and raise the question of how common such processes might be. A key question is whether such a mechanism applies only to reactions forming hydrogen, during which a light hydrogen atom may rapidly explore regions far from the conventional transition state.

- ***New Combustion Intermediates Discovered.*** A complete mechanism for the combustion of simple hydrocarbon fuels includes dozens of distinct molecular species and hundreds of chemical reactions. The identification of which molecules to include in a combustion chemistry mechanism still requires experimental detection, particularly for reactive intermediates. A class of unstable molecules known as enols, which have OH groups adjacent to carbon-carbon double bonds, are not currently included in standard combustion models. In work performed at the Advanced Light Source, significant quantities of 2, 3, and 4-carbon enols were observed using photoionization mass spectrometry of flames burning representative compounds from modern fuels. Concentration profiles of the enols taken in the model flames demonstrate that their presence cannot be accounted for by isomerization reactions that convert more stable molecules into enols. This leads to the conclusion that an entire class of important reaction intermediates is absent from current combustion models, and the models will need substantial revision.

- ***Unified Molecular Picture of the Surfaces of Aqueous Solutions.*** A long-term controversy exists regarding the detailed, molecular nature of the surface of an aqueous solution containing molecular ions (or electrolytes). Joint theoretical and experimental studies have led to a new, unified view of the structure of the interface between air and aqueous electrolytes. Molecular dynamics simulations have shown that in basic salt solutions positively charged ions (cations) are repelled from the interface, while negatively charged ions (anions) exhibit a propensity to migrate toward the surface that correlates with the anion's polarizability and physical size. In acidic solution, however, there is a high propensity for cations to be located at the air/solution interface. In this case, both cations and anions are concentrated at the surface and reduce the surface tension of water. These conclusions have been verified by surface-selective nonlinear vibrational spectroscopy experiments. Understanding the behavior of ions at aqueous surfaces is important to the heterogeneous chemistry of seawater aerosols and to the tropospheric ozone destruction in the Arctic and Antarctic due to reactions on ice pack covered with sea spray.

- ***Self-Assembled Artificial Photosynthesis.*** In natural photosynthesis, self-assembly of light-absorbing molecules, or chromophores, at specific distances and orientations is especially important in two parts of the overall photosynthetic system: the antenna component, where light is collected; and the reaction center, where charge is separated. Recently, a green organic chromophore was discovered that exhibits photophysical and photoredox properties similar to those of natural chlorophyll a. When conjoined with four similar chromophores, the molecules self-assemble in solution to form an antenna-reaction center complex. Self-organization of the large structure is believed due to the propensity of these similar chromophores to align in a cofacial stacking arrangement. The self-assembled organic has attributes that closely mimic the primary events in photosynthesis: efficient light energy capture over a wide spectral range, energy funneling toward a core electron-transferring unit, and excited-state symmetry breaking of a molecular pair resulting in charge separation. The structure of the new array was determined at the Advanced Photon Source.

- ***Two-Dimensional Spectroscopy Reveals Energy Transport Pathways In Photosynthesis.*** Photosynthetic antennas capture solar photons and transport the absorbed energy to the photosynthetic reaction center where charge separation occurs. Energy transfer by the antenna is nearly 100 percent efficient, although the mechanism for the process has been elusive. A novel spectroscopic technique known as a two-dimensional photon echo, commonly used in the infrared, has been extended to the visible spectral region and has revealed important details about energy transfer in photosynthetic light harvesting. In antenna pigments from green sulfur bacteria, distinct energy transport pathways have been identified that depend on the spatial properties of the pigment-protein complex. Contrary to the accepted model of a sequential cascade in energy from high- to low-lying excited states, these results reveal excited states that are distributed over two or more chlorophyll molecules and a pathway in which energy levels are skipped on the way to the lowest level. The new two-dimensional electronic spectroscopic method, which measures electronic couplings and maps the flow of excitation energy, opens the door to investigation of other photoactive systems and can be applied to improving the efficiency of molecular solar cells.

- ***How Water Networks Accommodate an Excess Electron.*** In bulk water an excess electron can become trapped within a cavity formed by a network of hydrogen-bonded water molecules. This "solvated electron" is a critical chemical intermediate in the radiolysis of aqueous solutions. One approach to understanding the solvated electron is to study the structure and dynamics of clusters of water containing an excess electron in the gas phase. This approach has not yet been successful because these anionic water clusters are hard to make and because an accurate theoretical description for them is lacking. Recent work has shown that anionic clusters containing four to six water molecules can be created within gas-phase matrices of inert argon clusters, where their infrared spectra can be obtained. Analysis of these spectra using density functional theory shows that the diffuse electron interacts most strongly with a single water molecule that is hydrogen bonded to two other waters in a rearranged network. The spectra also exhibit evidence for the rapid exchange of energy between the vibrations of the hydrogen atoms on the unique molecule and the excess electron. This new technique can now be extended to larger water clusters that better mimic the solvated electron in bulk water.

- ***Gold, a Magnificent Nanoscale Catalyst.*** When gold atoms are assembled as tiny clusters smaller than 8 nanometers and attached to the surface of titanium oxide, they acquire the remarkable ability to dissociate oxygen at room temperature and insert that oxygen into very specific locations in molecules. The origin of such unusual reactivity—discovered some 10 years ago—has until recently evaded a widely accepted explanation. Numerous parameters in the material are important and usually cross-correlated: gold particle dimension and shape, metal oxidation state, oxide support reducibility, and interaction of the gold with the support. Separating those parameters in these materials, which are macroscopically amorphous, would demand special analytical techniques that are able to focus on the detailed properties of individual chemical bonds in the solid. Therefore, researchers pursued a different route using existing and well-known surface science techniques: they accurately synthesized and stacked one-atom-thick layers of gold extended in two dimensions, and supported them on top of perfect oxide crystals of known structure. They demonstrated that the nanoscale properties of gold metal are achievable by controlling the layer thickness to between 2 and 3 atoms. Such knowledge can now be extended to the manipulation of selective oxidation chemistry or the discovery and assembly of new catalysts.

- ***Theory Guides Scientists on How to Extract Hydrogen from Natural Sources and Store it Efficiently.*** Two of the keys to a hydrogen economy are having an abundant supply of hydrogen and having materials that can store such hydrogen in a readily accessible form. Both of those challenges can be addressed by designing materials—chemical catalysts—that bind atomic hydrogen with medium strength and release molecular or gaseous hydrogen with very little heating. A random or systematic search for such catalysts, even with high-throughput techniques, would be very expensive and take many years. Scientists resorted to so-called density-functional theory, which is an electronic structure theory of matter, and other theories that describe chemical reactivity to design the ideal bimetallic catalysts, combinations of two metals, in special atomic arrangements that would result in solids with the desired properties. They arrived at a new theoretical construct called near-surface alloys of metals, such as a crystal of platinum containing a single layer of nickel atoms in its second row, that possesses the unique catalytic behavior sought. Having by now mapped entire families of such new theoretical materials—a feat unachievable by direct experimental means—these scientists have embarked on the challenge of fabricating these new structures and have already demonstrated their concept with a few successful examples.

- ***Devising the Next-Generation Wonder Molecules—Fine Chemistry inside Nano Cages.*** In the future drugs, fibers, fuel additives, molecular electronics devices, solar energy conversion dyes, and flavors may be synthesized in a similar manner using sets of discrete cavities to contain and isolate single molecules or just reacting pairs of molecules and catalysts. The "single-molecule catalysis" concept would allow maximum control of the environment surrounding a molecule, the spatial arrangement adopted by its atoms, the type of bonds made available for reaction, and even how the energy is coupled to and transferred to the molecule. Such level of control would result in the ability to break bonds or insert or remove atoms or change the spatial arrangement of atoms in very specific ways and not others. The resulting products would possess properties—chemical, biological, optical, electronic, or mechanical—superior to those achievable through less controllable chemistry. Researchers are beginning to show that this goal may be achievable. So-called supramolecular or larger-than-molecules cages made with organometallic compounds were used to host other organometallic complexes that have catalytic properties, such as the ability to specifically break carbon-hydrogen bonds. They have shown that certain carbon-hydrogen bonds are selectively broken and that only certain members of a chemical family undergo reaction, and not others. They have even shown that the constrained environment also leads to enhanced rate of production of the most desired product, which is in itself a revolutionary discovery.

- ***Controlling the Crash-landing of Biomolecules on Surfaces.*** Researchers have, for the first time, demonstrated that peptide ions retain at least one proton after soft landing on chemically modified, "fluffy" surfaces. Controlled deposition on surfaces holds great potential for applications such as selective chemical separations and analysis. Soft landing refers to the intact capture of large size-selected, charged molecules on surfaces of liquids or solids. Previous research suggests that soft landing provides a means for highly specific deposition of molecules of any size and complexity on surfaces using only a tiny fraction of material normally used in standard synthetic approaches. In the present studies, peptide ions are attractive as model systems that can provide important insights on the behavior of soft-landed macromolecules. The researchers used a specially designed mass spectrometer configured for studying interactions of large ions with surfaces. The special characteristics of the instrument enabled quantitative investigation of the effect of the speed and mass of ions on the soft landing process. For example, it was determined that even collisions with high energies can result in deposition of intact ions on surfaces.

- ***Removal of Radium Ions from Water using Special "Grabber" Molecules.*** Researchers demonstrated a process that is highly selective for binding radium cations. It is a significant challenge to remove radioactive radium cations from wastewater since the large excess of other non-radioactive ions in solution can interfere with the selective extraction of radium. In the new work, a specially designed molecule was used to selectively bind radium. This supramolecular assembly made from isoguanosine is just the right size to extract radium in the presence of other cations such as magnesium and sodium.

- ***How Molecules Move through Small Holes.*** Measurements of transport through 15-nanometer pores have been compared to theoretical results to yield new understanding of differential transport at small scales. This knowledge is important for an understanding of separation processes at the molecular level, and could lead to a new generation of analytical devices based on microfluidic platforms. By adjusting physical parameters such as the channel diameter, and applying the appropriate external electrical potential, arrays of nanochannels—formed by nanocapillary array membranes—can be made to behave like digital fluidic switches, and the movement of molecules from one side of the array to the other side can be controlled. Combining model calculations with experimental characterization provides important insights into the mechanism of molecular transport and, additionally, provides quantitative measures of the surface characteristics of the interior of the pores.

- ***Using Thorium and Uranium to Activate the Carbon-Hydrogen and Carbon-Nitrogen Bonds in Molecules.*** The extent of electron-sharing in bonds with metals is an important property in catalysis. The correlation of bond covalency with reactivity can be elucidated by determining the reactivity of actinide (thorium, uranium, and other elements in the same row of the periodic table) ions with multiply bonded functional groups. Pyridine N-oxide (C_5H_5N-O), which has a relatively stable benzene-like ring, can transfer oxygen atoms to certain transition metals. Chemists have discovered that some uranium and thorium compounds can make C-H bonds in pyridine N-oxide more reactive by forming metal-carbon bonds. The structures of the products produced in these new reactions have been confirmed by x-ray crystallography. These reactions provide examples of C-H and C=N bond activation that is mediated by actinide metals. These studies may offer insights into catalytic removal of nitrogen-containing compounds from petroleum feedstocks, which is necessary to reduce nitrogen oxide emission in fuels.

- ***Elusive Carbon Dioxide Binding Mode Discovered in New Uranium Complex.*** Carbon dioxide (CO_2) is a stable molecule with two strong carbon-oxygen bonds. Inorganic chemists seek to mimic the catalytic chemical processes by which carbon dioxide is modified by plants to form sugars. This process can remove CO_2 from the atmosphere and minimize atmospheric release of CO_2 in industrial processes such as refinement of hydrocarbons. A new exquisitely-designed uranium complex has been found to react with CO_2 such that one electron is transferred from the U^{3+} center to CO_2, producing a species with an unusual linear CO_2 that binds to uranium and has one weaker oxygen-carbon bond. Uranium is an essential component of this species because the U^{3+} ion is large, electron-rich, and has the right structure to participate in bonding. This species is unique in that the CO_2 remains linear, with one C-O bond longer and weaker than the other. The molecular structure, bond lengths and oxidation state were established experimentally. The linear M-O-C-O coordination had previously been seen only in an iron enzyme. The new uranium-CO_2 complex represents a chemical image of a catalytic process and may make it possible to design new catalysts to reduce the concentration of CO_2 in the atmosphere.

- ***Plutonium is Caged and Illuminated by Synchrotron Light.*** A new complexant, which was synthesized to extract plutonium and other actinide elements selectively, has shown promise to remove plutonium from mammals. Microscopic crystals (about the thickness of a human hair) of a plutonium complex have been produced to provide a structural model in order to design new actinide-selective binders. Using the Advanced Light Source, researchers determined the detailed structure of these crystals and showed that individual plutonium ions are trapped in cavities produced by eight oxygen atoms from the binder molecules. This structural determination will serve as a model of such complexes on which to base the design of novel molecules that are cages for toxic metals.

- ***Sheer Energy: Thinner, Cheaper Fuel Cell Catalysts.*** Fuel cells are a major source of clean energy in the hydrogen economy. Their economic development critically depends on cheaper electrocatalysts for oxygen reduction. The slow nature of this reaction causes a major limit in fuel cell efficiency. High precious metal content is another drawback of existing technology. Researchers coated five cheaper metals with a layer of platinum one atom thick and tested them. For most of the platinum "monolayers," the reaction occurred more slowly than it does on the thicker platinum layer currently used in fuel cells. But adding a monolayer of platinum to the cheaper metal palladium sped up the reaction. Theoretical computations predicted how the platinum monolayers are affected by atoms from the underlying layer of metal. The theory agreed well with the experiments and showed that a platinum monolayer on palladium balances two competing needs: it is reactive enough to break the bonds between oxygen atoms yet does not cling to the oxygen atoms so tightly that it prevents them from reacting with hydrogen. This method can dramatically decrease the expensive metal loading in fuel cells and improve cost and performance.

- ***Advances in Computational Chemistry Research.*** Basic research in computational chemistry has resulted in a superior method for the prediction of chemical behavior from computational quantum mechanics and statistical mechanics. The method is based on treating the solvent in which a molecule is placed as a continuum, and determining the cavity-formation energy from statistical mechanics, and the electric contributions from quantum mechanics. This work has now been published and a leading chemical process simulation company has incorporated this method into the most recent release of their industry dominating process simulator. This work will impact modern industrial plant and process design and lead to higher energy efficiencies through effective modeling of manufacturing processes.

- ***Is CO_2 Gone When You Put It In The Ground?*** There are only two options for dealing with increasing CO_2 concentrations in the atmosphere—get rid of new CO_2 actively or discontinue producing it and wait for natural processes to remove the excess over a very long time. Both approaches will likely be needed in the future. Researchers have been developing capabilities for realistic modeling of CO_2 injection into deep geological formations and for understanding dynamic processes associated with the injection in order to provide a scientific basis for evaluating the injections feasibility. Computational models were developed for coupling fluid properties, chemical and thermodynamic data, and rock-fluid interaction measurements. Reservoir dynamics were investigated on different levels of complexity and scale for natural and engineered systems. These types of calculations also form the basis for understanding possible leaks which may be major regulatory and insurance concerns for large scale geological CO_2 sequestration. The improved computational codes from this project were also used as the basis for design calculations for CO_2 injection at the Frio Test Site as part of the Office of Fossil Energy funded Climate Change Technology Program.

- ***Improving Our Vision of the Subsurface.*** Large scale subsurface seismic measurements, although adequate for simple oil and gas exploration or waste site characterization, are inadequate for high hydrocarbon recovery rates or more effective environmental remediation or monitoring. Research is providing a better understanding of geophysical measurements of compressional and shear wave velocities, elastic moduli, and seismic anisotropy as they vary as functions of porosity, permeability, fluid contents, and stresses. A fiber-optic "optical" strainmeter has been developed that provides spatially averaged properties over a centimeter or "core" length scale intermediate between point measurements and a meter-scale bulk-measurements. The increased accuracy and sensitivity in measuring elastic deformation during applied sinusoidal stress will enable better discrimination between strain (elastic wave transmission efficiency) and phase lags (attenuation indicative of fluid content and type). In addition, the highly precise optical strain gage measurements will allow higher resolution testing of the significance of different types of heterogeneity at the core scale, in order to enable prediction of these properties at larger scales. The fiber optic sensor has been demonstrated to have a significantly higher sensitivity than other strain gages.

- ***The Auxin Receptor: A Holy Grail in Plant Science.*** The plant growth hormone called auxin is a small molecule, indole acetic acid (IAA)—too small to have the expected breadth of "informational" content to achieve its myriad effects of controlling the growth of leaves, stems, roots, flowers, fruits, and growth changes in response to light and gravity. Recent research demonstrated that IAA interacts directly with a much larger molecule, a protein, which was earlier shown to affect plant growth by stimulating the expression (activation) of certain growth-related genes. Now the solution to the mystery of auxin action is becoming clear. It turns out to be similar to an electric switch, but a bit more complex. We are beginning to unravel the molecular details of auxin's biological activity.

Selected FY 2005 Facility Accomplishments

- **The Advanced Light Source (ALS)**

  Beam-Size Stability Improved. Over the last five years, elliptically polarizing undulators (EPUs) have been used very successfully at the ALS to generate high-intensity photon beams with variable photon polarization (from linear to circular). However, users were not completely satisfied with the EPUs performance because they degraded the beam quality by increasing the photon beam size. Based on detailed magnet measurements, a system was developed that maintains a constant beam size. It is now being employed in routine user operation solving a problem that has affected many other light sources.

  New Undulator Beamline for High-Resolution Photoemission Electron Microscopy. Beamline 11.0.1 is a new elliptically polarizing undulator (EPU) beamline dedicated to photoemission electron microscopy (PEEM) at the ALS. An EPU, the third installed at the ALS, delivers light into the new beamline, which began commissioning March 2005. With full polarization control and continuous coverage optimized over key energy regions, this beamline will be an attractive user facility for organic and magnetic polarization-contrast microscopy. This beamline will have an aberration-corrected photoemission electron microscope (PEEM-3) with a spatial resolution of approximately 5 nanometers.

  New In-Vacuum Undulator Beamline for Femtosecond X-ray Studies. Beamline 6.0.1 for soft x-ray science with ultrashort photon pulses of 200 femtoseconds was ready for commissioning in July 2005. The beamline is unique in the U.S. and will be made available to users in FY 2006. The primary components are a vacuum undulator to produce x-rays over a wide photon-energy range, optical components, including a spectrograph for recording an entire x-ray absorption spectrum from one photon pulse, and a high-repetition-rate femtosecond laser system.

- **The Advanced Photon Source (APS)**

  More Stable Beams. Using a technique pioneered at the APS, 175 girders supporting accelerator components in the APS storage ring have been displaced by as much as 6 mm during scheduled tri-annual maintenance periods over the last seven years, eliminating the stray radiation background signals. As a result, photon beam position monitors (BPMs) for insertion devices over the entire storage ring circumference are now operating on line. The APS leads the world in the use of photon BPMs for insertion device beamlines. Use of these monitors has improved long-term x-ray beam angular stability by more than a factor of five. Users are able to scan the x-ray photon energy by changing the insertion device gap on demand, while still maintaining superior photon beam stability on their samples. The payoff is improved ability to resolve micron and nanometer-sized features in samples

  Improved Timing Experiments. The x-ray pulse structure at the APS is on the order of 100 picoseconds. This pulse width enables special classes of timing experiments where the physical phenomena require fast time resolution. Recent experiments at the APS using this technique have involved the study of porphyrins that may one day form the building blocks of novel catalysts, photonic devices, and efficient solar-power units. The APS has a special operating mode to facilitate these types of measurements. In this mode, a single x-ray timing pulse is isolated from the other x-ray pulses. The intensity in the pulse is determined by the amount of charge stored in the isolated electron bunch that generates the photon pulse. Recent changes to the storage ring top-up injection method, which allows the APS linear accelerator to vary the injection charge along with increasing the injection frequency from two minutes to one minute, have resulted in doubling the single pulse-intensity without adversely affecting the non-timing experiments.

  Improved Mirrors for X-ray Focusing. Elliptically-shaped mirrors based on new technology developed at the Advanced Photon Source are being used to achieve unprecedented focusing of high-brightness x-ray beams. These mirrors are especially useful for producing the microbeams that are used to probe the composition and structure of materials. They are being applied to studies such as microstructural analyses of structural changes arising from welding operations and detailed investigations of the three-dimensional structure of complex crystalline samples.

Nanoprobe Beamline Commissioned for First Experiments. The world's first hard x-ray nanoprobe was activated in March 2005, at the APS. The Nanoprobe beamline is a central component of the new Center for Nanoscale Materials at Argonne National Laboratory. The x-ray nanoprobe will have a spatial resolution of 30 nanometers or better, the highest of any hard x-ray microscopy beamline in the world. It will offer fluorescence, diffraction, and transmission imaging in the x-ray spectral range of 3-30 keV, making it a valuable tool for studying nanomaterials.

- **The National Synchrotron Light Source (NSLS)**

New X-ray Micro-Diffraction Instrument. This instrument to be used for nanoscale research was developed at the X13B beamline to take advantage of the small source size of the in-vacuum mini-gap undulator in the X13 straight section of the NSLS x-ray ring. It consists of five main subsystems: monochromator, focusing optics, sample manipulator, charge-coupled detector (CCD) area detector, and a point detector with two degrees of freedom. The sample stages are equipped with integrated submicron position encoders for excellent positional precision and repeatability. The point detector assembly allows the use of analyzer crystals to obtain better resolution. A key design feature is the close attention paid to mechanical coupling of the focusing optics to the sample positioner to reduce vibrations and improve the microscope stability for the users.

Elliptically-Polarized Wiggler Beamline Upgrade. The Elliptically-Polarized Wiggler (EPW) located in the X13 straight section of the NSLS x-ray is a unique radiation source that produces time-varying elliptically-polarized x-rays for magnetism studies. A major upgrade was performed on beamline X13A to enhance its performance. It included replacement of the existing horizontal focusing mirror, which had been plagued by poor reflectivity as well as mechanical and thermal stability problems, with a new water-cooled spherical mirror. The new mirror system increases the horizontal photon collecting angle by a factor of two and is fully motorized to allow precise manipulation and optimization of the mirror's position. In addition, the beamline interlock and control systems were upgraded. The beamline upgrade has resulted in an order of magnitude increase in the photon intensity delivered to the sample, and the elimination of mechanical and thermal instabilities. These improvements have led to more efficient use of the beamline and increased magnetic sensitivity in the measurements.

Development of a Photon-Counting Silicon Microstrip Array Detector. The NSLS detector group has developed an extremely versatile 1-dimensional position sensitive detector. It is based on custom microelectronics developed at Brookhaven National Laboratory, and consists of a linear array of silicon photodiodes, each 0.125 x 4 mm, which is connected to a set of 32-channel custom integrated circuits and a microprocessor system. The detector system's performance is several orders of magnitude better than one can achieve with charge-coupled type detectors. It is easily adaptable to as large an array as is needed by the application. For example, arrays of 320 and 640 strips, 40 and 80mm long have been fabricated for real-time x-ray scattering.

X-ray Ring Lattice Symmetry Restored. The most direct benefit for the NSLS user community was the restoration of the x-ray ring magnetic field lattice symmetry, which for many beamlines resulted in a 25 percent reduction of the horizontal beam size and an increase in photon intensity delivered to a sample. The desired eight fold symmetry of the x-ray ring magnet lattice can be lost from errors in the x-ray ring quadrupole field strengths. The quadrupole errors can be partially compensated by trim coils available in the x-ray ring for one of the quadrupole magnet families. These errors were determined from an elaborate analysis of the electron orbit measurements taken as quadrupole magnet field strengths were systematically varied. This improvement allowed the NSLS to restore the eight fold symmetric x-ray ring magnet settings for routine operations.

- **The Stanford Synchrotron Radiation Laboratory (SSRL)**

First SPEAR3 Run Completed. In the commissioning run for the new SPEAR3 accelerator, the facility proved to be exceptionally reliable, providing very stable beam for a very high percent (97) of the scheduled time. This is higher than ever recorded with SPEAR2, and an exceptional achievement for a new storage ring. The user run commenced in March and the SPEAR3 storage ring operated at 3 GeV/100 mA and provided 30+ hour life times. (The average uptime over the past five years was 96%.) During the run, users on 239 different proposals received beam time in a total of 466 experimental starts involving 1,516 researchers.

First High-Current SPEAR3 Tests Performed. SSRL conducted three special 8-hour shifts of SPEAR3 operation with currents above the official safety envelope value of 100 mA. These high-current test shifts took place on swing shifts with the experimental floor cleared of non-radiation workers. The main purpose of these tests was to determine if multi-bunch electron beam instabilities will be encountered at higher current operation, in which case a program to implement a costly multi-bunch feedback system would have to be launched. Other potential problems, primarily excessive component heating, are also of concern. The current reached in these tests was limited to 225 mA by the power rating of some absorbers in a legacy insertion device chamber. This current was reached and a comprehensive search revealed no apparent beam instabilities.

New Methods Developed for Studying Structures of Nanomaterials. The reactivity and properties of nanomaterials are highly influenced by particle size and atomic-scale structure. Researchers at SSRL have recently demonstrated that the combined use of several x-ray scattering and absorption measurement techniques leads to quantum leaps in understanding the structures of nanomaterials. X-ray scattering measurements allow experimenters to combine size and shape information with structural information to remove the small-particle size contribution to x-ray diffraction peak broadening, whereas x-ray absorption measurements provide complementary, metal-specific information on local atomic structure in disordered materials. Measurements on zinc sulfide have conclusively demonstrated that structural relaxation of surface atoms causes inhomogeneous internal strain, markedly altering its material properties. This multi-technique nano-characterization approach has further been advanced by developing methods for the routine characterization of bacterial nano-minerals under fully-hydrated in-situ conditions. Bacterial nanominerals are an important class of naturally occurring nanomaterials that help to control the composition of the atmosphere, the potability of natural waters, and the arability of soils. This multiple-technique method provides unique information of wide interest to the nanoscience community.

- **The Intense Pulsed Neutron Source (IPNS)**

Simultaneous Measurement of Mixed-conductor Lattice Relaxation, Diffusion, and Gas Conversion. The General Purpose Powder Diffractometer (GPPD) at the IPNS is equipped with a specially designed controlled-atmosphere furnace, where samples in pellet or hollow-tube form are exposed to mixtures of gases to control oxygen and hydrogen content from highly oxidizing to highly reducing environments. Using two separate gas delivery "circuits," simulated membrane operation conditions can be achieved whereby the responses of oxygen-permeable membranes to strong oxygen partial pressure gradients can be studied. Exhaust gases are analyzed with a Residual Gas Analyzer to probe for leakage and to quantify gas conversion reactions. Dense ceramic components with mixed-conduction properties and high oxygen permeability are important as membranes for oxygen separation and solid oxide fuel cell applications. Membranes are typically operated at elevated temperatures (800-1000°C) and exposed to large oxygen partial pressure gradients. This experiment reproduces the conditions under which these membranes will be used commercially and provides insights into the unusual differential oxygen partial pressure stability of these materials.

Accelerator Systems Improvements. Efforts include: completion of the beamline-magnet power supply upgrades, replacing the originals with higher-efficiency and better regulated units; completion of a full year of operation of the first of two new kicker-magnet power supplies; and completion of full-power tests of the new third-rf system that will be installed in the synchrotron ring to provide new proton beam capture and handling capabilities.

National Neutron and X-ray Scattering School. During August 2005, Argonne National Laboratory again hosted the National School on Neutron and X-Ray Scattering. The school continues to attract outstanding graduate students and post-doctoral appointees with 150 applications for the 60 positions available in 2005. The intensive training introduces students to the theory of, and provides hands-on experimentation in, x-ray and neutron scattering.

- **The Manuel Lujan Jr. Neutron Scattering Center at the Los Alamos Neutron Science Center (LANSCE)**

  Neutron Scattering Winter Schools. The First and Second Annual LANSCE Neutron Scattering Winter Schools were held, with 30 students from a wide geographical distribution attending each School. The 2004 topic was magnetism and the 2005 topic was mechanical properties of materials. During nine intensive days in Los Alamos, students had lectures from world experts on the key materials issues for the School theme, modeling and theory, and neutron scattering techniques addressing these issues. In addition, the students had the opportunity to gain hands-on experience in neutron-scattering techniques and data analysis.

  New Sample Environments. A major emphasis on sample environments in FY 2005 has greatly enhanced the low temperature, high field, and high pressure possibilities for user experiments. Investments in new low temperature sample environments, high pressure instrumentation, sample goniometers, and support staff have made users more productive. Along with the 11-Tesla superconducting magnet commissioned in 2004, the Lujan Center's suite of sample environments for condensed matter physics has dramatically improved in FY 2005. A rheometer designed to synchronize with the 20 Hz Lujan Center pulsed neutron beam is expected to be tested in FY 2005. It will provide a unique capability to impose accurate hydrodynamic shear on polymer solutions and colloidal suspensions while performing structural measurements by small-angle neutron scattering.

  Instruments Enhancement. The High Intensity Powder Diffractometer (HIPD) and the Single Crystal Diffractometer (SCD) have received upgrades to software, shielding, alignments, and hardware that have increased their neutron intensity, user throughput, and efficiency. New hardware and software controls on the Low-Q Diffractometer (LQD) and a new detector have made small angle neutron scattering (SANS) more effective.

- **The High Flux Isotope Reactor (HFIR)**

  Common Guide Casings for Seven New Instruments Installed. Neutron guides transport cold neutrons (energies ~0.1–20 meV) with little loss in flux. This permits one to transport neutron beams from the source to instruments several tens of meters away. This lowers the instrumental background noise from gamma rays and unwanted neutrons since one can place the instruments far from the source. Also, the guides have a slight curvature which removes the "line-of-sight" view of the neutron source and further reduces this background. The guides are made by coating glass with layered coatings called supermirrors which are highly reflective for neutrons. These flat, coated glass plates are then assembled to form hollow rectangular cross-sectioned pipes with the coated sides forming the interior walls of the pipes. These guides will be illuminated with neutrons produced by the new HFIR cold source to be installed early in 2006.

  HB-4 Shield Tunnel and Velocity Selector Shielding Installed. A great deal of neutron shielding is required to shield the exit of the new HFIR cold source and components of the cold neutron beamlines. The first and largest general section of shielding for the new instruments was constructed. Also, the lead shielding for the velocity selectors for the two small angle neutron scattering (SANS) instruments was assembled. These components are essential for the new Center for Neutron Scattering cold neutron spectrometers.

  SANS 1 Detector Tank and Internal Components Installed. The largest component for the first Small Angle Neutron Scattering (SANS) instruments has been installed. This giant tank will contain the detector for this instrument. The 1 meter square detector will ride on rails inside the evacuated volume of the tank.

  The Neutron Reflectometer Commissioned. A new instrument, the neutron reflectometer, was commissioned for use in the general user program at the HFIR Center for Neutron Scattering. This machine is optimized for the studies of surfaces and interfaces. It is the fifth Cold Neutron Source instrument fully commissioned and will be used for the studies of polymers, biomaterials, thin solid films, and surfactants.

Selected FY 2004 Scientific Highlights/Accomplishments

Materials Sciences and Engineering Subprogram

- ***The Ultimate Analysis: Single-Atom Spectroscopy in Bulk Solids.*** A longstanding dream in materials sciences and engineering has been to see and study those specific individual atoms that are critical to bulk properties and to determine their location and active configuration. Now, through an enhanced scanning transmission electron microscope with improved optics, researchers are able to observe an individual atom within its bulk environment and characterize its chemical state via spectroscopic means, determining its valence and bonding with nearest neighbors. The advance was made possible by correction of lens aberrations in the electron microscope to give a smaller yet brighter beam with a diameter of approximately 1 Ångstrom. Single-atom sensitivity, the ultimate analysis, opens up all areas of materials science and engineering to fundamental investigations in a revolutionary way.

- ***New Thin-film Texture Discovered with Potential for Nanotech Applications.*** One of the most fundamental structural properties of a thin film is its "texture," which is the orientation of individual grains with respect to the deposition substrate. Three types of texture are commonly observed: random, where no single orientation is dominant; fiber-texture, where the film grains are parallel to the growth direction, but random about that direction; and epitaxial, where the film orientation is fixed in three dimensions with respect to the substrate. The new, fourth type of texture, named axiotaxy, was observed in a number of thin film systems in which the film and substrate share a common plane orientation as a consequence of crystal lattice matching. This new texture provides a potential method for assembling large numbers of nanocrystals in regular patterns for nanotech applications.

- ***Negative Refraction - New Frontier for Superlenses***. The first demonstration of negative and positive refraction of visible light at the same crystal interface was recognized as one of the "Top 15 Physics News Stories of 2003" by the American Institute of Physics. Nature provides us with optical refraction which is always positive: that is, the incident and transmitted light through an interface of two different media are on opposite sides of the interface normal. For negative refraction, they are on the same side of the interface normal. The beauty of negative refraction is total transmission and zero reflection, regardless of the angle of light incidence. These properties lend themselves to the creation of "super lenses." Laser beams can be steered in nano-photonic devices without loss, and optical telescopes can be built with higher resolution. The new interface uses a ferroelastic twin domain boundary such as a yttrium vanadate (YVO4) bi-crystal and is applicable to any frequency of the electromagnetic spectrum. As a vision for the future, electron beams could be focused more efficiently in highly sensitive electron microscopes.

- ***Multi-band Semiconductors for High Efficiency Solar Cells.*** A new semiconductor material has been discovered that has multiple energy gaps, instead of the usual one, allowing for ultra-efficient energy capture of sunlight. Multi-band semiconductors were theoretically predicted over 20 years ago, but only now through the properties of so-called "highly mismatched alloys" (HMAs) have they been achieved. HMAs are compound semiconductors in which a small fraction of the anions are replaced with more electronegative atoms, producing a material with a new band having a strong quantum mechanical interaction with either the occupied valence band or the empty conduction band of the host semiconductor. Using this approach it was predicted, and subsequently demonstrated experimentally, that a II-VI semiconductor compound (ZnMnTe) with a small fraction (~1%) of the group VI constituent, i.e., tellurium, replaced by oxygen operates as a multiband semiconductor. Theoretical evaluation indicates that a single junction solar cell fabricated from this material could achieve a power conversion efficiency of 56%.

- ***Individual Carbon Nanotubes as Nanoscale Light Sources.*** A single carbon nanotube with a diameter of only 1.4 nanometer was used to fabricate the smallest source of light that can be controlled by electric current. The emission spectrum (color) of the light varied as a function of nanotube length and diameter. The center of the spectrum is determined by the nanotube diameter while the width of the spectrum depends on the length of the nanotube. Long nanotubes (50,000 nanometers) had narrow, symmetric emission spectra (characteristic of cold electrons) centered at the bandgap of the nanotube, which is inversely proportional to the nanotube diameter. Short nanotubes (500 nanometers) were also peaked at the bandgap of the nanotube, but showed broad, asymmetric spectra with a tail on the high-energy side, characteristic of hot electrons. These spectra show the cooling of hot electrons in nanotubes as a function of length through excitation of vibrations of the nanotube. The demonstrated understanding and control of optical properties using nanotubes could be important for optoelectronic nanotechnology.

- ***Magnetic Resonance Imaging at the Nanoscale.*** An innovative magnetic resonance approach to characterizing nano-porosity in a variety of materials has been developed. Magnetic resonance imaging (MRI) has been tremendously successful in visualizing resident deformities and the presence of disease in soft, porous biological tissues of the liver or kidney, yet the limited resolution precludes characterization at the nanometer scale. By using a technique of percolating inert gas through a nanoporous structure and then determining both the "sticking coefficient" of the gas and the time it takes for the gas to move away from the pore structure, MRI can now evaluate both the pore size distribution and the nature of the pore connectivity. This allows the analysis of highly porous structures that are present in many living systems and those created artificially in the laboratory such as filters to sequester pollutants, catalysts for chemical reactions, highly efficient insulators, and high strength to weight ratio materials for structural applications. By understanding the relationship between processing parameters and porosity of the resultant materials, advances in porous materials can be made.

- ***Nano-Trains: Nanoparticle Transport Using Motor Proteins.*** An active transport system that can be used to pick up, transport, and deposit nanoparticles within a microfluidic system has been developed. The active transport system is powered by the motor protein kinesin, a naturally occurring molecular machine. In the presence of a fuel source (adenosine triphosphate, or ATP), the head groups in the motor proteins “walk” rapidly along protein fibers called microtubules. With the tails of kinesin fixed to a surface the proteins can be used to propel the microtubules across the surface. The microtubules can now be modified to carry various size particles, ranging from 10 micrometers to 10 nanometers, and in large quantities, by functionalizing segments of the microtubules to carry cargo, like train “cars,” while leaving other segments unfunctionalized to act as “engines” by allowing free interaction with the motor proteins. This discovery suggests that highly non-equilibrium structures could be developed using the same active transport strategies that organisms employ for tissue assembly and muscle actuation.

- ***How Do Complex Fluids Jam?*** Is the mechanism for flow jamming the same for solid particulate matter (such as powders, coal, grain, pills, etc.) as for foam (bubbles in a fluid)? Two processes that rely on flowing foam are oil extraction and mineral separation. A major feature of both is that the flow can spontaneously stop, or jam, as the bubbles block each other. A better understanding of the causes of jamming will improve processes relying on flow. Recent studies using model foam systems have measured the coexistence between a flowing phase and a jammed phase. A surprising result was that this behavior was different from jamming observed in solid particulate systems. It provided evidence for at least two different mechanisms of jamming, a critical step in furthering the understanding of the jamming process.

- ***Electron Transport in Semiconductor Quantum Wires.*** Spintronics (electronic phenomena that depend on electron spins) may provide a route to future generations of high-speed, low-power, nanoelectronics and may open up new areas of technology such as solid-state-based quantum computing. Significant challenges exist to realize these goals, including how to detect – or read – the electron spin in an electrical measurement. It has recently been demonstrated how such detection can be achieved in practice by exploiting the unique features of electron transport in semiconductor nanostructures known as quantum wires. Experiments show that the spin state of one quantum wire can be detected by studying the conductance of another wire located in close proximity. Theoretical work supports the idea that these experiments provide non-local detection of the electron spin opening pursuit of applications of this work to solid-state approaches to quantum computing.

- ***Superfluid Excitons at High Magnetic Field.*** A grand challenge for condensed matter physics is the observation of a new phase of matter created by the “condensation” of excitons, which are electron-hole pairs. Because excitons are bosons, any number can occupy a single quantum state. Thus, at low temperature, they should condense into the lowest energy level. Unfortunately, observation of this has been hindered by the rapid recombination of the electron and hole. Using magnetic fields to create stable exciton gases in doped double-layer semiconductor structures, the first evidence for condensation of an exciton gas was found in quantum tunneling measurements. The signature of the condensation was that both the conventional and Hall resistances of the sample become extremely small at low temperature. This nascent superfluidity is the strongest evidence yet for excitonic Bose condensation.

- ***Going from Good to Great: Doubling the Superconducting Upper Critical Field of Magnesium Diboride.*** In January 2001, a simple compound, magnesium diboride (MgB_2) was discovered to superconduct at a remarkably high temperature of 40 K, double the 20 K value for the niobium-based industrial standard. However, in its pure form, the material stops superconducting in a low magnetic field. During the past year, it was determined that the material continues to be superconducting in high fields if a small amount of carbon, about 5%, is substituted for boron. This has led to a better understanding of the superconductivity in this unique compound. The results indicate that, if the current carrying capability and mechanical properties can be further enhanced, carbon-doped MgB_2 could become the next industrial standard superconductor --better, cheaper, and lighter than niobium alloys.

- ***Wiring for Nanocircuits: Stabilized Silicon Nanotubes.*** Recent theoretical predictions have indicated that silicon nanotubes can be stabilized by attaching a string of 3d transition elements along the outside of the tube. These same calculations predict that the resulting nanotubes will be strongly conducting -- an important property needed by a candidate material for wiring together nanoelectronic components. The often considered carbon nanotubes, however, can be weakly metallic, semiconducting, or insulating depending on a property that is quite difficult to control-the winding ratio of the tube. The stabilization and metallization of the silicon nanotube can be accomplished with a small amount of nickel, about one nickel atom for every five silicon atoms. The compound tube structure studied is also smaller than most carbon nanotubes.

- ***Lashing Together Nanoparticles to Make Real Things.*** Theorists have shown that one can cause nanoparticles to self-assemble into ordered arrays by attaching short polymer strings to the particles to act as tethers. This is important because it is necessary to assemble large numbers of nanometer-sized particles to create something of size appropriate to our world. It must be done as a loose assembly of the nanoparticles to retain their special properties but often also be arranged in special geometric patterns to realize the desired property. The technique demonstrated by detailed simulations is to attach short polymer strands to the particles at specified points and then let nature take its course. While currently only a theoretical prediction, the scheme is quite feasible and is expected to be in use within two to five years. In the meantime, the theorists are busy developing a “handbook” of how to position the tethers, how long they should be, and what they should be made of to accomplish a particular desired structure.

- ***A New Class of White Light Phosphors: Advancing the Solid State Lighting Initiative.*** A new class of tunable, white light emitting phosphors based on single size semiconductor nanoparticles or quantum dots (QDs) has been discovered. This breakthrough meets one of the most critical needs in the Department’s Solid-State Lighting Initiative, whose aim is to replace present day highly inefficient light bulbs by solid state lighting devices and thereby have revolutionary effects on conserving electric energy. This accomplishment was made possible by the finding that, for sufficiently small cadmium sulfide and cadmium selenide QDs of diameters two nanometers or less, the onset of light absorption (determined by dot size) and the emission energy, or color (determined by interfacial chemistry), can be independently controlled. The decoupling of these two features allows wide separation of the absorption and emission to eliminate self-absorption of the emitted light, and allows one to tune the emission throughout the visible range from a population of single-size dots. Key to this discovery is the ability to tailor the energies and lifetimes of interface states by the addition of suitable surfactants that bind to selected sites on the QD surface (which determine the emission), or the addition of suitable electron or hole traps (e.g., zinc or sulfide ions, respectively).

- ***Catalyst Active Sites Imaged in Real Time.*** The atomic-scale formation and dynamics of active sites on a catalytic surface have been imaged for the first time. Using movies made from a series of state-of-the-art atomic-level scanning tunneling microscope images, the time-dependent behavior of sites on the surface of palladium metal was observed while diatomic hydrogen gas was adsorbed and then dissociated into two hydrogen atoms. The catalytic dissociation of hydrogen on a metal surface is pervasive in catalytic chemistry. Contrary to the prevailing view of the past three decades, it was found that three adjacent and empty surface sites are required for this process to occur - two empty sites are not sufficient. This surprising result calls into question the conventional thinking on the structure of active sites on catalyst surfaces. Further real-time measurements will help establish the molecular-level understanding of the formation of the active sites that determine the catalytic activity of a surface.

- ***Basic Research Leads to Terabit Memory Devices.*** A decade-long basic research project has led to the first successful application by industry of a novel approach in nanotechnology, 'molecular self-assembly,' to enable continued miniaturization of semiconductor circuitry such as FLASH memories. The essential element in this new approach lies in directing the orientation of highly-dense arrays of nanoscopic cylindrical domains in thin films of diblock copolymers (BC). Using routine lithographic processes, the BC films are transformed into large area arrays of cylindrical nanopores with very high aspect ratios. Establishing the ability to produce such high density arrays in a simple, robust, and inexpensive manner using conventional processing (new tooling is not required and will not be required with further advances in the self-assembly technique) has broken new ground in fundamental studies of nanoscience and the rapid transfer of this technology to the industrial sector.

- ***Fundamentals of How Liquid Metals Solidify Answered with Synchrotron Radiation Experiments.*** Materials properties are determined, in large measure, by the nature of the solidification process. During the cooling process, the metal atoms in the liquid phase are thought to pack together with almost the same order as the resultant solid. In fact, early experiments demonstrated that liquids cooled far below their melting point still maintain a large degree of disorder. As the temperature is further lowered, a well ordered crystalline solid is eventually reached, but the nucleation pathway to the crystalline form remained a mystery. By combining levitated molten metal drops with a newly developed, in-situ synchrotron x-ray diffraction technique for measuring structure during solidification, investigators have verified for the first time that atoms in a liquid metal arrange themselves with the local symmetry of an icosahedron, a Platonic solid consisting of 20 tetrahedra (4-sided pyramid shaped polyhedra). As cooling proceeds, the icosahedral arrangement transitions to the final crystalline form. This discovery proves that atomic scale structure in the liquid actually plays a role in crystallization, something that is not treated in current nucleation theory.

- ***X-Ray Microscopy in 3D on a Micron Scale***. Metal deformation, ranging from the centuries old heating and beating of sword edges to the rolling of metal sheets in modern industrial mills, is one of the oldest and most important materials processing techniques, yet it remains one of the least understood. Although elaborate recipes have been developed to produce alloys with desired properties, they are all based on expensive and inefficient search and discovery methods. To address this, a new, nondestructive, submicron-resolution 3D x-ray microscopy technique with high-precision nanoscale indentations to study the fundamental aspects of deformation in ductile materials has been developed. X-ray microscopy measurements made using penetrating synchrotron x-ray microbeams are providing detailed, quantitative information on the deformation microstructure for sizes below that of a human hair, but too large for electron microscopy. These results provide previously missing information that is critical for testing advanced theories and computer modeling and for making new materials, with predictable properties, in a more efficient manner.

- ***Understanding Fundamental Magnetic Properties Could Lead to Sensor Development.*** Magnetic excitations provide insight into the spin structure and spin dynamics of materials. One material studied exhibits colossal magnetoresistance, a property that makes it interesting for sensor applications. The magnetic structure of this material ($Pr_{0.5}Sr_{0.5}MnO_3$) was determined to be ferromagnetically aligned layers that are coupled antiferromagnetically. The magnetic excitations (also called spin waves) were measured using inelastic neutron scattering at the High Flux Isotope Reactor at Oak Ridge National

Laboratory. The spin wave dispersion follows the behavior expected from linear spin wave theory. With refinements in analyzer efficiency and film preparation techniques, the measurement technique will then be applied to thin films. This should allow a search for spin wave excitations in antiferromagnetic films of Fe-Pt.Bose

Chemical Sciences, Geosciences, and Energy Biosciences Subprogram

- ***Potential for Greatly Enhanced Efficiency in Nanocrystalline Solar Cells.*** An incident solar photon striking a semiconductor solar cell normally produces a single electron-hole pair (exciton) and some excess heat. Experimentalists have recently demonstrated that two or more excitons can be created by absorption of a single photon in an array of lead-selenide nanocrystals. This process is called "impact ionization" and is observed when the photon energy is greater than three times the band gap of the nanocrystal. Multiple excitons from a single photon are formed on the picosecond time scale, and the process occurs with up to 100% efficiency depending on the excess energy of the absorbed photon. If this process could be translated into an operational solar cell, the gain in efficiency for converting light to electrical current would be greater than 35%.
- ***High Order Harmonic Generation Using Ions.*** High harmonic generation (HHG) is a process in which highly nonlinear optical effects, driven by ultrafast, intense laser pulses in an atomic gas, are used to turn visible bursts of photons into bursts in the extreme ultraviolet and soft x-ray spectral regions. There is a cutoff at high frequencies for HHG that is determined by the ionization potential of the atom and by defocusing and phase mismatch of the pump-laser beam due to ionization. Recent experiments have significantly extended the range of HHG to photon energies up to 250 eV through the use of atomic ions, which have higher ionization potentials and are thus capable of producing more energetic harmonic orders. In this work an ultrashort, intense optical laser pulse was focused into a hollow fiber filled with low-pressure argon gas. The fiber serves as a waveguide to phase-match the fundamental excitation pulse with the HHG soft x-ray pulse. This work demonstrates that HHG from ions can extend laser-based, coherent up-conversion into the soft x-ray region of the spectrum.
- ***Manipulation of Carbon Monoxide Oxidation to Carbon Dioxide***. The formation of a chemical bond involves the approach of two reactants to short distances so that a new bond can form. How close do the two reactants need to be for them to interact with each other? In this novel experiment, a single carbon monoxide (CO) molecule on a surface was pushed toward two oxygen (O) atoms that were formed in the dissociation of O_2 by tunneling electrons. Using inelastic electron tunneling spectroscopy in a cryogenically cooled microscope, the hindered rotational mode of the CO molecule was measured as its distance from the two O atoms decreased. The change in this vibrational energy signaled the onset of a significant CO-O interaction prior to the formation of carbon dioxide (CO_2). A shift of 20% in the hindered rotation energy was observed when the CO molecule was within 2.50 Å from each of the two O atoms. Spatially resolved mapping of the hindered rotational mode led to a tilted CO in the O-CO-O complex. The controlled positioning of the two reactants allowed direct visualization of the chemistry. This research probed individual reactive encounters of the type that constitute a surface-mediated catalytic process. Exacting control of catalysis will require such molecular-level characterization.
- ***Direct Numerical Simulations of Homogeneous Charge Compression Ignition.*** Homogeneous charge compression ignition (HCCI) has the potential to reduce nitrogen oxide and particulate emissions from internal combustion engines while improving overall efficiencies. A major challenge posed by this method of combustion is control of the heat release rate, and in particular, a means to spread the heat rate out in time to suppress the occurrence of damaging engine knock. Direct numerical simulations (DNS) of lean hydrogen-air ignition at high pressure and constant volume in the presence of temperature inhomogeneities are helping researchers understand the HCCI combustion process. Starting from an initial distribution of fluctuating temperatures at high pressure, the evolution of localized ignition sites was studied in a constant volume DNS with detailed hydrogen/air reaction kinetics. For the first time, numerical simulations revealed that flame front and spontaneous ignition propagation can coexist in this environment. The simulations showed that the local nature of the ignition propagation is primarily dependent upon the inverse of the local temperature gradient. Criteria

were developed from the DNS data (e.g., speed of the ignition front and a critical temperature gradient at the front) to distinguish between the different modes of propagation.

- ***Charge Separation by Carbon Nanotube/Ferrocene Nanohybrids.*** Carbon nanotubes, which are chemically stable and electrically conducting, have been modified for the first time by attachment of electron donors, in this case, ferrocene molecules. When excited with visible light, these carbon nanotube-ferrocene hybrids exhibit intramolecular electron transfer to yield long-lived charge-separated species. The carbon nanotube serves as the electron acceptor in the donor-acceptor ensemble, distributing the charge over its extended π-electronic system. The separation of charge is sufficiently long lived to show promise for future development of solar photoelectrochemical cells based on modified carbon nanotubes.

- ***They Bend Before They Break: Fast Scission of Chemical Bonds.*** Bond-breaking reactions in liquid solution which are so fast that the rates could not previously be measured, have recently been studied at the new picosecond Laser-Electron Accelerator Facility (LEAF) at Brookhaven National Laboratory. A large class of molecules known as aryl halides was studied, in which a halogen atom, such as chlorine or bromine, dissociates from a sizable planar ring structure, breaking its bond. The newly measured rates can only be explained theoretically if the bond breaks by the halogen atom bending out of plane by about 30 degrees before bond breaking, in a bent transition state. Such fundamental knowledge of the reaction mechanism may lead to improvements in energy efficiency and fewer toxic by-products in large-scale industrial processing.

- ***Protein-Nanoparticle Hybrid Systems for Light Energy Conversion.*** Novel protein-nanoparticle hybrid assemblies have been developed that employ semiconductor nanoparticles for initial light-induced charge separation and biomolecules for subsequent chemical/electrical conversion. The end-to-end, wire-like nanorod structures are based on nanoscale metal oxide particles, in which the ability to systematically manipulate size and shape of the nanoparticles was exploited in synthesis of axially anisotropic tubes, cubes, rods, or stars. The nanoparticles were oriented into organized architectures using biolinkers, such as the biotin molecule, that bind strongly to the protein, avidin. Photoexcitation of the wire-like architecture resulted in charge separation originating at the tips of the nanorods: the photogenerated electrons being localized at the semiconductor, and holes at the protein. Thus, a rational design of protein-nanoparticle hybrid architectures enables coupling of photoinduced charge separation in nanocrystallites with the charge-transfer induced chemistry on proteins. The hybrid architectures and ensuing chemistries can either use or alter protein functionality, and could be used for construction of solar-based molecular machines.

- ***Reverting Carbon Dioxide into Valuable Chemicals.*** An inexpensive, low-temperature synthetic route for the conversion of carbon dioxide into useful chemicals and fuels is a long-standing challenge. Despite extensive research, current catalysts still use expensive complexes of platinum-group metals. Recent work has led to a breakthrough in the catalytic addition of hydrogen to carbon dioxide to produce formic acid. Using sophisticated high-throughput techniques to rapidly search for promising catalytic structures, investigators have identified the broadest range to date of hydrogenation catalysts that can sustain high activity for many cycles. These structures consist of phosphine-complexes of copper, chromium, iron, indium, molybdenum, niobium, nickel, or tungsten, all of which are abundant and inexpensive metals. Detailed structural and mechanistic studies have led to even further improvement of the activity and durability by surrounding the metal centers with ligands designed to provide optimum electronic structure while protecting the metals from degradation. The new nickel, copper, and iron phosphine-cyano complexes carry out the production of formic acid at 40 bar and 50 ^{o}Celsius with limited deactivation for periods of days.

- ***Pure Hydrogen from Alcohol through Microsecond Catalysis***. Researchers have recently shown that it is possible to selectively extract pure hydrogen from ethanol, a renewable fuel made from biomass, in a matter of microseconds. The process is based on a high-temperature ceramic catalyst containing rhodium metal and cerium oxide. At about 800 ^{o}C, wet ethanol, contacted with the catalyst for about one microsecond, undergoes oxidative dehydrogenation to hydrogen and carbon dioxide, with 95% conversion and 100% selectivity to hydrogen. This remarkable catalytic performance and the low-cost wet alcohol source could result in an economically feasible hydrogen production process for the future, especially as many of these very rapid oxidation reactions are self-sustaining even at 800 ^{o}C or higher and do not require external heat sources. Advances in this hydrogen production process might provide an alternative to steam reformation of hydrocarbons as a source of hydrogen.

- ***Benign Polymerization Chemistry Leads to New Polymers.*** The demand for polymeric materials continues to rise at an impressive rate and, in the near future, environmental conservation may become a major constraint in this expansion. Researchers have long pursued catalysts that take molecules derived from biomass, such as sugars, alcohols, and esters, and convert them with high yield and no waste into synthetic plastics, such as polyethers, polyesters, and polycarbonates, with controlled characteristics. Besides having appropriate thermal and mechanical properties, a significant fraction of future polymers should be biodegradable or biocompatible for use in large-scale packaging or in smaller-scale biomedical applications: drug release membranes, synthetic tissue, and sutures. Recently, investigators have successfully synthesized a family of metal alkoxide catalysts that produce polyesters and blends via ring-opening polymerization of cyclic esters derived from renewable sources. Examples are the synthesis of polylactides from lactides derived from corn and the formation of polycarbonates by ring-opening copolymerization of epoxides-oxiranes and carbon dioxide. The latter is a chemically benign alternative to the current technology for polycarbonate synthesis that uses phosgene, a highly poisonous gas. Through mechanistic, microstructural, and kinetic studies, these investigators are arriving at fundamentally new rules and new catalysts for transformations of oxygenated molecules that may dramatically change the landscape of polymerization chemistry.

- ***Fundamental Studies on Crown Ethers Benefit Cleanup of Nuclear Waste at Savannah River.*** Fundamental research has provided the foundation enabling innovative technology for nuclear-waste cleanup at the Savannah River Site (SRS). In early 2004, a large contract was awarded for the design, construction, and commissioning of the Salt Waste Processing Facility (SWPF) to clean up a major portion of some of the nation's most dangerous Cold War era nuclear waste stored at the SRS. Approximately 34 million gallons of waste from nuclear-weapons production are stored in tanks at the SRS. Over 31 million gallons of that waste is solid or dissolved salts in which the fission product cesium-137 comprises more than 98% of the total radioactivity in the salt. In 2001, the Office of Environmental Management chose the Caustic-Side Solvent eXtraction (CSSX) process developed at Oak Ridge National Laboratory for removing cesium-137 from the waste in the SWPF. The selection followed an intensive period of evaluating candidate technologies by a multi-site team of scientists and engineers over a four-year period. Selection was based on the ability of candidate technologies to meet difficult processing requirements, including the ability to remove 99.9975% of the cesium-137 from the waste. Such extraordinary performance requires extraordinary chemistry, which had its roots in fundamental research which focused on the principles of host-guest chemistry, emphasizing the synthesis of tailored molecules that selectively bind (or host) target species. The understanding of host-guest chemistry from this research led to the ability to design the synthesis of crown ethers with appropriate architecture to complex with alkali metal ions to effect extraction with high selectivity.

- ***Improved Analysis for the Next Generation of Electronic Devices.*** New research has shown that by covalent Fluorescent Labeling of Surface Species (FLOSS), the inherent sensitivity of fluorescence spectroscopy can be exploited to identify and quantify low concentration functional groups on surfaces. FLOSS enables the detection of surface chemical groups as low as 1011 molecules/cm^2 (0.01% of the surface) by specific covalent attachment of fluorescent chromophores to surface functionalities. Advances in electronics and sensors have been made by decreasing the size of the components making electronics faster and sensors more sensitive and selective. These advances provide an important step in our ability to control size and thickness of insulating layers for modern electronic devices. The technique used to develop these films is to expose the surface, such as silicon, to a long chained molecule, and allow it to self assemble on the surface. The length of these chains can then be reduced to control the resistivity by reaction with electrons or ozone, and the pattern they make on the surface can be controlled by ion or electron bombardment using a mask or laser ablation by rastering the beam across the surface. Understanding and controlling the chemistry of these reactions is critical to make the next generation of devices.

- ***Building Polar Actinide Materials.*** Compounds that adopt polar structures are able to exhibit a wide range of important technological properties such as second-harmonic generation (nonlinear optics), piezoelectricity, and pyroelectricity. One strategy for constructing polar structures is to use oxoanions containing heavy atoms such as selenium, tellurium, and iodine. These oxoanions share a common feature: they contain a nonbonding pair of electrons that can be aligned during crystal formation to create polar structures. These anions have been combined with the actinide elements uranium, neptunium, and plutonium to create novel polar actinide materials. Some of the neptunium compounds are further unusual in that the distance between neptunium atoms within the crystals can be controlled, allowing magnetic interactions to take place between the actinide elements. This work allows detailed structure-property relationships to be developed in polar actinide materials. These relationships elucidate the properties of 5f electrons, which contribute uniquely to the bonding in actinide materials and provide models for polar materials of nonradioactive transition metals.

- ***Plutonium Oxide Unraveled.*** A collaboration of research groups has developed sophisticated quantum chemistry software to model the electronic properties of actinide materials. These computational programs solve the first-principles, basic equations governing the quantum mechanics of electrons and nuclei, to yield predictions about conducting properties, equilibrium structure, and other electronic properties of materials like plutonium oxide (PuO_2). In a recent series of calculations on a cluster of high-performance computers, it was predicted for the first time that PuO_2 is an insulating material with a band gap of a few eV and with ferro- and anti-ferromagnetic phases in close energetic balance. These results are consistent with subsequent experimental data obtained by other researchers. A successful description of electronic properties of PuO_2 is a prerequisite for more elaborated modeling of the interaction of PuO_2 surfaces with water and other environmental species. Understanding these basic processes is essential to predict the long-term stability of PuO_2 when it is exposed to air, water, and other common substances.

- ***Bioelectrochemistry on Nanostructured Surfaces.*** A defining feature of modern bioelectrochemistry is extraction of functional biomolecules and their reconstitution on patterned surfaces in defined geometries. The bioelectrochemical process of solar energy absorption and subsequent conversion of light energy uses two molecular reaction centers operating in series, Photosystems I (PSI) and II (PSII). Photon absorption triggers electron transfer reactions that generate an electric voltage. It is this electrochemical potential that is the source of free energy for conversion of light energy into chemical energy. It has been demonstrated for the first time that PSI molecules can be oriented by elementary dipole forces that exist at the air-water interface and the dipole points predominantly towards the water. Orientation was demonstrated by measurement of the magnitude and sign of the electrostatic potential above the PSI-containing air-water interface. Bioreaction centers supported in nanoporous media enable the construction of bioelectrochemical systems for both basic and applied needs.

- ***Thermophysical Properties of Macromolecular Systems in Nanoscopic Structures.*** An important part of nanotechnology is to understand whether the properties of polymeric systems in nanoscopic structures are different from those of the bulk. Theoretical studies have established for the first time that nanometer-length structures of polymer glasses exhibit a glass transition temperature which is significantly lower than that of the corresponding bulk polymer. These studies also established that the elastic properties of the polymer in such structures are considerably "weaker" than those of the bulk. Finally, and perhaps most importantly, it has been demonstrated that the elastic moduli of nanoscopic polymeric samples are highly anisotropic, raising serious concerns about the applicability of continuum-mechanics computational approaches for study of such systems. These predictions indicate that the mechanical stability of features smaller than 50 nm is severely degraded. Extrapolation of current technology as applied in the microelectronics industry might not be possible.

- ***Structure of Electric Double Layer at the Rutile Surface from Molecular Dynamics Simulations.*** Rutile (α-TiO2) is the protective surface phase that will cover the drip shields over the waste canisters at the Yucca Mountain waste repository. It is also an important mineral in the chemical and materials industries as a catalytic substrate, photocatalyst, pigment, and ceramic raw material. Molecular simulation of the structure of the relaxed rutile (110) crystal surface in contact with aqueous solutions were performed to determine the structure of water molecules near the interface, adsorption of ions, identification of several modes of binding of adsorbed ions with surface oxygens, and static and dynamic properties of the surface. Quantitative experimental data provided by synchrotron x-ray investigations determined the distribution of adsorbed water molecules and cations at the rutile (110) surface and verified the predictive capabilities of the computational approaches. Computational chemical physics demonstrated the utility of classical models of the macroscopic properties of the electric double layer. Solid-liquid surface properties (colloidal stability, structure of micelles, membranes, metallurgy, chemical sensors, catalysis, and synthesis of nanophase materials) can now be linked to the atomic-level structural information.

- ***Water-Driven Structural Transformation in Nanoparticles at Room Temperature.*** Natural mineralogical nanoparticles exist at ambient temperature, pressure, and humidity in the geosphere. Research on nanoparticulate mineral phases provides understanding of the role of natural nanoparticles and in predicting what the future of "new" nanoparticles will be in the environment. Zinc sulphide nanoparticles (~3nm, 700 atoms) synthesized in methanol exhibited a reversible structural transformation accompanying methanol desorbtion. The binding of water to the as-formed particles at room temperature led to a dramatic structural modification, significantly reducing distortions of the surface and interior to generate a structure close to that of the mineral sphalerite. This shows one route for post-synthesis control of nanoparticles structure, and the potential use of the nanoparticles' structural state as an environmental sensor. The results also demonstrate that the structure and reactivity of natural nanoparticles will depend both on the particle size and on the nature of the surrounding molecules.
- ***A Molecular Switch Controls Cell Identity.*** Like its fuzzy, dwarf namesake from the "Star Wars" movie, the YODA (YDA) mutant in Arabidopsis is small but powerful. Recent molecular genetic experiments reveal that YODA acts as a negative regulator of plant cell fate decisions following asymmetric cell divisions. This regulation is essential for establishing normal cell patterns for stomata, tiny surface pores in leaves and shoots. Pore size is regulated by a pair of flanking guard cells that serve as gas valves controlling carbon dioxide and water vapor movement in or out of the leaf. Early in development these cells make an irrevocable decision on whether they will end up as epidermal cells, or undergo an asymmetric division and become guard cells. YODA's kinase activity sends the signal that decides this developmental fate, thus determining the number of stomates on a leaf surface. So as plants grow and form new leaves, they can adjust to factors such as carbon dioxide, and water and light availability by changing stomatal density and distribution. This illustrates how protein-gene interactions within complex regulatory feedback loops and pathways can be deciphered to understand how a group of cells can grow, develop, and adapt to an ever-changing environment in the coordinated form of a whole plant.
- ***Structural and Functional Analysis of a Minimum Plant Centromere.*** Every chromosome, the carrier of hereditary information in all living organisms, contains three essential elements: the telomere ends, the origin of replication that initiates copying of genetic information, and the centromeres that direct the partitioning of chromosomes during cell division. Scientists have made a startling discovery about the nature of these centromeres in rice plants. Their sequencing of the centromere of rice chromosome 8 revealed the presence of four active, expressed genes. This discovery refutes long-held scientific beliefs that centromeres contained only structural information for chromosome segregation, programmed within vast stretches of "junk DNA" consisting of repetitive, rearranged and noncoding sequence tracts. This work, significant for being the first completely sequenced plant centromere, complements the international effort to complete the sequence of the rice genome, and represents the first step toward achieving such practical applications as the creation of artificial chromosomes for precision plant engineering.
- ***The Glass Bead Game of Molecular Detection.*** A significant challenge in the study of biological systems is the ability to detect molecular interactions with sensitivity and accuracy. Scientists have developed a novel technique for detecting substrate binding to proteins embedded within cellular membranes. Their technique uses the fundamental qualities of colloidal particles, which self-assemble into a variety of ordered phases in a manner driven by the pair interaction potential between particles. Colloidal suspensions of membrane lipids linked to a specific substrate were coated onto silica beads. When a protein binds to this immobilized substrate, it causes small perturbations on the membrane surface that result in visible reorganization of the colloid, such that the coated beads disperse. The ability to sense molecular interactions without the use of expensive fluorescent probes has practical implications for rapid, high-throughput screening of a variety of interactions between biological molecules.

Selected FY 2004 Facility Accomplishments

- **The Advanced Light Source (ALS)**

  New Insertion Device Installed for Ultrafast X-Ray Pulses. Light from a high-power, ultrafast laser will travel with the electron beam through the new permanent-magnet wiggler at the ALS, thereby modulating the energy of a portion of the electron beam. The energy modulation results in a spatial separation of the modulated slice of the beam, which is only 200 femtoseconds long, so that it can be used to generate ultrafast x-ray pulses for experiments at photon energies from 100 eV to10 keV.

  High-pressure Facility Enables State-of-the-art Geophysics and Materials Research. At the newly commissioned ALS research facility, x-rays from a superconducting bend-magnet source, a high-efficiency micro-focused beamline, and a high-power laser-heated high-pressure cell (diamond anvil cell) will be used for a wide range of experiments, such as determining the high-pressure/high-temperature phase diagrams and equations of state of materials at pressures up to the Mbar range and at temperatures up to several thousand Kelvin.

  New Research on Solvated or Buried Systems Possible. Real-world materials that inhabit wet environments or are buried in the interior of more complex structures pose challenges to researchers. *In situ* electronic and structural properties of such materials are now accessible due to the high brightness of third-generation synchrotron radiation sources and the development of liquid-cell sample chambers. The technology developed at the ALS has already been demonstrated for the characterization of nanoparticles and opens the way for studies of advanced battery and hydrogen storage material.

  Fast Orbit Feedback Stabilizes Electron Beam Position. Today's synchrotron radiation instrumentation requires that the position of the illuminating x-ray beam be rock solid, which in turn imposes the same condition on the position of the electron beam. ALS scientists and engineers have commissioned a new feedback system (fast orbit feedback) that senses the beam position and sends signals to the control system to correct any vertical and horizontal position errors to within 2 μm and 3 μm, respectively.

- **The Advanced Photon Source (APS)**

  A New Technique for Understanding Materials under Extreme Conditions. Nuclear resonant inelastic x-ray scattering and extreme-brilliance x-ray beams are being used to measure, for the first time, the velocity of sound in tiny samples of materials under extreme conditions. The ability to obtain detailed information from minuscule amounts of materials under extreme conditions is critical to many experiments, from geophysics to national security.

  Taking the Heat from Higher-Brightness X-rays. Two new beamlines require two or three in-line undulators to achieve the required high photon intensity. To accommodate the expected higher APS storage ring beam current and concurrent heat loads that will be more than three times hotter than the surface of the sun, a novel insertion device front end has been developed.

  Powering Up to Higher X-ray Beam Brilliance. Radio frequency (rf) technology at the APS is one of several innovations laying the foundation for an eventual increase in storage ring current to 300 mA. This power exceeds the rf output power of all the TV and radio stations in a major U.S. city such as Washington, D.C., and will provide researchers with more brilliant x-ray beams.

  Glowing Results from a Unique Application of X-ray Fluorescence. The intense photon flux from an APS insertion device beamline has been used for the first application of x-ray-induced fluorescence techniques to perform in-situ measurements in high-pressure metal-halide arcs. These data, not obtainable in any other way, are essential to developing a clearer understanding of high-pressure arc systems, among the most energy-efficient sources of white light.

- **The National Synchrotron Light Source (NSLS)**

  Superconducting Undulator Test Facility Constructed. A state-of-the-art cryogenic Vertical Test Facility was designed and constructed for use in developing superconducting undulators (SCU). This device allows precise magnetic field mapping of superconducting undulator prototypes at cryogenic temperatures and measures thermal performance and quench behavior under realistic operating conditions, including simulated beam heating. A SCU design has been developed which incorporates a novel cryogenic thermal management system to intercept the high beam heat loads expected in future ultra-high brightness synchrotron light sources.

Hard X-ray Microprobe Completed for Environmental Sciences. A new hard x-ray microprobe beamline, X27A, will provide additional and enhanced x-ray micro-spectroscopy capabilities to the NSLS environmental science user community. The beamline can be operated in three different modes and can focus x-rays to a spot the size of a few microns. The detector array will enable both elemental mapping as well as fluorescence yield x-ray absorption spectroscopy studies of complex environmental samples.

Infrared Spectrometer Installed on Surface Science Beamline. Corrosion and catalysis involves the interaction between gas molecules and another material such as a metal surface. Infrared spectroscopy from metal surfaces is an important tool for studying the interactions with adsorbed molecules. A portion of the U4IR surface science beamline was re-built to incorporate a new infrared spectrometer. This new spectrometer provides improved spectral resolution, spectral range, and increased collection rates over the previous instrument.

X-ray Beamline Renovated for Materials Sciences. The X21 hybrid wiggler x-ray beamline and two experimental stations have been substantially rebuilt to accommodate new experimental programs that address elastic x-ray scattering studies of materials under high magnetic fields, thin films grown in-situ, and materials studied with small angle x-ray scattering, with appropriate setups permanently installed in the stations.

- **The Stanford Synchrotron Radiation Laboratory (SSRL)**

  SPEAR3 Project Completed. The four-year SPEAR3 Upgrade Project, jointly funded by the Department of Energy and the National Institutes of Health, was completed on time and within budget (SPEAR stands for the Stanford Positron Electron Accelerating Ring). The 3-GeV SPEAR3 light source produces x-ray beams having 1 to 2 orders of magnitude higher photon brightness than the SPEAR2 accelerator it replaced, enabling enhanced scientific capabilities comparable to those of other third generation light sources.

  SPEAR3 Commissioned and Operation for Users Commenced. The SPEAR3 storage ring was commissioned within a remarkably short time, beginning with equipment turn-on in mid-November 2003, and ending with the first 100-mA beam delivery to users in early March 2004. The speedy commissioning enabled the SSRL user program to begin again only 11 months after the SPEAR2 shutdown.

  First Diffraction Patterns are demonstrated with the SPPS. The first measurements of diffraction patterns from several prototypical samples were achieved at the sub-picosecond pulse source (SPPS). The first signals from the electro-optic pulse length and jitter experiment have been recorded yielding resolution limited pulse lengths of 1 picosecond. The preliminary jitter results indicate root-mean-square timing of the order of 250-300 femtoseconds.

  Source of Excessive Beam Emittance Found. Important progress in understanding the sources of excessive electron beam emittance from a photo-cathode gun has been made at the SSRL Gun Test Facility, setting the path for achieving the design goal for the Linac Coherent Light Source (LCLS) electron gun. The discovery indicates that a time dependent kick significantly increases the projected beam emittance. Eliminating the beam kick will enable operation of the high-charge gun with a sufficiently low emittance for x-ray Free Electron Laser operation at the LCLS.

- **The Intense Pulsed Neutron Source (IPNS)**

  IPNS Instruments Upgraded. The IPNS continues to make major instrument upgrades to maintain world class science capabilities for its users: 1) more than one half of the user instruments have migrated to a new data acquisition system that enables faster and more flexible data binning; 2) installation of neutron guides and frame definition choppers has boosted flux on sample for some instruments by 2-20 times; and 3) improved detectors and collimation and larger detector coverage have significantly reduced the time required to collect neutron data. Successful commissioning of a new IPNS target from recycled disks recovered from end-of-life targets has provided a cost effective alternative to the construction of entirely new IPNS targets and enables IPNS operations for an additional six years.

IPNS Hosts the National Neutron and X-Ray Scattering School. During the two-week period of August 15-29, 2004, Argonne National Laboratory again hosted the National School on Neutron and X-Ray Scattering. The school continues to attract outstanding graduate students and post-doctoral appointees with 134 applications for the 60 positions available in 2004.

- **The Manuel Lujan Jr. Neutron Scattering Center at the Los Alamos Neutron Science Center (LANSCE)**

  Goniometer Installed on Small-Angle Neutron Scattering Instrument. The goniometer is able to position the sample in the neutron beam with any orientation. Thus, it provides for a complete measurement of diffraction space, giving information on the crystal three-dimensional structure over large length scales from 1 to about 100 nm. Research problems that will benefit from this new capability include flux-lattice studies in superconductors, super lattice structures, and self-assembling colloidal structures.

  Spin Echo Spectrometry Demonstrated. This technique, achieved for the first time at a pulsed neutron source, has application to diffraction problems in nanoscale materials systems and was demonstrated on a dilute solution of 58 nm diameter polystyrene spheres in deuterium oxide.

  High-Intensity Powder Diffractometer (HIPD) Refurbished. The instrument is now fully operational for studies of atomic and magnetic structure of crystalline and noncrystalline powders, liquids, phase transitions, small samples, and absorbing materials. Due to its very high counting rates, time-resolved measurements are also possible as recently demonstrated in a diffraction study of the curing process of cement.

- **The High Flux Isotope Reactor (HFIR)**

  Operational Milestone Celebrated. On April 21, 2004, HFIR began its 400th operating cycle in its 38 year history. The length of an operating cycle depends on the time it takes for the reactor's uranium fuel to become depleted. A celebration marking this anniversary was held on May 15.

  Neutron Scattering Instruments Upgraded. The upgraded HFIR has state-of-the-art neutron scattering instruments that are among the world's best. In FY 2004, the HB-2B Residual Stress Diffractometer was brought into operation in the HFIR Beam Room. The HB-2D triple-axis monochromator shield was installed at the end of the HB-2 tunnel, and the Reflectometer and SNS Detector Station on this beam tube are operational. The WAND diffractometer, one of the instruments in the US-Japan International Collaboration, will also be operational, completing an important milestone in the HFIR Upgrade project.

  Cold Source Comprehensive Hazards Analysis Completed. One of the premier features of the HFIR upgrade will be the addition of an environment of super-cold liquid hydrogen. This environment literally chills the neutrons so they have less thermal energy with longer wavelengths, which make them valuable tools for the study of larger, more complex atomic and molecular structures. The HFIR Cold Source Comprehensive Hazards Analysis was completed and submitted to DOE in support of the October 4, 2004 milestone.

  Reactor Equipment Upgraded. New Instrument Air System compressors, dryers and receivers were installed in FY 2004. These components replace obsolete equipment and will simplify the system by reducing the number of valves in the system significantly.

- **The Combustion Research Facility (CRF)**

  Sample Preparation Laboratory Ready for Advanced Microscopy. A laboratory has been converted to a sample preparation space for the research activities in the Advanced Microscopy Laboratory. The new lab is equipped with instrumentation and supplies for preparing ultra-clean samples critical to single molecule imaging of biomolecules and nanomaterials.

  Optically Accessible Engine Facility Established. The facility’s new automotive-scale Homogeneous-Charge Compression-Ignition (HCCI) engine provides versatile optical access, accommodating the study of combustion via a laser-based investigation of in-cylinder processes. The facility is well suited for the examination of advanced fuel-air mixture preparation strategies that have been proposed as a way of achieving the strong potential of HCCI engines.

New Instrument Developed to Investigate Complex Reaction Processes. A new instrument consisting of an ion- and laser-beam surface analysis system coupled to time-of-flight and high-resolution Fourier Transform ion cyclotron resonance mass spectrometers has been built and tested. The instrument is used to investigate complex spatiotemporal reaction processes related to the aging of materials and biological processes at the cellular level.

New Laser Diagnostics Measure Diesel Particulate Emissions. Laser-induced incandescence (LII) and Laser-Induced Desorption with Elastic Laser Scattering (LIDELS) are new diagnostic techniques that provide previously unobtainable time-resolved measurements critical for the optimization of engine performance. Real-time measurements are particularly crucial for the development of regeneration strategies for lean NO_x catalysts and diesel particulate filters.

Selected FY 2003 Scientific Highlights/Accomplishments

Materials Sciences and Engineering Subprogram

- ***Towards an Exciton Condensate – A New Form of Matter.*** A Bose-Einstein condensate, a form of matter heretofore observed only in atoms chilled to less than a millionth of a degree above absolute zero, may now have been observed at temperatures in excess of one Kelvin in excitons, the bound pairs of electrons and holes that enable semiconductors to function as electronic devices. Researchers have observed excitons in a macroscopically ordered electronic state, indicating the formation of a condensate. The observations were made by shining laser light on specially designed nano-sized structures called quantum wells, which were grown at the interface between two semiconductors – gallium arsenide and aluminum gallium arsenide. These quantum wells allow electrons and electron holes (spaces in the crystal that are positively charged) to move freely through the two dimensions parallel to the quantum well plane, but not through the perpendicular dimension. Under photoluminescence, the macroscopically ordered exciton state appeared against a black background as a bright ring that had been fragmented into a chain of circular spots extending out to one millimeter in circumference. Just as the Nobel prize-winning creation of Bose-Einstein condensate atoms offered scientists a new look into the hidden world of quantum mechanics, so, too, will the creation of Bose-Einstein condensate excitons provide scientists with new possibilities for observing and manipulating quantum mechanical properties. The observation also holds potential for ultrafast digital logic elements and quantum computing devices.
- ***Magnetic Nanocomposites: The Next Little Thing.*** Magnetic materials are indispensable to a modern industrial society; however, it is no longer possible to squeeze significantly better performance out of today's most advanced magnets. A new approach is to create a composite material of two magnetic materials combined on the nanoscale to create a material with better performance than either taken separately. The boundary between the two magnetic materials is exceedingly important. Studies of bilayers of magnetically-hard and magnetically-soft magnetic materials have revealed that diffusion between the two materials alters the interface between them, resulting in improved magnetic properties. Theoretical modeling confirms that interfacial modification can enhance interlayer magnetic coupling. The results reveal the potential of careful interfacial control for improving magnets through manipulation of the material at the nanoscale.
- ***Tuning the Properties of Materials at the Nanoscale.*** As the size of silicon electronic devices shrinks toward the nanometer scale, the properties of the nanometer-thick silicon thin film in the devices depart from those of the bulk form of silicon. Nanostressors will be able to tune the properties of such thin films. For example, germanium islands grown on silicon act as nanostressors to shape the silicon film. The induced bending of the silicon film modifies the local electronic and optical properties of silicon. This ability to "tune" the properties of solid thin films is expected to become more prominent as semiconductor devices shrink to ever smaller scales.

- ***New Nanoscale Structures Form where Grain Boundaries Meet Surfaces.*** A newly discovered nanoscale "defect" may be connected to unusual behavior of metal catalysts and thin films, which are critical to the chemical and electronic industries. A distinct channel with a V-shaped cross section has been observed along the intersection of a grain boundary with an external surface. Atomic-resolution observations of gold surfaces in combination with atomic-scale simulations show that this channel has a different crystal structure than the remainder of the material. One implication is that when the grains become sufficiently small, these channel regions may dominate the surface and result in very different reactivity and catalytic activity than expected based on the bulk structure. These channel defects may also pin grain boundaries, slowing or preventing their motion and affecting the processing of thin films for microelectronics. Furthermore, the channels can be thought of as naturally occurring nanoscale wires along the surface of a material, whose arrangement could be controlled by appropriate processing.

- ***Imaging Single, Individual Molecules.*** By using a tightly focused beam of electrons less than a nanometer in diameter and by reconstructing images from the electron scattering data, the exact atomic positions in an individual carbon nanotube have been determined. Images of high resolution and high contrast can be obtained as has been shown by solving the structure of a single, double-walled carbon nanotube – a very complicated problem involving one tube nested in another. The technique has the potential to allow imaging of atomic arrangements in individual non-periodic structures such as biological macromolecules.

- ***Nanofluids Improve Heat Transfer.*** Suspensions of nanoscale metal particles or carbon nanotubes in fluids exhibit unusual enhancements in thermal conductivity. Picosecond measurements using laser techniques have been used to make the first quantitative measurements of heat transfer at the solid/fluid interface. Very large improvements for thermal conductivity are expected based on simple theory for carbon-nanotubes, but are not observed. The picosecond data shows that the thermal coupling between the nanotube and the surrounding matrix is weak, greatly impeding heat transfer in the carbon-nanotube composite. The results also indicate that the thermal conductance at the particle/fluid interface is highly sensitive to both structure and chemistry.

- ***Silicon: From Information Age to an Efficient Light Emitter****?* Silicon is the bedrock on which the information age is built, but it is a notoriously poor light emitter. The holy grail of silicon technology is to make silicon an efficient light emitter so that digital information can be converted to light for the ultimate transmission speed across optical fiber networks. New calculations have shown that a novel impurity superlattice structure of thin-layer oxide could do precisely that by altering silicon electronic charge characteristics to couple directly to light. This breakthrough opens the door so that the light-emitting efficiency of silicon could be drastically enhanced. This discovery will dramatically impact the microelectronics industry by significantly reducing the cost and complexity associated with the integration of optoelectronics into silicon-chip products.

- ***Synchrotron Light Sources Help Reveal Secrets of Welding****.* Welding is a critical metal joining technology used worldwide in the energy, automotive, aerospace, construction, and chemicals industries. Rapid cooling during welding induces numerous phase changes in the metal. Theories have been developed to describe this, but they have never been verified experimentally. Time-resolved x-ray diffraction using synchrotron radiation has now been used for the first time to monitor in-situ phase evolution of a multi-component steel weld during melting and subsequent solidification. The results show that equilibrium theories applied to rapid cooling conditions are not valid for steel welds containing fast diffusing (carbon) and slow diffusing (aluminum) atoms. This new ability to observe the competition of multi-component phases at the microstructural level will make it possible to design stronger and tougher welds, chemically tailored for optimum performance.

- ***Ultrathin, Laminar Films for Instantaneous Computer Boot-up.*** A new technique has been developed to deposit metal atoms onto thin oxide layers. This technique will help next-generation computers boot up instantly by making entire memories immediately available for use. The method anchors ultrathin metallic cobalt layers on sapphire by using a surface chemical reaction that overcomes an island formation problem that has long plagued researchers. The new, inexpensive trick to prevent island formation is as simple as exposing thin oxide films to water vapor before depositing the metal layer. The thin metal layer achieves crystallinity after the deposition of only a few atomic layers. This process should be applicable to a wide range of metals on metal oxides.

- ***Novel Synthesis of Shape-Controlled Nanostructures.*** Fabricating shape-controlled nanostructures such as nanowires and nanodots plays a central role in nanoscale science and technology. A novel electrodeposition process has been developed to self-assemble an array of nanostructures on flat surfaces. The new technique is based on the application of an electric field to ions on graphite substrates immersed in an aqueous solution. A large variety of voltage-controlled nanostructures have been grown such as cubes, pyramids, pentagons, hexagons, nanowires and snowflakes in superconductors and ferromagnets as well as in emerging application systems such as catalytic silver and hydrogen-sensing palladium. These unique nanostructures provide a new theater to explore shape effects on quantum confinement and present new opportunities for nanoelectronic applications.

- ***Biomolecular Route to Photovoltaic and Semiconductor Nanocrystals***. Biology exhibits a remarkable ability to control the nanostructures of materials, such as the exquisitely shaped microscopic shells of diatoms and radiolarians, with a precision that far exceeds the capability of present human engineering. Now, the biomolecular mechanism that directs the nanofabrication of silica in living organisms has been harnessed to direct the synthesis of photovoltaic and semiconductor nanocrystals of such materials as titanium dioxide, gallium oxide, and zinc oxide -- materials that biology has never used in structures before. Proteins from a marine sponge – and their counterparts produced from cloned, recombinant DNA – were used to catalyze and structurally direct the growth of the inorganic semiconductors at low temperature and under mild conditions, in marked contrast to the need for elevated temperatures and caustic chemicals presently required by conventional manufacturing methods. The nanocrystallites of gallium oxide formed in this process show a preferential alignment directed by the underlying proteins, revealing a template-like structure-directing activity of the biomolecules. Furthermore, the proteins working at low temperature produce and stabilize crystal forms of gallium oxide and titanium dioxide normally seen only at very high temperatures. Such biomolecular routes may lead to new, environmentally benign routes to semiconductor and photovoltaic materials with improved control over both nanostructure and performance, as well as improved interfaces between optoelectronic devices and living systems.

- ***The Impact of a Single Atom***. Never before has it been possible to identify single atoms within bulk materials and determine the influence of a single atom on its surroundings. Isolated atoms can significantly modify the physical properties of many of the technologically most relevant and scientifically interesting materials. While it has long been known that in semiconductors, for example, the presence of a single dopant atom among 10^{19} host elements drastically modifies the macroscopic properties, the possibility of identifying, localizing, and even measuring the electronic properties of single atoms becomes of fundamental importance in the nanotechnology era. We now have that capability. The aberration-corrected scanning transmission electron microscope allows not only the imaging of individual atoms inside a crystal, but their chemical identification. This remarkable improvement in sensitivity reaches the quantum limit of information, the ability to probe the electronic environment of a single atom.

- ***Molecular Cages under Pressure***. The isolation, removal, and entombment of radioactive waste are challenging scientific problems. Structural data from high-pressure x-ray powder diffraction has demonstrated that cage-like zeolites can potentially separate toxic waste from the environment. Using reversible superhydration -- the selective absorption of excess water under pressure into fully hydrated zeolites — the immobilization of commonly occurring radioisotopes such as ^{90}Sr, ^{137}Cs and ^{60}Co via a “trap-door mechanism” may be realized. By exchanging ions at high pressures, the holes of the zeolites will expand due to the excess water entering the zeolite cages. After pressure release these holes contract again, essentially closing the trap door and sealing the waste inside the zeolite for good.

- ***Biocompatible Lasers for Ultrasensitive Detection***. A highly sensitive quantum optics device using a biocompatible semiconductor laser microcavity has been devised that can analyze and characterize spore simulants. This device is 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 light squeezing enables even tiny spores to generate a very large signal which, when analyzed, yields critical biological information including the spore’s protein coat morphology, shape, intracellular granularity, protein density, and uniformity. This field-deployable biolaser should be able to identify different types of spores (for example, anthrax) within a large population of harmless spores rapidly and effectively.

- ***Electrocatalyst Design for Fuel Cells***. Electrocatalytic fuel cells at ambient temperature require materials with high catalytic activity and high tolerance to poisons such as carbon monoxide and sulfur. The use of alloys presents inherent limitations including a random distribution of the constituent elements and their propensity to segregate. The use of ordered intermetallics provides stable ordered phases. Based on studies of model systems, it is predicted that the ordered intermetallic bismuth-platinum (BiPt) should exhibit high catalytic activity and greatly reduced poisoning from carbon monoxide. These predictions, based on electronic and geometric effects, respectively, were borne out by experiments. BiPt catalyzes the oxidation of formic acid is a better material than pure platinum in some ways; moreover, it exhibits catalytic currents that are about 30 times those on platinum and is virtually immune to carbon monoxide poisoning. Although the focus has been on anode materials, this new design paradigm has clear implications in the design of cathodes as well as reformer catalysts and could usher a new era in fuel cell R&D.

Chemical Sciences, Geosciences, and Energy Biosciences Subprogram

- ***Emergence from the Primordial Soup***. Fifty years ago, Miller and Urey (Science, 1953) showed that simple inorganic molecules presumed present in the early earth atmosphere could yield amino acids after exposure to an electric discharge. Subsequent models of the chemical origin of life were complicated by the requirement to explain the asymmetric (chiral) nature of DNA and its components. Both of these elements are addressed in recent work using advanced mass spectrometric tools to study amino acid aggregation and reaction products in the gas phase. The simple amino acid serine is the commonly accepted product of formaldehyde and glycine, both known to exist in interstellar space. Using sonic-spray ionization with mass spectrometric detection, researchers have shown that certain, especially stable, clusters of serine are homochiral, that is, exclusively one of the possible symmetries. Furthermore, in reactions of the cluster with other important biological molecules, the asymmetry is passed on to the reaction products. These observations rationalize a model of prebiotic chemistry beginning with the assembly of homochiral serine octamers. Following selection of a particular homochiral cluster by an unknown asymmetric species, reactions with other biologically relevant molecules could pass on the asymmetry as further chemical reaction led to the formation of chiral, self replicating, life forms.

- ***Designer Solvents.*** Ionic liquids have already replaced volatile, polluting hydrocarbon solvents in some industrial processes, and progress is being made in using ionic liquids for inherently safe processing of nuclear fuel and radioactive waste. It is important to understand how chemical reaction patterns are influenced by the unusual environment of ionic liquids. New studies have explored fast reactions in ionic liquids by pulse radiolysis and have shown that charged species, such as a bare electron surrounded by solvent, move more slowly in ionic liquids in comparison to neutral species, just the opposite of what is seen in normal solvents. Also discovered was a reactive and highly mobile form of the electron that exists for only a few trillionths of a second in normal solvents but persists thousands of times longer in ionic liquids.

- ***Reactivity within Nanovessels.*** The elusive challenge of attaining chemical selectivity close to 100 percent for reactions in aqueous solution may eventually be achieved by mimicking Nature's most selective catalysts – enzymes. Researchers are attempting just that by synthesizing stable and semi-rigid inorganic cage structures that are able to sequester organometallic catalysts in their interior. By using the restrictive environment of the nanovessel cavity, they have shown reactant-selective organic transformations. As a dramatic demonstration of reactant selectivity, they have shown that these encapsulated complexes react with aldehydes with rates that depend on the size of the molecule, unlike the same complexes in solution, which cannot discriminate among aldehydes of different length.

- ***Fundamental Studies of Water.*** It is difficult to identify a quantity more fundamental to chemistry than the O–H bond dissociation energy of water. Its importance arises from its ubiquity, which ranges from elementary reactions to those in complex environments such as flame chemistry or atmosphere chemistry. A joint experimental/ theoretical study recently revised the value of this bond dissociation energy by a small amount. Although a relatively small change, the impact of this correction is enormous. It will cause changes in the gas-phase acidity of water, several proton affinities, all R-OH bond dissociation energies, reaction enthalpies of all OH reactions, and heats of formation computed relative to H_2O or OH bond dissociation energies.

- ***Storing Energy in Dendrimer Trees.*** Dendrimers are nanoscale molecules constructed from branches connected to a central core. If a dendrimer is built with an electron acceptor in the core and electron donors on the branches, the molecule can capture and temporarily store energy from light by moving electrons from the branches to the core. Further chemistry can then be used to capture the energy permanently before it is dissipated by electron transfer back to the branches. A dendrimeric system has been designed that functions as an electron antenna, absorbing several photons to create a core with a long lifetime. The stored energy can be lost if the electron returns to the "hole" it left behind. However, for dendrimers with branches long enough to allow their tips to touch, the holes are trapped on pairs of molecules at the tips, and the charge-separated state lasts for a long period of time.
- ***Coherent Surface Plasmons in Nanoscale Systems.*** One of the great promises of nanotechnology is the localization of phenomena on the nanoscale. Theoreticians have recently described the nanoscale analog of a laser in which coherent optical-frequency radiation fields are confined and amplified in nanosystems. They show that quantum generation of surface plasmons for a nanoscale v-shaped metal or semiconductor pattern can lead to stimulated emission and gain for certain highly localized plasmon modes. Such a device has been christened a SPASER, for Surface Plasmon Amplification by Stimulated Emission of Radiation. If realized, the SPASER has enormous potential applications in nanotechnology, including optical detection and information processing.
- ***Triple-Action Catalytic Polymerization.*** Catalysts that involve multiple functions working in concert at the molecular level offer dramatic advantages over single-function catalysts by reducing intermediate separation steps and achieving unusual reaction selectivity by controlling the competitive interplay of catalytic sites and the various molecular species present in the solution. Triple functions were synthesized on a complex catalytic compound that is active for ethylene polymerization. The terfunctional catalyst produces branched polyethylene with regular structures that cannot be obtained with a single catalyst or a pair of catalysts working in tandem. The extent and type of branching exhibited by the polymers, and therefore the chemical, mechanical, and optical properties of those materials, can be controlled by adjusting the ratios of the different functionalities.
- ***Multidimensional Chemical Analysis of Attomole Sample.*** Modern applications of chemical analysis, ranging from pollution studies to homeland security, increasingly require the ability to interrogate extremely small sample sizes. These mass-limited situations might arise because the sample is incredibly expensive, unusually toxic (biothreat agents), or inherently difficult to obtain in large quantities (intracellular signaling molecules). Conventional instrumentation is challenged, because their requirement for large sample volumes leads to extremely diluted samples. Researchers are developing solutions to this conundrum by exploiting the special electrokinetic flow properties of tiny cylindrical capillaries to create multilayer chemical instrumentation capable of addressing samples as small as 1,000,000 molecules and below. Because the capillaries are less than 100 nanometers in diameter, they can control fluid flow among layers of microchannels, thereby making it possible to sequentially link separate chemical manipulations. For example, scientists recently demonstrated the use of a nanocapillary molecular gate to detect and capture a 100 attomole (10^{-16} moles) band from a chip-based electrophoretic separation, establishing a new low for preparative chromatography of mass-limited samples.
- ***DNA Transport through a Single Carbon Nanotube.*** Carbon nanotubes have been proposed as useful media for a variety of applications such as hydrogen storage, chemical separation, and ultrasensitive sensors. A common research theme among these applications is the need to understand mass transport through such nanoporous materials. In a dramatic demonstration of its separations capability, a single, multiwalled carbon nanotube has been immobilized within an electrophoretic membrane test chamber and the passage of single DNA molecules has been monitored by fluorescence microscopy. Individual DNA molecules having a diameter smaller than the nanotube's opening were observed to readily pass through, whereas larger DNA molecules exhibited behavior consistent with trapping and hindered

passage. Because of the simple structure of the nanotubes, modeling can yield insight into the mass transport properties of its very small pores.

- ***Actinide Supramolecular Chemistry: Giant Rings for Heaviest Atoms***. Supramolecular chemistry is the controlled formation of large molecular aggregates from smaller subunits. The formation is controlled in order to achieve or optimize specific chemical properties. Actinide ions, the largest metal ions, have unique electrons configurations and represent materials that can be extremely useful or extremely dangerous. Supramolecular assemblies called helicates have been created where six thorium ions are encapsulated in a "box" (cluster) that self-assembles from eight smaller assemblies, which will now be investigated for their ability to remove toxic ions such as the actinides from the body.
- ***Targeted Recognition of Actinide Ions.*** Fundamental research on the selective complexation of specific ions of radioactive elements with disk-like complexants has led to simple and sensitive detection of these ions. Several classes of disk-like complexants create strong bonds between actinide ions, all of which are radioactive, and nitrogen atoms in the cages. These bonds cause transitions in electronic and vibrational spectra that result in visible color changes that occur only when specific actinide ions, in particular ions of neptunium and plutonium, are present. These colored complexes are important because of the changes they cause in electronic and vibrational structure and because they represent opportunities for detection of potentially hazardous radioactive ions that could be released into the environment – or to reassure first-line responders and the public that such species have not been released.
- ***Life Cycle of a Water Molecule on an Electrode.*** Technological progress towards a future hydrogen economy relies on understanding molecular-level phenomena governing conversion hydrogen formation at the electrodes in electrolyzers and fuel cells. Ruthenium dioxide is unsurpassed at enhancing catalytic activities in room-temperature fuel cell anodes, and it is a very promising electrocatalyst. Using synchrotron x-ray studies, fascinating sequential rearrangements of surface water molecules were discovered, evolving from a loose hydrogen-bonded water layer, to a hydroxide layer, and to a dense form of water, which exist on the ruthenium dioxide surface at different applied potentials. These interfacial forms of water may be the intermediates long suspected to be responsible for promoting oxidation of hydrogen and methanol in the fuel-cell environment as well as promoting the oxygen-evolution reaction. These previously unavailable molecular-level details of the energy-conversion processes provide scientific impetus for a more rational design of high performance electrocatalysts. This first-of-its-kind study was possible because of the unprecedented level of sensitivity afforded by the high brilliance of today's synchrotron radiation light sources.
- ***Identification and Structural Determination of a Novel Protein Motif.*** The protein machinery within a biological cell is manufactured via a complex assembly line that stretches from decoding DNA into RNA and translating the message into a polypeptide chain. Subsequent assembly into larger complexes and covalent linkage of the peptide chain with other carbohydrate or lipid components may also occur to provide additional chemical reactivity or specificity. The photosynthetic machinery that captures light energy and turns it into chemical energy is assembled in just such a fashion, with both large and small subunits of the carbon-fixing enzyme, Rubisco, undergoing methylation on lysine residues. A novel protein motif called the SET domain that carries out the methylation of Rubisco has been identified and its structure determined. The SET domain has been found in many other enzymes in a variety of biological contexts ranging from enzyme substrate recognition to scaffolding and stabilizing DNA. The common function of recognizing a molecular structure for subsequent covalent modification may lead to a common code for deciphering regulatory mechanisms of catalysis and molecular recognition.
- ***First measurement of how much energy is required to insert a single new protein into a chloroplast.*** The presence of internal organelles within the plant cell poses numerous challenges for the coordinated synthesis and trafficking of new proteins, which often must be synthesized in one part of the cell and directed to another sub-cellular compartment. The latter process necessitates the movement of the new protein across one or more membranes. Plant chloroplasts represent a unique opportunity to study the energetics of a mixed transport system that incorporates the cellular challenges of both eukaryotes and microbes. The energetic cost of this process is a fundamental unanswered question in plant biology, since the majority of photosynthetic apparatus proteins are continuously synthesized and imported into

the chloroplast, then rapidly degraded. DOE/BES support has led to the first measurement of how much energy is required to insert a single new protein—an astonishingly high proton flux that is equivalent to the energy stored within 10,000 ATP molecules! Thus approximately 3% of the total energy output of the chloroplast from photosynthesis is devoted to maintaining the photosynthetic machinery. This knowledge provides the foundation for future strategies for more efficient light-harvesting applications for renewable energy.

Selected FY 2003 Facility Accomplishments

- **The Advanced Light Source (ALS)**

  Record Low Vertical Emittance Demonstrated. The emittance is a key parameter that describes the circulating particle beam in a storage ring. Accelerator scientists have reduced the ALS vertical emittance to 5 picometer-radians during accelerator physics experiments. This is the lowest emittance value ever realized in any storage ring. While this emittance is a factor of 20 lower than the value normally used in ALS operation for users, it will be especially important for future spectroscopy studies in which the highest possible resolution is important.

  Femtosecond R&D Program Launched. The study of ultrafast dynamical processes on the time scale of fundamental processes, such as a molecular vibration, is one of the most active areas of modern science. An ALS R&D program was initiated that aims to produce ultrafast x-ray pulses by means of a technique known as electron-beam slicing. To generate x-rays from soft to hard x-ray energies with the maximum intensity the first, narrow-gap, in-vacuum undulator will be installed in the ALS.

  Beamline Devoted to Study of Soft X-Ray Coherent Science. Exploitation of the coherence of undulator light has not kept pace with that of other properties, such as brightness. To address this issue at the ALS, a branchline dedicated to coherence has been added to an existing undulator beamline that will produce microwatts of tunable coherent soft x rays. This new capability will allow users to carry out a wide range of experiments in both scattering and fundamental optics.

  Next-Generation Detector for Synchrotron Radiation Developed. The brightness of third-generation synchrotron radiation sources often generates huge signal rates that overwhelm the capabilities of existing detector systems. Often, the detector saturation problem both prevents the fullest utilization of the synchrotron light and limits the realization of certain new types of experiments. To overcome this bottleneck, the ALS has developed and successfully tested a high speed (more than 1 GHz), next-generation detector based on high-energy physics technology.

- **The Advanced Photon Source (APS)**

  A Bull's Eye for Storage Ring Beam Orbit Stability. Stable x-ray beams are critical for all users of x-ray facilities, particularly those users who microfocus x-rays onto small samples. X-ray beam-position monitors developed for the APS insertion device beamlines are providing beam stability that is now equivalent to firing a stream of bullets through the bull's eye of a target from several miles away.

  New Information from APS Could Lead to Improved Data Storage. A surface twisted magnetic state predicted 15 years ago has, for the first time, been confirmed using a new experimental technique at the Basic Energy Sciences-funded X-ray Operation and Research sector 4 at the APS. Twisted magnetic states of materials have important ramifications for applications in the development of improved magnetic memory.

  EPICS Collaboration Helps APS and the World. EPICS (Experimental Physics and Industrial Control System) software developed at two U.S. Department of Energy national laboratories is being used worldwide to control complex mechanical systems, from accelerators that reveal the nature of subatomic particles, to observatory telescopes that view distant galaxies, to industrial control processes such as semiconductor wafer manufacturing.

  Optics Capabilities at the APS Enable New Dynamical Studies of Liquids and Solids. Inelastic x-ray scattering (IXS) is a synchrotron x-ray tool that opens new vistas for the study of high-temperature materials. The x-ray optics capabilities of the APS have reached a level that makes possible implementation of an IXS spectrometer with exceptional resolving power.

A Breath of Fresh Air for Insect Physiology. A technique that couples phase-enhanced x-ray imaging to the intensity of APS x-ray beams has revealed a previously unknown insect breathing mechanism. Further development of this technique could have important implications for human health care and afford the potential for a wide variety of other materials-related applications, including detecting and studying cracks, voids, and other boundaries inside optically opaque structures; studying fluid flow in rocks and soils for oil exploration and recovery; and characterizing advanced materials, such as ceramics and fiber composites.

- **The National Synchrotron Light Source (NSLS)**

High Gain Harmonic Generation (HGHG) FEL Reaches Saturation in Ultraviolet. The NSLS is pioneering the development of laser seeded Free Electron Lasers (FEL). The HGHG FEL makes uses of a Ti-Sapphire seed laser to produce fully coherent 266 nm light. This marks the first HGHG FEL to successfully reach saturation in the ultraviolet regime and thereby obtaining sub picosecond pulses with energy in excess of 100 microjoules.

New Powder and Single Crystal Diffraction Beamline Completed. A new bending magnet beamline, X6B, has been completed. The beamline was constructed to meet the increasing demand of nanoscience users for powder and single crystal x-ray diffraction. The beamline consists of a Si(111) monochromator, tunable from 5 keV to 20 keV, and a double focusing mirror. The beamline is designed to perform (a) time-resolved powder diffraction, (b) combined x-ray spectroscopy and x-ray diffraction, (c) single crystal diffraction, and (d) measurement of electron density of excited states.

Superconducting Wiggler Beamline Upgraded. The X17 superconducting wiggler beamline is the only high-energy x-ray insertion device at the NSLS. It serves a large and very productive earth science and high-pressure users community. In FY 2003, two new experimental hutches were constructed so that a materials science instrument, a large volume press instrument and a diamond anvil cell instrument will each have a dedicated experimental hutch. All three programs will be able to operate simultaneously, thus significantly increasing the amount of beam time available to these user communities.

Low-Energy X-Ray Beamline Upgraded. The low-energy x-ray region is important because it covers the K absorption edges of Si, S, P, Cl, and L edges of 4d transition metals. X-ray spectroscopy and x-ray resonant scattering in this energy range are valuable tools in catalysis, environmental science, magnetism and bio-materials. A new monochromator was designed and installed in FY 2003 to improve the cooling of the monochromator crystals in X19A beamline. The new design has led to better energy and intensity stability of the beamline.

- **The Stanford Synchrotron Radiation Laboratory (SSRL)**

First Beam from the Sub-Picosecond Pulse Source (SPPS) is Achieved. Ultrafast pulses of x-rays are key tools for probing the electronic and structural changes in materials during fast chemical reactions and phase changes. To this end, the SPPS was installed in the SLAC Final Focus Test Beam Facility, which generates pulses of 8-10 keV x-rays with 10^7 photons/pulse at a pulse rate of 10 pulses per second. The peak brightness of these x-ray pulses exceeds that of any existing x-ray source. The SPPS is planned to operate 3-4 months per year through 2005, when it will be displaced by the construction of the Linac Coherent Light Source, a much more intense source of short x-ray pulses.

SSRL's Final Run with SPEAR2 Ends on a Perfect Note. SSRL's most recent experimental run prior to the decommissioning of SPEAR2 ended very successfully with SPEAR delivery of scheduled beam time to users at the 100% mark during the last week of operations. Even though the FY2003 run was shortened by about 4 months due to the beginning of the SPEAR3 installation, a total of 813 users came to SSRL during the run to conduct experiments on 32 stations. The up time average for the entire FY2003 run was 96.8%.

SPEAR3 Installation Program Proceeding on Schedule. The SPEAR3 Installation Program began on schedule on March 31, 2003. The Installation Program involves three phases: demolition of SPEAR2, modification of the facilities to meet SPEAR3 needs, and finally the actual installation of SPEAR3 technical systems and components. Each phase is a complex procedure that is planned in great detail with overall completion by the end of October 2003.

New Experimental Station Developed on BL11. A new experimental station that will be used for both materials scattering and macromolecular crystallography has been commissioned on BL11. This new station will help relieve the significant over subscription on BL7-2 for users performing x-ray structural studies of thin films as well as provide for single- or multi-wavelength anomalous dispersion (SAD and MAD) experiments to be carried out at the Se edge for macromolecular crystallography applications.

- **The Intense Pulsed Neutron Source (IPNS)**

  Upgrades of IPNS Instruments Continue. IPNS continues to make major instrument upgrades and source improvements to maintain world class science capabilities for U.S. users: 1) an upgrade project for a powder diffractometer, GPPD, has been completed putting the instrument on a par with the fastest powder instruments in the world; 2) installation of a guide on QENS, a quasi-elastic spectrometer boosted flux on sample by a factor of five; 3) redesigning the moderator/reflector assembly resulted in a gain of 60% neutrons-on-sample for small angle scattering applications.

  Outstanding Operations at IPNS Continues. For the sixth consecutive year, the IPNS has exceeded its goal of offering at least 95% reliable operations, achieving a figure of 97% in FY 2002. This reliability assures users that experiments can be performed as planned and offers additional evidence that pulsed neutron sources can be run in a reliable manner.

  IPNS Hosts the National Neutron and X-Ray Scattering School. During the two-week period of August 10-24, 2003, Argonne National Laboratory again hosted the National School on Neutron and X-Ray Scattering. The school continues to attract outstanding graduate students and post-doctoral appointees with 143 applications for the 60 positions available in 2003.

- **The Manuel Lujan Jr. Neutron Scattering Center at the Los Alamos Neutron Science Center (LANSCE)**

  First Results with the 11-T Magnet at Lujan Center. The newly commissioned 11-T superconducting magnet provided Lujan Center users with the first results of an intensity image (reflection) of neutron data collected from an antiferromagnetic material on the new Asterix instrument. Significantly, the mass of material contributing to the reflection is only about 100 micrograms. Moreover, exceedingly good thermal stability was achieved during the measurements.

  Upgraded NPDF Produces 300 Data Sets. The Neutron Powder Diffractometer (NPDF) opened its shutter for the first time and produced over 300 experimental data sets during the run cycle. Promising results obtained during the run cycle not only put NPDF at the cutting edge of local-structure determination but also served as a development platform for a new structure-analysis tool based on pair-distribution functions in disordered and nanostructured materials.

  Upgrades to SPEAR Improve Reflectivity Measurements. Upgrades to SPEAR have simplified the operation of the instrument and provided more precise and reproducible reflectivity measurements. SPEAR is a time-of-flight neutron spectrometer ideally suited to study thin organic and inorganic layers in a variety of environments. A recent experiment on SPEAR provided fundamental information about the stability of model biomembranes in the presence of large electric fields.

  Upgrades to LQD Enables More Sophisticated Small-Angle Scattering Experiments. Small-angle scattering has been improved at the Lujan Center to keep apace with the significantly increased cold-neutron flux available to LQD (Low-Q Diffractometer), which has been increased by approximately a factor of five. These upgrades will allow more measurements, higher-quality data, and the ability to perform more sophisticated experiments.

- **The High Flux Isotope Reactor (HFIR)**

  World-Class Triple-Axis Spectrometers Installed at HFIR. These spectrometers, designated HB-1, HB-1A, and HB-3, are exceeding performance goals and are equal to the highest intensity instruments of their kind in the world. The installation of three additional world-class instruments is under way at the HB-2 shielding tunnel, which was completed in March 2003. The first of the new instruments should be available in early fall 2003 with the other two to follow by the end of 2003.

Shield Tunnel Installed for the HFIR HB-2 Neutron Beam. The tunnel extends the neutron beam into the beam room and provides full neutron beam access to four instruments with individual instrument shutters. Installation of the instruments will result in a significant increase in the number of experiments that can be performed using the HB-2 neutron beam.

Construction of the Small Angle Neutron Scattering (SANS) Guide Hall Completed. The high bay guide hall will house the new 40m and 35m SANS instruments and supporting lab space. It will provide a research environment away from the reactor building that will be used by numerous facility users for physical and biological material studies.

- **The Combustion Research Facility (CRF)**

  New Capability Developed for Three-Dimensional Measurements in Turbulent Flames. Lasers and digital camera systems for imaging of laser-induced fluorescence in two intersecting planes were added to existing systems for line-imaging measurements of temperature and major species in turbulent flames. The combination yields information on the magnitude and effects of three-dimensional scalar dissipation, which is a central quantity in combustion theory and modeling.

  Station Established to Generate Periodically Poled Lithium Niobate (PPLN). A station has been designed and built to pole lithium niobate at the CRF. PPLN is a quasi-phase-matched crystal that is significantly more efficient and tunable than conventional crystals. Recent major advances in nonlinear optical materials have opened up many new possibilities for chemical sensing. In particular, the development of PPLN has sparked the advent of broadly tunable, compact, highly efficient infrared laser sources. This technology could be applied to problems such as medical monitoring or transient molecule detection.

Selected FY 2002 Scientific Highlights/Accomplishments

Materials Sciences and Engineering Subprogram

- ***Giant Magnetoresistance (GMR).*** GMR is revolutionizing the magnetic recording and data storage industry by enabling major increases in data density and ease of read/write processes. GMR is the term applied to layered magnetic systems that undergo very large changes in resistance in the presence of a magnetic field. The origin of GMR and its relationship to layered structure is unknown. New experiments in which the GMR is measured with current flowing perpendicular to the layer interfaces have yielded insight into the factors underlying the effect. Measurements of the GMR in samples with quantitatively determined interfacial structure, characterized by microscopy and x-ray scattering, have shown a direct relationship between the GMR and the interfacial roughness. Since most GMR-based devices rely on the magnitude of the effect, these results provide guidance for their optimization by interfacial roughness tailoring.

- ***Multifunctional Materials.*** For the first time, organic materials that exhibit bistability simultaneously in three channels – magnetic, optical, and electrical – have been produced. The new materials have many interesting properties. In one state, they are paramagnetic (attracted to a magnetic field), infrared transparent, and electrically insulating; in the other state, they are diamagnetic (repelled by both poles of a magnet), infrared opaque, and electrically conducting. The switching between the two states is thermally driven, and a switching temperature just above technologically useful room temperature has been achieved. These multifunctional materials have the potential for use in new types of devices for electronics, computers, and data storage where multiple channels are used for reading, writing, and transferring information.

- ***Transparent Electronic Devices.*** Rather than ordinary glass, imagine that your window panes at home are a multi-functional wide band-gap semiconductor device that might serve as: an energy generator, a microprocessor, a detector, and a light modulator. The potential of wide-gap semiconductors is enormous, ranging from highly efficient solid-state light sources and high-density data storage to invisible monitoring devices for national security. The key in making this dream a reality is to be able to dope these materials with impurities to achieve both the n- and p-type mechanisms of electrical conduction. Achieving p-type doping had been an insurmountable problem. The root cause was found to be twofold: the spontaneous formation of native defects and the low-dopant solubility. Suppression of the defect formation was achieved by chemical design of the band structure of the semiconductor oxides. This approach has led to a family of new p-type transparent conducting materials. These studies have facilitated the experimental exploration of transparent electronic device materials.

- ***World's Smallest Ultraviolet Nanolasers.*** The world's smallest ultraviolet-emitting lasers, based on "nanowires" of zinc oxide, have a broad range of potential applications in fields ranging from photonics – the use of light for superfast data processing and transmission – to the so-called "lab on a chip" technology in which a microchip equipped with nano-sized light sources and sensors performs instant and detailed analyses for chemistry, biology, and medical studies. The nanolasers were fabricated using a new processing method that can grow arrays of zinc oxide nanowires between 70 and 100 nm in diameter with adjustable lengths between 2 and 10 microns. This development continues the progress in semiconductor laser research, providing new materials that extend the availability of these versatile and inexpensive light sources from the near infrared and red regions of the spectrum into the green-blue and near ultraviolet.

- ***Nanotubes Increase Heat Conduction in Fluids.*** Fluids containing 1 percent carbon nanotubes in oil exhibit a 250 percent increase in heat conduction. This addition of nanotubes resulted in the highest thermal conductivity enhancement ever achieved in a liquid – ten times higher than predicted by existing theories. This has required the development of new heat conduction models for solid/liquid suspensions. This research could lead to a major breakthrough in solid/liquid composites for numerous engineering applications, such as coolants for automobiles, air conditioning, and supercomputers.

- ***Molecular Based Spintronic Material.*** For years scientists have dreamed of separately controlling the spin and charge of the electron to create "spin electronics" or spintronics for next generation electronic devices. We have advanced one step closer to this goal with the fabrication of a new molecular solid integrating alternate layers of spin networks with organic metal networks through crystal engineering. The close proximity of the spin to the metal – less than one nanometer apart – promises strong communication of spin and charge while allowing each to be manipulated separately. The new material is made by relatively inexpensively using bottom-up self-assembly as opposed to the elaborate and expensive top-down lithography for other semiconductor materials.

- ***Deformation at the Nanoscale.*** Large-scale atomic-level simulations reveal how and why conventional dislocation deformation processes in materials break down at the nanoscale. Nanostructures can experience very high internal stress levels; thus, mechanical stability and compliance represent major obstacles in the development of nanodevices. The computer simulations demonstrated that, as the grain size becomes ever smaller, a material becomes harder to deform. However, at a critical size, dislocations no longer can exist, because they are comparable to that of the grains themselves, and the material suddenly softens again due to the onset of novel deformation mechanisms mediated by the grain boundaries that contain the grains. This "strongest size" was shown to be a function of not only the material itself but also the stress level to which it is subjected. These insights will enable the design of nanodevices with tailored mechanical performance, capable of withstanding the very high stresses under which they often operate.

- ***Nano-onions.*** Carbon "nano-onions," generated by carbon-arc discharge in deionized water, are the latest entry in the fullerene family. Their structures resemble onions, with a fullerene at the core, surrounded by multiple layers of fullerene-like carbon. The arc method produces "nano-onions" with diameters from about 10 to 150 nm. These "Buckyonions" are easily fractionated on the basis of diameter by using flow field-flow fractionation, with small particles eluting before larger ones. Characterization of these "nano-onions" using electron microscopy and light scattering methods could lead to new and novel applications for these materials.

- ***A Trillion Elements per Square Inch.*** Magnetic storage arrays with more than a trillion elements per square inch, ultrahigh resolution field emission displays, and high resolution, on-chip macromolecular separations devices have been constructed using a new, patented technique of self-assembly of polymers. By means of routine chemical etching processes, large area arrays of nanopores (4-50 nm in diameter) with very high aspect ratios are produced in a simple, robust manner. These serve as templates for pattern transfer to substrates and as scaffolds to direct surface chemistry or electrochemical deposition of metals for the generation of ultrahigh density, multilayered nanowire arrays. The simplicity of this technique has a broad impact across many disciplines ranging from bioactivity to semiconductor devices.

- ***Molecules of Gases and Water Swim Upstream.*** A theoretical analysis has shown that molecules of hydrogen, oxygen, and even water can travel across conducting membranes in opposite directions from what would normally be expected. An understanding of these membranes is important in the development of advanced materials systems for energy storage such as fuel cells. The analysis pertains to a class of materials called perovskites that can, under some circumstances, conduct charge via both individual electrons and ionized atoms of hydrogen and oxygen. Individual chemical species can move in the "wrong" direction from areas where they are at a lower concentration to areas of higher concentration. This is normally explained by other driving forces that are taken into account in a quantity referred to as the chemical potential. In mixed-conducting membranes, however, the new analysis shows that neutral (uncharged) molecules can even move contrary to the gradient in the chemical potential as a result of the simultaneous, coupled transport of multiple species.

- ***Ultra-Sensitive Sensors.*** A new principle for chemical sensors with ultra-high sensitivity has been developed and successfully demonstrated based on computer simulations of the structure and properties of particle composites. These sensors are fabricated by dispersing electrically conducting magnetic particles into an insulating liquid, then organizing the particles into chains with a magnetic field while the liquid solidifies by polymerization. These materials are referred to as Field-Structured Composites. The particle chains conduct electricity quite well. When exposed to certain chemical vapors, the polymer absorbs the chemicals and swells. The chains are stretched ever so slightly to create gaps between the particles, resulting in conductivity decreases of ten billion or more. The unprecedented magnitude of this effect makes these materials sensitive to even trace amounts of vapors. Inexpensive, portable devices for chemical identification can be achieved by making an array of sensors, each of which is fabricated with a polymer having unique chemical affinities, so that any single vapor leaves an identifying signature on the array.

- ***New Analysis Method Enables Prediction of Dendritic Pattern Formation.*** Just as water freezes into the elaborate patterns of snowflakes, so do metals form highly branched patterns called dendrites. These dendrites control many aspects of the processing and microstructure that determine alloy properties and hence our ability to use materials. Dendrite patterns are controlled by minute variations of the interface between the material and its melt. While simulations have modeled the atomic processes that occur during solidification, they have proven inadequate to extract the more subtle information about the anisotropy. An entirely new method to extract the anisotropy of energy and mobility from supercomputer simulations has been devised. The critical step was the identification of a related quantity that can be calculated with sufficient precision and then used to simulate dendritic growth. Additional supercomputer simulations have exploited this new information to predict the precise nature of dendritic pattern formation in a range of materials from silicon to nickel.

- ***Superconductors Show Their Stripes.*** Like tigers and zebras, superconductors are distinguished by their stripes. Some physicists believe that electricity runs without resistance along “stripes” of electric charge in these materials. Stripes have now been observed for the first time the most widely studied of the cuprate high-temperature superconductors. The material consists of planes of copper and oxygen atoms located in a square pattern. Some of the electrons are missing in these planes leaving positively charged holes that pair together to produce superconductivity. In a standard superconductor, these pairs travel through the material without hindrance producing the perfect conductivity inherent to a superconductor. However, in the cuprate materials, the copper atoms have a magnetic moment that makes conductivity in the planes difficult. Recent neutron scattering measurements made at the High Flux Isotope Reactor show that the holes form lines or stripes in the superconductor in which there are no magnetic moments. The holes can thus move along the stripe in an unimpeded manner.

- ***Neutron Instrumentation for Nanoscience.*** Nanoscience requires the study of structures ranging from a few nanometers to a few microns. A new neutron scattering technique for study of materials in this size range has been developed. The method uses the fact that the spin of the neutron has unique behavior in a magnetic field -- the spin precesses like a top in a magnetic field so that the total rotation angle of the spin depends on the time the neutron spends in the magnetic field. By appropriately designing the magnetic fields, the rotation angle can be made to depend on the direction of travel of the neutron with respect to some fixed spatial direction, effectively "coding" the trajectory angle into the value of the neutrons spin. This technique can easily be implemented and could be perfected in time to impact early measurements at the Spallation Neutron Source.

Chemical Sciences, Geosciences, and Energy Biosciences Subprogram

- ***Catalytic Chemistry of Gold Nanoparticles***. Gold spheres of 2.7 nm diameter supported on titanium oxide are able to oxidize carbon monoxide, and spheres of 2.4 nm diameter are able to activate oxygen from air and insert it into propene readily and very selectively. Yet bulk gold metal is inert, and particles of slightly smaller or larger diameter than those cited are also unreactive or unselective. Using a variety of spectroscopic and chemisorption techniques, atomic-resolution microscopy, and theoretical electronic structure calculations, it was shown that decreasing metal particle size provokes changes in the electronic structures of gold and titanium oxide such that the particles are able to acquire a partial charge. Those variations are shown to decrease the binding energy of gold on titanium oxide (and thus alter the morphology of the clusters), as well as increase the binding energy of reactants such as oxygen, carbon monoxide, and propene to gold. The results explain why gold clusters are active and selective oxidation catalysts and provide a semiquantitative framework to predict catalytic reactivity on the basis of electronic structure of metal clusters.

- ***New Nanoporous Catalysts Developed.*** Nanocrystalline materials possess unique properties and offer great promise for promoting selected physical and chemical processes. Crystalline films of magnesium oxide that consist of tilted arrays of filaments attached to a flat substrate have been synthesized by impinging a magnesium atom beam in an oxygen background toward a surface off-normal by 70° to 85°. The individual filaments are thermally stable, highly ordered and porous, and contain enormous numbers of binding sites in comparison to a magnesium oxide flat surface deposited on a substrate. The high surface area (~1,000 m^2/g) and high density of binding sites potentially render these nanoporous materials extraordinary catalysts.

- ***Multidimensional Catalyst Arrays***. Studies of the affects of particle spacing on the reactivity of catalysts has been hampered by the inability to produce uniform nanoparticles that are regularly distributed in a supporting matrix. Recent work shows that two- and three-dimensional arrays of platinum nanoparticles are achievable. Two-dimensional arrays of platinum supported on 4-inch silicon wafers were produced using electron beam lithography and spacer photolithography. The latter technique permits variation of particle size from 600 nm to 10 nm. More recently, three-dimensional arrays of 2-5 nm platinum nanoparticles of vary narrow size distribution were prepared, and the resulting x-ray and electron diffraction patterns are typical of crystallinity, hence regularity. The results significantly enhance enable the production of designer catalysts and will answer fundamental questions in catalysis.

- ***Nanostructured Anodes***. There is considerable interest in tin/lithium anodes for high-energy electrochemical storage systems because, in principle, they can deliver substantially more storage capacity than carbon based lithium ion batteries. However, the tin-based anode functions by reversibly alloying lithium into the tin, and a very large volume expansion occurs when lithium is alloyed (as much as 300 percent). As a result, the tin based anode system typically has poor cycle life because the volume expansion and contraction during cycling causes the anode to self-destruct. New research has shown that nanostructured tin/lithium anodes prepared via a membrane template method do not suffer from this loss of cycle life, even after 1,400 charge discharge cycles. The nanostructured electrode gives good cycle life because the absolute volume change for a nanofiber is correspondingly small and because the brush like configuration of nanofibers provides room to accommodate the volume expansion.

- ***Nanometer-Scale Faceting of Metals, a Means to Control Reactivity.*** Bimetallic catalysts are providing new insights into chemical reactivity. Upon annealing at elevated temperatures, the atomically rough, "unstable" surfaces were observed to undergo massive reconstruction at the nanometer scale, in some instances leading to the formation of surface alloys. These structural rearrangements were accompanied by corresponding changes in electronic structure, morphology, and catalytic activity. Time-dependent, atomically resolved images allowed the measurement of the rate of facet growth and of their reconstruction in the presence of adsorbates such as sulfur and oxygen. Catalytic activity was found to dramatically depend on the composition, structure, size, and shape of the facets exposed under reaction conditions.

- ***Organic Semiconductors.*** Molecular and polymeric semiconductors are very important organic compounds that have the potential to replace inorganic semiconductors for applications in photoelectrochemical and photovoltaic cells for solar energy conversion of sunlight to electricity and solar fuels (hydrogen, methane, and alcohols). Photoconversion devices based on organic semiconductors could be much less expensive and easier to produce and process because of the present vast technology available for polymer and molecular processing into continuous thin films and sheets. Doping the molecular semiconductors to produce the required n-type and p-type electrical conductivity to create p-n junctions has been problematic as the dopant has not become part of the molecular or atomic structure of the compound. Recently, scientists successfully doped molecular semiconductors and increased the conductivity by five orders of magnitude.

- ***Long-Lived Charge Separation in a Novel Artificial Photosynthetic Reaction Center***. Fullerenes and porphyrins have molecular architectures that are ideally suited for photochemical conversion and storage of solar energy. Their use as three-dimensional electron acceptors holds great promise because of their small reorganization energy in electron transfer reactions that can significantly improve light-induced charge-separation processes. Recent research indicated a 24 percent efficient charge-separation within a molecular tetrad. In this linear array, a light harvesting antenna assembly composed of two porphyrins and a fullerene-ferrocene photosynthetic reaction-center mimic were integrated into a single molecule. The 380 millisecond lifetime of the spatially-separated and high energy radical pair, a product of sequential short-range energy and electron transfer reactions, enters a time domain that has never been achieved in an artificial reaction center.

- ***New Technique for Detection of Impact Ionization in Semiconductors***. The thermodynamic conversion efficiency with which solar radiant energy can be converted to electricity or to stored chemical energy in solar-derived fuels is limited by the energy loss of high energy electrons and positive holes created by the absorption of high energy solar photons in the photoconversion device. The thermodynamic efficiency limit can be more than doubled if the high energy photons can be used to create additional photogenerated current through a process called impact ionization. For the first time, scientists have demonstrated a contactless, optical method to detect impact ionization in semiconductors useful for solar photoconversion. The method is based on femtosecond time-resolved visible pump-infrared probe spectroscopy, and can be used to study impact ionization in colloidal semiconductor quantum dots where electrical contact to the colloidal particles is not possible. Impact ionization in semiconductor quantum dots is expected to be greatly enhanced.

- ***Gas-Phase Chemistry of Actinide Ions.*** The studies of gas-phase reactions of ions provide important insights into fundamental chemistry. Such studies have previously been limited to transition metal ions and to thorium and uranium in the actinide series; however, recent work has expanded this approach to the radioactive actinides, which cannot easily be studied by conventional techniques. One type of reaction that has been particularly enlightening involves the metal- or metal-oxide-catalyzed removal of hydrogen from alkene hydrocarbons. In these alkene dehydrogenation reactions, the neptunium ion is highly reactive, the plutonium ion is significantly less reactive, and the americium ion is essentially unreactive. This provides clear evidence that the 5f electrons of the actinides beyond neptunium are inert in these organometallic reactions. Results for the actinide oxide ions have also been illuminating, revealing a decrease in reactivity between uranium oxide ions and heavier actinide-oxide ions. The role of 5f electrons in bonding is central issue in contemporary actinide science, and these results provide experimental evidence for a change in the bonding nature of the actinide 5f electrons in molecular compounds, ranging from being chemically active for the early members of the series to being inert for the actinides beyond neptunium.

- ***Lattice Disorder and f-electrons: Evidence For a New State of Matter.*** An important question is the nature of the non-superconducting high-temperature superconducting (HTSC) ground state from which superconductivity arises. Intermetallic alloys containing *f*-electron elements, in which superconductivity is absent or is easily suppressed, allow one to explore this question. Like HTSCs, *f*-electron intermetallic alloys often behave as "non-Fermi liquids" (NFL), so named because they are not consistent with Fermi liquid theory, which, until recently, has been the basis for explaining the properties of metals. Of specific interest is how the atoms surrounding an *f*-electron atom, and how disorder in their arrangement, affect magnetic and conducting properties. A recent study of these arrangements in the NFL compound UCu_4Pd showed that significant lattice disorder exists. Although such disorder can produce NFL behavior within a Fermi liquid model, the study showed that there is insufficient disorder for the model to match the measured magnetic and conductivity data. That is, the system acts as though it is more disordered than it actually is. These results strongly imply that lattice disorder precipitates NFL behavior in this material, perhaps by amplifying the effect of the disorder, and thereby the possibility of a new type of metallic ground state.

- ***Cellulose Biosynthesis.*** The detection and isolation of cellulose synthase genes is driving new efforts to understand how cellulose acquires its structural characteristics in hopes of eventually devising methods of tailoring these characteristics to facilitate its use as a renewable resource. Scientists have provided a key piece of information in the biochemical dissection of the three steps of cellulose synthesis: 1) initiation of the sugar chain; 2) adding sugars to the growing chain; and 3) stopping the process at a predetermined length. A single copy of a cellulose synthase gene was introduced into yeast cells that do not normally make cellulose. The result was the formation of a specific lipid-sugar compound that serves as a primer for subsequent chain growth. Understanding the critical steps in the synthesis of cellulose, the most abundant biomolecule, will lead to understanding the function of plant cell walls and to engineering modified renewable resources.

- ***Boron in Plant Cell Walls.*** Research has confirmed the role of the element boron in the growth and development of plant cell walls. Over 90 percent of a plant's boron is associated with the cell wall, and boron deficiency leads to stunted plants with malformed and brittle leaves. Arabidopsis thaliana mutants with a small change in the structure of a major type of cell wall carbohydrate show the same characteristics but can be rescued by feeding with excess borate. This defect was shown to reduce the plant's ability to bind the borate that is needed to form and stabilize the cross-linked cell wall. Future mechanistic studies relating borate-carbohydrate crosslinking to physiological growth could lead to improved strategies for the development and production of renewable biomass resources.

- ***Naturally Occurring Organochlorine Compounds***. Organochlorine molecules are commonly observed in natural soils and have been attributed to pollution from manmade sources. Natural organic matter, such as humic and fulvic acid, in the shallow subsurface is both universal and little understood. It has no fixed stoichiometry or structure, cannot be crystallized, and is famously difficult to characterize reproducibly. Synchrotron x-ray spectroscopy has been used to document changes in the chemical state of chlorine in humic materials. This research confirmed the startling conclusion that natural organochlorine compounds are common in soil and that there is a net transfer of chlorine from inorganic to organic forms with common weathering. Abundant catalytic peroxidase facilitates the chlorination of natural aromatic organics. These results add strong support to the hypothesis that chlorination of organic compounds in humic materials is widespread, and may explain the puzzling organochlorine concentrations found in otherwise unpolluted environments. Accurately understanding natural conditions is critical in identifying and taking action to correct man-made problems.

- ***Quantum Degenerate Fermi Gases***. A new theoretical formulation predicts an unusually high critical temperature for the onset of superfluidity in a gas of fermionic potassium atoms. This new form of quantum matter, which lies between high-temperature superconductors and systems that undergo Bose-Einstein condensation should soon be achievable experimentally using optical traps. The ultimate goal of these experiments is to achieve Cooper pairing, in which pairs of fermionic atoms "condense" and occupy the lowest quantum states available to the ensemble of trapped atoms. Such an accomplishment would permit studies of the underlying mechanism of superconductivity.

Selected FY 2002 Facility Accomplishments

- **The Advanced Light Source**

  Superbend Magnets Extend Synchrotron Spectral Range. Originally designed for highest brightness at longer x-ray wavelengths (soft x rays), the ALS has been retrofitted with superconducting bend magnets (superbends) that dramatically boost the synchrotron radiation intensity at shorter x-ray wavelengths (hard x rays) without disrupting the soft x-ray performance of the existing beamlines, thereby allowing the ALS to service a broader user community.

  Higher-Order-Mode Dampers Increase Storage Ring Stability. The beam in the ALS storage ring comprises more than 300 discrete "bunches" of electrons spaced more or less equally around the ring, but interactions between the bunches can cause the beam to become unstable. Addition of antennae to the radio-frequency (RF) cavities that power the storage ring has substantially improved the reliability of the feedback system that combats beam instabilities.

  A New Radio-Frequency (RF) Feedback Loop Saves Electrical Power and Money. Driven by the soaring costs that came with the California energy crisis, staff at the ALS found a way to reduce the electricity bill an estimated 11% by implementing a feedback loop that reduced power consumption by a klystron power amplifier without interfering with other RF-cavity controls.

  Beamline for Ultrahigh-Resolution Chemical Crystallography Commissioned. Based on a novel miniaturized design that is low-cost yet robust and high-performance, the ALS has put into operation a new beamline that meets the demands of chemists for a tool to rapidly determine the atomic structure of molecules with sub-angstrom resolution from solid samples (crystals) as small as a few micrometers on a side.

  An Experimental Station Has Been Designed to Study Magnetic Nanostructures. Consisting of multiple layers of magnetic and nonmagnetic materials, each only a few atoms thick, magnetic nanostructures are the foundation for advanced magnetic devices. The new station at the ALS will allow complete magnetic characterization of each layer separately with x rays that are polarized in any desired orientation.

- **The Advanced Photon Source**

  Operating in Top-up Mode. One of the principal operational goals has been to run the storage ring in the "constant current" or top-up mode. Top-up mode consists of injecting a small amount of charge into the storage ring at regular intervals in order to maintain a 100 mA current. The major benefit of top-up operation is the virtual elimination of the beam lifetime (the decay of beam current over time) as a factor in further improvements or enhancements of the storage ring performance. As an example, the APS can now operate efficiently with a lower horizontal emittance, which reduces the source size by a factor of two. This reduction in size provides a smaller beam spot that can be used to illuminate smaller samples. Normally, the decrease in beam lifetime would severely reduce the average current available to the users, but with top-up, the reduction is non-existent. Top-up operation is now the standard and comprises 75 percent of the total operating time of the APS. The APS is the first synchrotron facility to have conceived and implemented top-up operation.

  Canted Undulators for Increased Beamline Capacity. New technologies devised to offset the ever-increasing demand for beamline access include the "canted undulator" configuration that produces two beamlines originating from one point on the ring.

  New Information on High-Pressure Fuel Sprays. An x-ray imaging technique devised at the Basic Energy Sciences-funded Synchrotron Radiation Instrumentation Collaborative Access Team (SRI-CAT) has produced unprecedented details of the structure of diesel fuel sprays, including the first evidence of supersonic shockwaves in sprays as they leave high-pressure fuel injectors. This information may lead to improvements in fuel injector-engine emissions and efficiency, and earned a 2002 National Laboratory Combustion & Emissions Control R&D Award from the Department of Energy.

  Nanotomography of Integrated Circuit Interconnects. A high-resolution scanning transmission x-ray microscope is providing superior 3-D images of the tiny wire interconnects and other embedded structures in computer chips without damage to the chips. This unique capability makes it possible to more easily identify and correct manufacturing problems, and ultimately to build faster, smaller, more-efficient, and more-reliable computers.

New Lens for Imaging. An offshoot of APS expertise in x-ray beamline instrumentation is the first full-scale crystal-diffraction medical-imaging lens. Resolution with this lens is a factor of three better than with most current imaging systems. It can be applied to small test animals used by the pharmaceutical industry and to imaging small parts of the human body. There are also many possibilities for nonmedical applications, including examination of nuclear fuel elements and location of radioactive material within a larger mass.

- **The National Synchrotron Light Source**

Source Development Laboratory Laser at 400 nm. The Deep Ultra-Violet Free Electron Laser (DUV-FEL) facility marked an important milestone, generating laser light at 400 nm by the process of Self Amplified Spontaneous Emission (SASE). Achieving intensity 20,000 times higher than the spontaneous emission, the result showed that the electron beam and the undulator system can support lasing down to 88 nm, which has strong user interest in the chemical physics community.

Soft X-ray Undulator Beamline Monochromator Upgrade. A new water-cooled, 6-position interferometrically controlled grating chamber was installed at beamline X1B. At present, four new gratings (300, 600,1200, and 1600 lines/mm) covering the soft x-ray photon energy range from 100eV to 1600eV were outfitted. Resolving power of more than 10,000 was achieved. The high energy resolution and extended energy range provided by the new monochromator will benefit greatly all the experimental programs using the beamline, including soft x-ray resonant scattering, emission, and imaging.

Ultra-high Vacuum Compatible Soft X-ray Scattering End Station. A novel resonant soft x-ray scattering instrument has become operational at the X1B undulator beamline. The instrument combines the element and electronic state specificity of soft x-ray spectroscopy with x-ray diffraction, which enables the direct probing of intrinsic inhomogeneities in strongly correlated electron systems and nanoscale magnetic systems. For example, the spatial distribution of the doped holes in an epitaxial film of oxygen-doped $La_2CuO_{4+\delta}$ was determined recently using this instrument for the first time.

New End Station for Soft X-ray Coherent Scattering and Imaging. To facilitate nanoscience research, imaging techniques with nanometer spatial resolution are needed. A new end station for soft x-ray coherent scattering and imaging was designed and constructed. It will be used to develop two and three dimensional diffraction imaging and tomography with tens of nanometer spatial resolution for nano-magnetic, organic, and biological systems

- **The Stanford Synchrotron Radiation Laboratory**

Accelerator Modeling Toolbox Developed. An interactive accelerator modeling software tool called Accelerator Toolbox has been developed that greatly increases productivity and flexibility in interactive computer modeling. By making the Accelerator Toolbox available to other laboratories via the web, a community of users has grown who share code and experience in solving similar accelerator modeling problems.

High Power X-ray Monochromators Deployed. X-ray monochromators with high-efficiency crystal cooling utilizing liquid nitrogen have been designed, fabricated and successfully installed on four high-power wiggler beam lines. Their enhanced performance under high heat loads has already resulted in significant improvements in the stability and throughput of these beam lines. These monochromators and others to be implemented will be critical elements in obtaining the ultimate performance available from the SPEAR3 accelerator when it becomes operational in 2004.

Improved Microfocusing System for X-ray Microspectroscopy. Improved tapered metal capillary focusing optics with a 5 micrometer focal spot have been successfully integrated into a new system for performing microspectroscopy measurements. These developments, which included sample scanning capabilities and software for mapping the chemical states of the elemental distributions, will ultimately be propagated to a number of beam lines to enable microspectroscopy research in biology, materials sciences, and environmental sciences.

Major Progress in SSRL Beamline Upgrade Program. A beam line upgrade program is underway whose goal is to bring all SSRL beam lines to optimal performance with SPEAR3 running at 500 mA. Improvements to date include high-stability mirror systems for the insertion device-based beam lines, new permanent magnet wigglers, a high-resolution soft x-ray monochromator, and new liquid nitrogen-cooled two-crystal x-ray monochromators. Some upgrades have been completed during the current SPEAR2 operations phase, bringing higher performance to the ongoing user research programs.

- **The Intense Pulsed Neutron Source**

Upgrades of IPNS Instruments. 1) A project was initiated for the development of a large-aperture, magnetic bearings-suspension, high-resolution chopper system for the HRMECS and LRMECS chopper spectrometers at IPNS. 2) A new scattering chamber for the Small Angle Diffractometer is being installed. It will improve the data quality and collection rates. 3) Through an IPNS/RIKEN collaboration a neutron compound refractive lens based on an assembly of MgF2 single-crystal prism elements was tested on the POSY II beamline for focusing cold neutrons.

Operations at IPNS Continues Outstanding. For the fifth consecutive year, IPNS has exceeded its goal of offering at least 95% reliable operations. This includes delivering the 7 billionth pulse to the target. This accomplishment constitutes more pulses delivered to target than any other pulsed neutron source in the US. In May of 2002, IPNS was designated a Nuclear Historic Landmark by the American Nuclear Society.

IPNS Hosts the National Neutron and X-Ray Scattering School. During the two-week period of August 12-23, 2002, Argonne National Laboratory once again hosted the National School on Neutron and X-Ray Scattering. The school continues to attract outstanding graduate students and post-doctoral appointees with 160 applications for the 60 positions available in 2001.

- **The Manuel Lujan Jr. Neutron Scattering Center at the Los Alamos Neutron Science Center**

Four Instruments Commissioned. Four world-class neutron scattering instruments completed commissioning and entered the user program. These are HIPPO, SMARTS, Protein Crystallography Station, and Asterix. New data acquisition systems were completed and installed on the new instruments.

Pharos Rebuilt. Inelastic chopper spectrometer Pharos enjoyed substantial upgrades, including detectors on the wide-angle bank, commissioning of the new vacuum system, new data acquisition electronics and computer system, and a new chopper control system. Pharos took its first data and accepted its first users since 1997.

Designed and Installed New Robust Target System, Mark II. Using a simplified Monte Carlo model, the new target improves cooling in Mark I moderator and upper target. A beryllium reflector replaced the lead reflector, cooling was simplified, and cadmium decoupling in the reflector was removed for more robust operation. The target received first beam on July 8, 2002, as scheduled.

Completed Basis for Interim Operation for actinide experiments. The new authorization basis enabled over a dozen plutonium and uranium studies to be completed and restores an important capability to the DOE science complex.

New Shutters and Interlocks. Greater safety, reliability and performance were achieved by replacement of Personnel Access Control Systems interlocks on all flight paths, replacement of all mercury reservoirs and plumbing, and installation of a new fire detection system. Two new mechanical shutters and over 300 tons of shielding were installed to enable two new flight paths for new instruments.

Proton Storage Ring Instability Tamed. A series of successful Proton Storage Ring development tests confirmed that the “e-p instability” could be controlled at accumulated charge levels approaching 10 μC, well above the goal of 6.7μC.

- **The High Flux Isotope Reactor**

Major Refurbishment of Reactor Vessel Completed. The refurbishment of the pressure vessel's internal components included replacing the permanent and semipermanent beryllium reflectors and their support structures. This required maintenance was accomplished without incident and will support the substantial upgrade in neutron scattering research capabilities at HFIR.

HFIR Cooling Tower Replaced. The original 36-year-old wooden cooling tower had significant structural degradation, required excessive maintenance, and could no longer reliably support reactor operations. The more efficient replacement tower will cost less to operate and should last for the remaining life of HFIR.

New Thermal Neutron Beam Tubes Installed at HFIR. The new beam tubes, which replaced existing tubes that had reached their end of life, are capable of providing more neutrons to a greater number of scientific instruments.

Operational Readiness Review (ORR). The ORR at HFIR was the first to be conducted at any Category 1 DOE facility since the current ORR guidance was issued. The ORR included a comprehensive restart plan, independent-contractor and DOE reviews, and close coordination with DOE headquarters and the site office. Reactor operations were resumed on December 18, 2001

Facility Improvements Support Neutron Scattering Instrument Upgrades. New monochromator drums were fabricated for the triple-axis spectrometers at HB-1, 2, and 3. A shielding tunnel and neutron guide were fabricated for HB-2, where a 20-cm-diameter beam tube was installed with beryllium inserts to support four beam lines. The resulting beam intensity is expected to be three times that of the original design for some of the instruments.

- **The Combustion Research Facility**

  Stagnation-flow Reactor Designed to Probe High-temperature Chemistry. Chemically reacting flows at interfaces are an important class of processes occurring in combustion, catalysis, thin film formation, and materials synthesis. An innovative stagnation-flow reactor with access for optical diagnostics and mass spectrometry is nearing completion and will provide a valuable tool for probing high-temperature chemistry for a broad range of industrially relevant processes.

  Fiber-based Laser Systems Developed. Fiber lasers and amplifiers are unique optical sources that provide many advantages for detection of chemical and biological compounds. The CRF has established the capability to fabricate them in-house. The facility will allow the pursuit of new research in optical diagnostics and will help DOE remain at the forefront of this field.

  New Reactor Allows Investigation of Gasification Processes. The design and facility modifications have been completed for a new reactor that will allow unprecedented optical access to pressurized combustion and gasification processes. This reactor will give the CRF the capability to investigate gas-phase kinetics, materials behavior, advanced diagnostic development, and solid and liquid fuel combustion chemistry and physics under pressurized conditions.

Selected FY 2001 Scientific Highlights/Accomplishments

Materials Sciences and Engineering Subprogram

Micro-size Light Emitters for Solid State Lighting Applications. Energy savings of tens of billions of dollars per year could be achieved by replacement of household 100-watt light bulbs by white light emitting diodes (LED) made by mixing LEDs emitting primary colors. However, improved LED efficiency is necessary before such replacement becomes feasible. New research has shown that interconnecting hundreds of micro-size LEDs to replace larger conventional LEDs can boost the overall emission efficiency by as much as 60 percent.

A New Method for Obtaining Crystal Structures Without Large Crystals. High-resolution x-ray diffraction using polycrystalline samples ("powders") rather than traditional single-crystal samples has advanced to the point where the structures of complex materials including oxides, zeolites, and small organic structures can be solved. Advantages of powder diffraction are that it is not affected by crystal fracture and polycrystalline samples can be formed over a much wider range of conditions than large single crystals. Recently, powder diffraction was demonstrated for large molecules, such as proteins, that were considered far too complex for powder diffraction experiments. In addition to the many important applications to materials sciences, this technique will also be useful in chemistry and biosciences.

NMR and MRI Outside the Magnet. NMR (nuclear magnetic resonance) imaging and MRI (magnetic resonance imaging) have required large high-field magnets that impose extremely uniform magnetic fields upon the sample. In many circumstances, however, it is impractical or undesirable to place or rotate objects and subjects within the bore of such a large magnet. A new approach for the recovery of highly resolved NMR spectra and MRI images of samples in grossly non-uniform magnetic fields was recently demonstrated. The approach will be useful for the enhanced study of fluids contained in porous materials, such as deep underground oil-well logging studies, and is expected to have dramatic research applications in chemistry, materials sciences, and biomedicine.

Terabit Arrays (One trillion bits per square inch). A 300-fold increase in magnetic storage density has been achieved using a patented technique of self-assembly of block copolymers under the influence of a small voltage. The new technique is simple, robust, and extremely versatile. The key to this discovery lay in directing the orientation of nanoscopic, cylindrical domains in thin films of block copolymers. By coupling this with routine lithographic processes, large area arrays of nanopores can be easily produced. Electrochemical deposition of metals, such as cobalt and iron, produces nanowires that exhibit excellent magnetic properties, key to ultrahigh density magnetic storage. The nanowires are also being used as field emission devices for displays.

Observations of Atomic Imperfections. A new electron beam technique has been developed that has measured atomic displacements to a record accuracy of one-hundredth of the diameter of an atom. Such small imperfections in atomic packing often determine the properties and behavior of materials, particularly in nano-structured devices. This capability has been made possible by a new technique that couples electron diffraction with imaging technology. The result is a greatly enhanced capability to map imperfections and their resulting strain fields in materials ranging from superconductors to multi-layer semiconductor devices.

Semiconductor Nanocrystals as "Artificial Leaves." Recent experiments demonstrated that carbon dioxide could be removed from the atmosphere with semiconductor nanocrystals. These "artificial leaves" could potentially convert carbon dioxide into useful organic molecules with major environmental benefits. However, to be practical, the efficiency must be substantially improved. New theoretical studies have unraveled the detailed mechanisms involved and identified the key factors limiting efficiency. Based on this new understanding, alternative means for improving efficiency were suggested that could lead to effective implementation of artificial leaves to alleviate global warming and the depletion of fossil fuels.

"Magic" Values for Nanofilm Thickness. A key issue for nanotechnology is the structural stability of thin films and the devices made from nanostructures. It was recently demonstrated that nanofilms are significantly more stable at a few specific values of film thickness. The origin of this effect arises from the confinement of electrons within the film leading to electronic states with discrete energy values, much as atomic electrons are bound to the nucleus at discreet energy levels. Calculations demonstrated that increased stability occurred when the number of electrons present in the film completely filled the set of available states, just as filled electronic shells make the mobile gases very stable.

Materials Resistant to Damage from Nuclear Waste. The ability to predict the composition and structure of materials that are resistant to radiation damage, such as in nuclear waste storage, has been formulated on a firm scientific basis. Current nuclear storage materials cannot resist radiation damage for the required thousands of years because radioactive emissions in a storage material jostle atoms out of their carefully ordered arrangements. These materials become unstable and eventually leach into the environment. Computer simulations and experiments revealed that a special class of complex ceramic oxides called fluorites is able to resist this fate. The fundamental principle is rather simple: the configurations of atomic arrangements in these oxides are relatively disordered to begin with allowing them to tolerate displaced atoms caused by radiation.

Brilliant X-Rays Shine Light on Welds. Using high-brightness synchrotron radiation, the details of microstructural changes of welds were mapped and studied for the first time. This advanced capability shows how the welding process alters the structure and changes the properties of metals. Its application is virtually unlimited, since it can investigate dynamic changes in crystal structure near the melting point of any metal. Knowledge gained from this award winning work on titanium and stainless steels is being used to advance and refine theories and numerical models of welding fundamentals. Dramatic savings to the U.S. economy would result from better quality, more reliable welds.

***Micro Lens for Nano Research*.** A silicon lens that is 1/10 the diameter of a human hair has been fabricated and used to image microscopic structures with an efficiency 1,000 times better than existing probes. The combination of high optical efficiency and improved spatial resolution over a broad range of wavelengths has enabled measurement of infrared light absorption in single biological cells. This spectroscopic technique can provide important information on cell chemical composition, structure, and biological activity.

***Nanofluids*.** Nanofluids (tiny, solid nanoparticles suspended in fluid) have been created that conduct heat ten times faster than thought possible, surpassing the fundamental limits of current heat conduction models for solid/liquid suspensions. These nanofluids are a new, innovative class of heat transfer fluids and represent a rapidly emerging field where nanoscale science and thermal engineering meet. This research could lead to a major breakthrough in making new composite (solid and liquid) materials with improved thermal properties for numerous engineering and medical applications to achieve greater energy efficiency, smaller size and lighter weight, lower operating costs, and a cleaner environment.

Chemical Sciences, Geosciences, and Energy Biosciences Subprogram

Capturing Molecules in Motion with Synchrotron X-Ray Pulses. Photochemical conversion of solar energy depends on light-driven chemical reactions. Absorption of light ultimately leads to atomic rearrangements necessary to produce photochemical products. The intermediate molecular configurations created by absorption of light are short-lived and their structures are largely unknown. In novel experiments at the Advanced Photon Source, molecular structures of laser-generated reaction intermediates in solutions, having lifetimes as short as 28 billionth of a second, have been obtained. Future experiments are planned that will allow for capture of intermediate structures on even shorter time scales. These studies are providing the fundamental knowledge needed to develop artificial photoconversion devices.

***Early Precursor Identified in Water Radiolysis*.** Radiolytic decomposition of water produces hydrogen gas, which is flammable and potentially explosive. This is of concern in maintenance of water-moderated nuclear reactors, long-term storage of transuranic fissile materials containing adsorbed water, and management of high-level mixed-waste storage tanks. In recent studies on the effects of ionizing radiation on condensed media, a common precursor to essentially all hydrogen from irradiated water has been discovered. This precursor is a solvated electron. External intervention and capture of this precursor can prevent the generation of hydrogen gas from water. The reactivity of the precursor with a large number of scavengers has previously been determined in pulse radiolysis experiments, thus a priori predictions can be made on the efficiency of the intervention and prevention of gas generation.

***The World's Smallest Laser*.** A team of materials scientists and chemists has built the world's smallest laser - a nanowire nanolaser 1,000 times thinner than a human hair. The device, one of the first to arise from the field of nanotechnology, can be tuned from blue to deep ultraviolet wavelengths. Zinc oxide wires only 20 to 150 nanometers in diameter and 10,000 nanometers long were grown, each wire a single nanolaser. Discovering how to excite the nanowires with an external energy source was critical to the success of the project. Ultimately, the goal is to integrate these nanolasers into electronic circuits for use in "lab-on-a-chip" devices that could contain small laser-analysis kits or as a solid-state, ultraviolet laser to allow an increase in the amount of data that can be stored on high-density optical disks.

Polymerization to Make Plastics. The discovery of metallocene catalysts caused major advances in polymer production (e.g., polyethylene, polypropylene), the most widespread of synthetic materials. The ability to control the orientation of each link of a polymer chain allows control of crystallinity, density, softening point, and other important properties. A recent improvement in these catalysts is the synthesis of bimetallic complexes in which two catalytic centers and two cocatalytic centers are held in close proximity in solution or adsorbed on surfaces. By altering the nature of the centers, it is possible to control rate of reactivity, the degree of chain branching, and plastic rigidity.

First Ever Chemistry with Hassium, Element 108. Element 108 - hassium - was discovered in 1984. It does not exist in nature but must be created one atom at a time by fusing lighter nuclei. Recently, the first experiments to examine its chemical properties were performed by an international team (German, Swiss, Russian, Chinese and American scientists) at the Gesellschaft für Schwerionenforschung (GSI) in Darmstadt, Germany using novel techniques developed at the Lawrence Berkeley National Laboratory. Energetic magnesium projectiles bombarded targets of curium, a rare artificial isotope produced and processed at Oak Ridge National Laboratory. The hassium atoms formed by impacts between beam and target reacted with oxygen to form hassium oxide molecules enabling the study of the properties of this new chemical compound. The chemistry of man-made and heavy elements, particularly chemistry impacting environmental insults, is of major interest, and these experiments are a first step for this element.

Improved Materials for Fuel Cells. Major impediments for the commercialization of fuel cells include the inability to use hydrogen fuel containing traces of carbon monoxide and the necessity of using large amounts of expensive platinum catalysts. A novel ruthenium/platinum catalyst has been produced through a new preparation method involving spontaneous deposition of platinum on metallic ruthenium nanoparticles. The resulting catalyst has a higher carbon monoxide tolerance than commercial catalysts and uses smaller amounts of platinum.

Platinum Encrusted Diamond Films. Research on new catalytic electrodes, e.g., for fuel cells, has shown that synthetic diamond thin films are excellent supports for catalysts because of their corrosion resistance. The challenge to produce an electrode is to incorporate nanometer sized platinum and platinum/ruthenium catalyst particles into the surface structure of the diamond film. Recently, the ability to incorporate 10 to 500 nanometer diameter particles into the bulk structure of the films has been demonstrated. These new surface modified systems may result in significantly improved catalytic activity and stability, and could have even broader applications in chemical synthesis, toxic waste remediation, and chemical and biomedical sensors.

Complex Flow in the Subsurface. Recovery of subsurface fluids, whether oil and gas or contaminants, requires understanding the way fluids flow within porous and fractured rocks and soil. This is particularly complicated when there are multiple fluids (oil-methane-water; water-carbon dioxide). New experiments combined with theory and computational modeling have tracked the simultaneous flow of two fluids in fractured and porous media. Flow paths of both fluids are significantly longer than under single fluid conditions and transport is very sensitive to differences in fluid structure.

Complete Plant Genome of the First Model Plant. The first complete sequencing of a plant genome was completed by an international consortium of researchers from Europe, Japan and the U.S. The DOE was one of the supporters of the U.S. effort. The sequencing of the genome of Arabidopsis will provide the information needed to increase food production in an energy-efficient and environmentally friendly manner, provide increased wood and fiber production, and increase the use of plant materials for energy and the production of petroleum-replacing chemicals.

Selected FY 2001 Facility Accomplishments

The four synchrotron radiation light sources and three BES neutron scattering facilities served 6,982 users in FY 2001 by delivering a total of 26,476 operating hours to 204 beam lines at an average of 96.1% reliability (delivered hours/scheduled hours)[1]. The High Flux Isotope Reactor at Oak Ridge National Laboratory did not operate in FY 2001 due to the installation of upgrades. Statistics for individual facilities are provided below. In one instance, less time was needed for maintenance activities than was scheduled, so more time was delivered to users than planned.

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[1] BES defines "users" as researchers who conduct experiments at a facility (e.g., received a badge) or receive primary services from a facility. An individual is counted as one user per year regardless of how often he or she uses a given facility in a year. “Operating hours” are the total number of hours the facility delivers beam time to its users during the Fiscal Year. Facility operating hours are the total number of hours in the year (e.g., 365 days times 24 hour/day = 8,760 hours) minus time for machine research, operator training, accelerator physics, and shutdowns (due to maintenance, lack of budget, faults, safety issues, holidays, etc.).

The maximum number of total operating hours for these 7 facilities is estimated to be about 37,100 hours. Most of the BES facilities already operate close to the maximum number of hours possible for their facility. The next priority is to support and maintain beamlines and instruments at the state-of-the art. For the synchrotron radiation light sources and the neutron scattering facilities, the number of beamlines and instruments would need to be increased in order to achieve the full capacity of each of the facilities. Capacity at the light sources could increase by nearly a factor of two if all beamlines were fully instrumented. Capacity at the neutron sources could also increase substantially by upgrading existing instruments and fabricating new ones.

The Advanced Light Source (ALS) served 1,163 users in FY 2001 by delivering 5,261 operating hours to 37 beam lines at 96.2% reliability (delivered hours/scheduled hours). The ALS is supported by the Materials Sciences and Engineering subprogram.

A new beamline for x-ray microscopy of polymers. Owing to its elemental and chemical specificity, x-ray microscopy is a superior tool for the study of multicomponent polymers. A scanning x-ray microscope that is specifically optimized to the demands of polymer research is being commissioned.

Ambient-pressure photoemission spectroscopy. The real world of chemistry, biology, and environmental science is a world that is frequently wet, hot, and under atmospheric or higher pressures, whereas experimental measurements are often best done under vacuum with cold samples. One step toward bridging the gap is the development of a new experimental chamber for *in-situ* investigation of samples under ambient conditions.

Interferometer controls scanning x-ray microscope. In scanning microscopy, it is essential to locate and control the position of the probe over the sample. A control system developed for a scanning x-ray microscope is able to position the x-ray beam with nanometer accuracy, so that features in the sample can be studied at the finest spatial resolution of the instrument.

Superbend beamlines developed. To broaden the spectral range of the Advanced Light Source to cover shorter wavelengths, superconducting bend magnets were designed. The first two beamlines will be implemented sequentially over the next year to serve protein crystallographers and to provide much needed harder x-ray sources for ALS diffraction studies.

The Advanced Photon Source (APS) served 1,989 users in FY 2001 by delivering 4,788 operating hours to 37 beam lines at 95.8% reliability (delivered hours/scheduled hours). The APS is supported by the Materials Sciences and Engineering subprogram.

Storage ring "top-up operation" becomes routine. After successful tests with 25% of the scheduled user-beam time dedicated to top-up operation, the APS is scheduling the majority of future operations for top-up mode. During top-up operation, injecting a pulse of electrons once every two minutes holds the stored current constant to 0.2 percent. This operating mode delivers a constant heat load on x-ray optics and various accelerator components, thus improving the x-ray beam stability. It also allows flexibility in operating modes, which are traditionally limited by the short lifetime of the stored beam. Top-up operation has significantly enhanced the research capabilities of the APS.

Two undulators on a single straight section deliver two independent x-ray beams to users. For the first time, a novel concept of spatially separating the beams from two insertion devices placed on single straight section was realized. This was accomplished by placing the undulator axes at a small angle with respect to each other. Successful implementation of this concept enabled 100% efficient utilization of the delivered beam.

Low-emittance lattice developed. Machine studies have successfully established operating conditions for the APS storage ring with the horizontal emittance reduced by approximately a factor of two. This reduces the horizontal source size and divergence of the x-ray beam and results in at least a factor of two improvement in the overall brilliance. Initial user results are encouraging and routine operation with this mode is scheduled for the near future.

The National Synchrotron Light Source (NSLS) served 2,523 users in FY 2001 by delivering 5,556 operating hours to 86 beam lines at 100.0% reliability (delivered hours/scheduled hours). The NSLS is supported by the Materials Sciences and Engineering subprogram.

Polarization modulation spectroscopy for magnetism research. A new high-resolution soft x-ray beamline and a phase sensitive detection system were completed to take advantage of the fast switching capability of the Elliptically Polarized Wiggler. The new system provides high sensitivity and enables magnetic field dependent studies.

Focusing of high energy x-rays with asymmetric Laue crystals. Theoretical prediction and experimental verification of a new concept for focusing of high energy x-rays was demonstrated. This new design results in a more than 100 fold increase in the photon flux delivered to the sample. A new monochromator based on this design was constructed and implemented at the superconducting wiggler beamline for high pressure and materials research.

High magnetic field, far-infrared spectroscopy beamline commissioned. A new high magnetic field, far-infrared beamline was commissioned with a far-infrared spectrometer and 16 Tesla superconducting magnet. Combining this with a high-field magnet system opens up new opportunities for measuring electron spin resonance (ESR), cyclotron resonance, and other magneto-optic effects in solids.

X-ray optics for microbeam diffraction, elemental mapping, and high pressure research developed. A new system for micro-focusing of x-rays was implemented, achieving a focus of 3 microns (vertical) by 9 microns (horizontal). The system has been used in the study of bone diseases, materials under high pressure, and semiconductors.

High gain harmonic generation (HGHG) free electron laser (FEL) achieves saturation. By frequency multiplying and amplifying a seed laser signal, an HGHG FEL imposes the properties of the laser onto the FEL output beam. In a demonstration, light at long wavelength was frequently doubled. Full characterization of the FEL light and its harmonics agreed with theory and demonstrated the utility of an HGHG FEL for producing intense coherent light pulses.

The Stanford Synchrotron Radiation Laboratory (SSRL) served 907 users in FY 2001 by delivering 4,539 operating hours to 25 beam lines at 94.9% reliability (delivered hours/scheduled hours). The SSRL is supported by Materials Sciences and Engineering subprogram.

Stanford-Berkeley synchrotron radiation summer school. The first Stanford-Berkeley summer school on synchrotron radiation and its applications was held with 36 students from a diverse range of scientific fields. The goal was to introduce young scientists to the fundamental properties of synchrotron radiation and the understanding and use of several techniques, including spectroscopy, scattering, and microscopy.

New actinide facility commissioned. Synchrotron-based measurements are a crucial part of chemical and materials research programs involving radionuclides and radiologic materials. In order not to limit the scope of experiments that can be performed, a radiologic sample analysis facility has been integrated into a modern synchrotron beamline. This combination insures safe handling of actinide and other radiology materials and also provides state-of-the-art measurement capabilities that have proven extremely useful in remediation efforts.

Materials science small angle x-ray scattering beamline facility completed. The materials science small and wide-angle x-ray scattering station is now in full user operation. The integrated beamline and experimental equipment facility allows for studies of weakly scattering systems, such as dilute polymer solutions.

Microfocus optics system for X-ray micro-spectroscopy. An experimental apparatus employing tapered metal capillary optics for conducting X-ray micro-spectroscopy is now in operation. This capability allows X-ray micro-spectroscopy experiments in the materials, biological, and environmental sciences.

Successful 3 GeV injector test. The SPEAR injector was successfully run at 3 GeV, proving that it is ready to provide at-energy injection for SPEAR3. The 3 GeV test came toward the end of the two-year Injector Upgrade Accelerator Improvement Project, in which power supplies, magnets, and diagnostics were upgraded to insure reliable 3 GeV operation. At-energy injection will improve SPEAR3 performance by providing better fill-to-fill orbit reproducibility and thermal stability.

RF waveguide dampers improve beam stability and lifetime. RF waveguide dampers were installed in the two radio frequency (RF) waveguides in the SPEAR storage ring to eliminate high frequency oscillations excited by the electron beam in the RF cavity/waveguide system. The dampers not only eliminated the instabilities but they allowed the use of operations parameters that gave a 20% improvement in the electron beam lifetime.

The Intense Pulsed Neutron Source (IPNS) served 240 users in FY 2001 by delivering 3,968 operating hours to 13 beam lines at 102.6% reliability (delivered hours/scheduled hours). The IPNS is supported by the Materials Sciences and Engineering subprogram.

IPNS hosts the national neutron and x-ray scattering school. In August 2001, Argonne National Laboratory again hosted the two-week National School on Neutron and X-Ray Scattering. The school continues to attract outstanding graduate students and post-doctoral appointees with 179 applications for the 60 available positions.

Upgrade of IPNS instruments. The High Resolution Medium Energy Chopper Spectrometer (HRMECS) instrument was completely upgraded and a chopper was added to the General Purpose Powder Diffractometer (GPPD). The HRMECS upgrade included the complete overhaul of data collection/control software and hardware, addition of position-sensitive detectors at low scattering angles and improved neutron choppers. The T0 chopper on GPPD blocks high energy neutron from entering the diffractometer.

Auto-anneal capabilities added to moderator system. Regular annealing required for IPNS's unique ultra-cold moderator has been accomplished by installing a system that automatically anneals the solid methane moderator every three days. This automation allows for reduced manpower and improved operation of the IPNS target moderator assembly.

The Manuel Lujan Jr. Neutron Scattering Center at the Los Alamos Neutron Science Center LANSCE served 122 users in FY 2001 by delivering 2,364 operating hours to 6 beam lines at 82.0% reliability (delivered hours/scheduled hours). The Lujan Center is supported by the Materials Sciences and Engineering subprogram.

HIPPO diffractometer commissioned. Following three years of design and construction, the recently completed HIPPO (High Pressure, Preferred Orientation) diffractometer took its first neutron-beam-related diffraction pattern on a sample of nickel on July 7, 2001. The scientific thrust of this new state-of-the-art spectrometer is the investigation of dynamic processes in heterogeneous bulk materials in a variety of environments.

SMARTS will provide new capabilities in materials research. SMARTS, a third generation neutron diffractometer for the study of polycrystalline materials, received its load frame and furnace, which were successfully tested onsite during 2001. SMARTS is scheduled to receive first beam in August 2001, followed by commissioning through the remainder of the year.

BES partners on new institutional instruments. Three institutionally funded instruments, ASTERIX, PHAROS, and IN500 were supported in part under the auspices of BES. ASTERIX produces a highly polarized intense beam of cold neutrons that has a very large cross section and covers a wide wavelength range while minimizing the fraction of the neutron beam that is not used. PHAROS, a high-resolution chopper spectrometer, is designed for low-angle studies. IN500 is a cold neutron time-of-flight spectrometer, which will offer all the advantageous capabilities of reactor-based instruments.

Instrument performance improves with use of new chopper technology. All of the Lujan Center's new instruments and some of the existing instruments have enjoyed dramatic improvements in chopper technology in FY 2001. These performance improvements in two technical areas, timing reference generators and chopper controls, now enable the accelerator and all neutron choppers to run as slaves of the master timing generator. This success in chopper technology has drawn the attention of several other spallation neutron facilities and has redefined the timing specifications for the Spallation Neutron Source.

Upgrades to small-angle scattering instrument. A new frame-overlap chopper was procured and installed, which enables the small-angle scattering instrument, LQD, to make full use of the higher flux it enjoys from the hydrogen moderator installed over the last two years. Recent additions to LQD also include a gravity-focusing device, which compensates for gravitational drop, especially for slow neutrons.

Upgrades to SPEAR improve instrument performance. SPEAR (Surface Profile Analysis Reflectometer) is used for determining chemical density profiles at solid/solid, solid/liquid, solid/gas, and liquid/gas interfaces. Upgrades to SPEAR during 2001 included the installation of shutter hardware to reduce closure time, and additional automation of flight-path components. For better performance, an evacuated flight path, and two digital chopper controllers were added. In addition, a new collimation system, together with improved software, allowed for the first real-time reflectivity measurements. These upgrades were made to make the instrument user-friendlier.

The High Flux Isotope Reactor (HFIR) served 38 users in FY 2001 by delivering 8 operating hours for materials irradiation and institutes that utilize the transplutonium program and medical isotopes. The reactor was shut down at 8:00 a.m. on October 1, 2000, for the scheduled replacement of the beryllium reflector and installation of upgrades and remained shutdown for the remainder of the year. The HFIR is supported by the Materials Sciences and Engineering subprogram.

Installation of new components enhances scientific capabilities at HFIR. Many of HFIR's internal components have been replaced with new, upgraded components that will significantly enhance its neutron scattering research capabilities without diminishing its isotope-production or material-testing capabilities. Replaced components include the beryllium reflector, its support structure, and three of the four neutron beam tubes. Beam intensity for some instruments is expected to be three times that of the original design.

Cold Source Project progress. The moderator vessel has been fabricated and has passed acceptance pressure tests at room and liquid-nitrogen temperatures.

Spectrometers for cold neutron research. The cold source to be installed at HFIR will provide long wavelength neutron beams that are unsurpassed worldwide. Instrumentation has been designed to make optimum use of the cold neutron beams. Instruments include small angle spectrometers for measurements on large-scale structures, reflectometers for the study of surface phenomena, and triple-axis spectrometers for the determination of low-energy excitations.

Spectrometers for thermal neutron research. The larger beam tubes and new mochromator drums installed at HFIR will permit considerable gains in intensity for the thermal neutron spectrometers, by as much as a factor of five.

The Combustion Research Facility (CRF) is supported by the Chemical Sciences, Geosciences, and Energy Biosciences subprogram.

New capabilities. The CRF provides a primary interface for the integration of BES programs with those of DOE's Offices of Energy Efficiency and Renewable Energy and Fossil Energy related to combustion by collocating basic and applied research at one facility. Three laboratories were completed. The particle diagnostic laboratory can now generate flames with controllable fuel and oxidizer feeds to develop a fundamental understanding of small particle formation from combustion sources. A time-resolved fourier transform spectrometer for chemical kinetics and dynamics studies is now available in the kinetics and mechanisms laboratory. Related to applied research, the investigation of a novel engine combustion concept is being conducted in the new homogeneous-charge, compression-ignition engine laboratory.

Selected FY 2000 Scientific Highlights/Accomplishments

Materials Sciences Subprogram

Magnetism at the atomic scale. When information is written to a computer hard drive, local magnetic moments associated with atoms in a small region of the surface reverse direction like sub-microscopic compass needles. A new theory has helped explain these dynamical processes. This work recently received the Gordon Bell Award for the fastest real supercomputing application and was named to the Computerworld Smithsonian 2000 collection for being the first supercomputing application to surpass one teraflop.

Functional nanostructured materials that replicate natural processes. A newly developed class of nanostructured materials can selectively filter molecules by their size and chemical identity. These remarkable materials are made from a solution of molecular building blocks that spontaneously arrange themselves into a porous solid as the solvent evaporates. This achievement involved creating the self-organizing precursors, controlling the pore size, and employing a novel evaporation process that promotes self-assembly. These materials hold the promise for significant applications. For example, in the future we may wear “breathing” fabrics that block hazardous chemicals while admitting benign species like oxygen.

The Library of Congress on a single disk? The vision that information can be written and erased near the single molecule limit has been realized for the first time. Disordering and re-ordering tiny regions of a thin film show promise for storing a million times more information than with today's computer disks with no increase in space. The film is made of organic material and supported by graphite. It is so thin that 40,000 layers would be only as thick as a sheet of paper. By exposing the film to voltage pulses with a scanning tunneling microscope, nanometer-sized regions can be switched from crystalline to disordered, increasing their ability to conduct electricity by 10,000 times. Each tiny region is one bit of information, not much bigger than a single molecule of the film.

Analyses of nanocrystals using coherent (laser-like) synchrotron radiation. A powerful new x-ray diffraction method for characterizing the structure of nanocrystalline solids has been developed. Tailoring nanocrystalline properties for specific applications depends critically on detailed knowledge of three-dimensional structure. Traditional x-ray diffraction methods are inadequate; however, coherent x-ray diffraction patterns of gold nanocrystals show surface facets, fringes due to interference among facets, nanocrystal lattice distortion, and, ultimately, equilibrium nanocrystal shape.

Ion-implantation for strong metal-ceramic bonds. Ceramics are hard and corrosion resistant but fracture easily. Metals resist fracture but are not as wear or corrosion resistant as ceramics. Coating a metal with a ceramic is a way to improve both. However, current coating technologies can degrade the performance of metals. A new approach has been successfully developed that employs ion-beam intermixing of the coating with the metal from collision cascades, which are microscopic (nanometer-sized) “hot-zones” formed along the ion track. Since the heating in collision cascades is very short and localized, macroscopic heating of the metal does not occur. A patent has been filed using this new approach to improve hip, knee, and dental prosthetic devices. Ion implantation is used to coat the bone mineral (hydroxyapatite) on titanium starting with a high density layer bonded well to the titanium and changing progressively toward a porous bone mineral outer surface that promotes bone growth and bonding to bone.

Long-term storage of plutonium. Worldwide, nuclear energy production and defense programs have created 1,350 metric tons of plutonium. Because plutonium is radiotoxic and has a long half-life (24,500 years), a long-term storage solution must immobilize plutonium in materials that are resistant to radiation damage for millennia. Using heavy-ion irradiation, advanced characterization techniques, and computer simulation methods, researchers have discovered that highly durable gadolinium zirconate can lock plutonium into its structure while remaining resistant to radiation damage for millions of years.

Boron doping of silicon semiconductor devices -- faster, lower-power computing. Boron doping of silicon improves electrical conductivity and other important aspects of silicon device performance. A fifty-fold increase in active boron doping -- far above nature's maximum of 0.01 percent -- has been achieved using a new process involving atomic hydrogen. Resulting ultra-highly doped silicon layers provide self-aligned "metallic" contacts, improve semiconductor devices, eliminate etching steps in device fabrication, reduce manufacturing costs, and minimize the use of toxic etching gases and chemicals.

Seeing electrons. A novel, quantitative, and highly sensitive method has been developed to image and measure the distribution of valence electrons, which are responsible for chemical bonding and the transport of electrical charge in solids. This new technique, combining imaging and diffraction in the electron microscope, was used to reveal the spatial distribution of valence electrons in complex structures of high-temperature superconductors. The ability to directly observe and measure valence electron distributions with atomic scale resolution will greatly help in the search for better superconductors, ferroelectrics, and semiconductors.

Fluctuation microscopy. Fluctuation microscopy, a new discovery, challenges the common perception that glassy materials have no organization. Fluctuation microscopy relies on the ability of the electron microscope to measure diffraction from tiny volumes (~1000 atoms). It is based on detailed computational simulations coupled with computer-assisted statistical analysis of multiple electron images. It has required development of advanced image-detection methods. In one of the first applications of this method, studies of amorphous silicon and germanium show that both are highly organized over distances of tens of atoms, even though other measurement techniques see these atoms as completely random. This finding is critical to improving the ability of amorphous solar cells.

A smart transistor. A breakthrough in developing the world's smartest transistor has been accomplished. Germanium-based transistors using a new ferroelectric dielectric would be "smart" devices capable of remembering their state. The heart of this new scientific advance is the understanding of the relationship between polarization and microstructure and how to control it. This breakthrough offers enormous potential for energy savings in a myriad of electronic sensors and devices as no power is necessary to maintain a given on/off state. A low-power, gigabyte chip could thus serve as a computer hard drive.

Design of semiconductors with prescribed properties. A theoretical method has been invented by which one can first specify the properties desired in a semiconductor and then work backward to predict the structure of the material that will show those properties. This work was featured in *Fortune Magazine*.

Chemical Sciences Subprogram

Direct measurement of chemical reactions in turbulent flows. Long known for their dramatic advancements in laser instrumentation for monitoring gas-phase reactions and chemically reacting flows, scientists at the Combustion Research Facility have for the first time monitored multiple flame species directly and simultaneously. These measurements provide a powerful test of combustion models that could lead to improved combustion efficiency.

Dynamics of a single molecules. Reactions of single molecules have been observed by monitoring molecular fluorescence using newly developed experimental methods, thus separating the effects of the motion of one molecule from the ensemble motion of the molecule in its environment. The dynamics of a single molecule have been shown to be significantly different from motion in an ensemble, and should lead to the development of new theories for predicting chemical reactivity.

Blinking quantum dots. Quantum dots -- nanometer-size particles in which electrons are confined in a relatively small volume -- have recently been shown to emit light at multiple wavelengths, blinking on and off on a time-scale of seconds. This remarkable behavior, attributed to luminescence from different electronic states, has potential applications for optical logic and photonics and may one day lead to nano-scale computers and/or portable analytical instrumentation.

Generation of laser-like x-ray beams. Combining state-of-the-art ultrafast laser systems with evolutionary computer algorithms has led to a dramatic new demonstration of the controlled generation of coherent x-rays. This represents an important new source of ultrafast, coherent soft x-rays for studies of materials properties and chemical physics.

Biomolecular photobatteries. Voltages have been measured from a single photosynthetic reaction center -- the five nanometer wide molecular structure in green plants that captures solar energy and converts it into electrical energy. The reaction center may be thought of as a tiny photobattery. The reaction center functions as nanometer-sized diodes with possible applications to molecular scale logic devices and computers.

Radiation induced chemistry. Solid particles have been found to enhance the effects of water radiolysis and the resulting production of hydrogen. Furthermore, gas bubbles form on the particles and that impedes the continuous, safe release of hydrogen from the suspension. These results may provide an explanation for the "burps" in storage tanks containing aqueous suspensions and radioactive material.

Plutonium chemistry in the environment. Using newly constructed beamlines at the BES synchrotron radiation light sources, scientists are now able to study small quantities of radioactive materials. X-ray absorption studies on plutonium-containing soils from Rocky Flats revealed that the plutonium is predominantly present as the solid oxide, PuO_2, a form substantially less mobile in soil and ground water than other possible forms. This result demonstrates that the plutonium will remain stable and has led to substantial cleanup cost savings.

Actinide supramolecular complexes. Researchers have for the first time built a supramolecular actinide complex. Supramolecular complexes are molecules that are built from smaller subunits, yet retain their own distinct molecular properties. While there may be future applications in separation science and catalysis, the current worldwide effort in supramolecular chemistry is to understand the principles that govern assembly of such molecules.

Molecular theory of liquids. A molecular theory for the liquid state, which has eluded scientists for years, has now been developed. This provides new opportunities in one of the most important areas for process engineering and one of its most perplexing problems - the prediction of liquid-gas equilibria based on the well-known properties of molecules.

Engineering and Geosciences Subprogram

Engineering at the nanoscale. Using nanoscale devices in real-world engineered systems is one of the greatest challenges facing nanoscale research. A portfolio of research activities explores how to engineer at the nanoscale. Recent activities include the development of physics-based models to represent crack initiation as a nanoscale phenomenon; studies of the frictional response of nanochains; electric charge transfer in semiconductor nanostructures; nanoscale quantum-dot self assembly using DNA templates; and the integration of nanoscale biomotors with mechanical devices. In this last activity, researchers constructed integrated nanoscale devices that are powered by biomolecular motors and fueled by light. In one such system, a protein from a photosynthetic bacterium generates an electrochemical gradient across an artificial membrane system. This system is chemically closed, enabling the motors to be continuously supplied with fuel using a total light collection area less than 400 square nanometers.

Geosciences imaging from the atomic scale to the kilometer scale. Advances in geosciences imaging were demonstrated this year at a variety of disparate length scales. At the smallest length scale, the GeoCARS beamline at the Advanced Photon Source was used to examine the interaction of liquid water with alumina as a model for understanding aluminum containing minerals such as clays. Unlike other techniques used to characterize surfaces, the new beamline can study wet crystal surfaces. The result showed a significant change from the experiments using dry surfaces and will help researchers understand water-solid interactions in nature at the atomic level. At an intermediate length scale, researchers are using advanced laser scanning confocal microscopy to image, reconstruct, and characterize fluid flow through pores and cracks. Predicting the magnitudes and directions of flow in earth material is critical in performance assessment of oil and gas reservoirs. Finally, at the largest length scales, researchers are using specially instrumented regions in an earthquake zone to help model and improve geophysical imaging on the kilometer scale.

Biogeochemistry. It is increasingly evident that living processes play a fundamental role in determining the geochemistry of groundwater, near-surface sediments, and deeper rocks. Microbes affect the weathering of rocks and minerals, and microbial metabolism affects the accumulation of heavy metals in soils or their release to groundwater. These and other processes determine how soils, sediments, and ore bodies form and how water quality is affected. Work identifying how microbes affect the fate of zinc released to groundwater percolating through lead-zinc mines and other biogeochemistry work recently led to the award of MacArthur Foundation Fellowship to a BES supported researcher. Biogeochemistry, which links three BES subprograms, is expected to play an increasingly important role in addressing DOE missions.

Energy Biosciences Subprogram

Completion of the gene sequence of* Arabidopsis thaliana*, the first plant genome. *Arabidopsis thaliana*, a small weed belonging the mustard family, became the world's "model" plant owing to its small physical size, small genome size, low level of junk and repetitive DNA, short life cycle, large number of mutations, and ease in genetic analysis. An international collaboration involving scientists from the U.S., Europe, and Japan announced the completion of the complete sequence of this plant genome in December 2000. The *Arabidopsis* genome is entirely in the public domain, making the results available to scientists worldwide. The Energy Biosciences subprogram has been a partner in this project since its inception; support for research on *Arabidopsis* dates to the early 1980s.

Snapshot of a light-driven pump. Sunlight causes the bacteriorhodopsin protein to change shape, and in the process transport protons across a membrane to provide chemical energy. X-ray crystallographic structure determinations of this light-driven proton pump captured for the first time the molecule frozen mid-stroke of this shape modification. This novel view of the intermediate conformation enables us to see how biological nanostructures capture and transform energy.

Selected FY 2000 Facility Accomplishments

The four BES synchrotron radiation light sources served 6,009 users in FY 2000 by delivering a total of 19,854 operating hours to 184 beam lines at an average of 99.5% reliability (delivered hours/scheduled hours). The three BES neutron scattering facilities served 524 users in FY 2000 by delivering a total of10,395 operating hours to 34 beam lines at an average of 94.7% reliability (delivered hours/scheduled hours). Statistics for individual facilities are given below.

"Users" are defined by BES as researchers who conduct experiments at a facility (e.g., received a badge) or receive primary services from a facility. An individual is counted as one user per year regardless of how often he or she uses a given facility in a year. "Operating hours" are the total number of hours the facility delivers beam time to its users during the Fiscal Year. Facility operating hours are the total number of hours in the year (e.g., 365 days times 24 hour/day = 8,760 hours) minus time for machine research, operator training, accelerator physics, and shutdowns (due to maintenance, lack of budget, faults, safety issues, holidays, etc.).

The Advanced Light Source (ALS) served 1,036 users in FY 2000 by delivering 5,367 operating hours to 34 beam lines at 95.0% reliability (delivered hours/scheduled hours). The ALS is supported by the Materials Sciences subprogram.

> *New technique for improved storage-ring stability.* The electron beam parameters in the storage ring determine x-ray beam lifetime and stability. Using a mathematical technique, accelerator physicists have understood the strength and location of harmful resonances that cause irregular, chaotic electron behavior leading to loss of electrons from the beam.
>
> *Third-harmonic cavities enhance beam lifetime.* The electron beam lifetime in a synchrotron-radiation source determines how long users can record data before being interrupted when accelerator operators replenish the train of short bunches that make up the beam. A desirable way to increase the lifetime is to lengthen the bunches. Five new third-harmonic cavities accomplish the bunch lengthening and have increased electron beam lifetime increased by about 50%.

X-ray science possible at femtosecond speeds. X-ray experiments to study physical, chemical, and biological processes that occur on a time scale of one molecular vibration (typically 100 femtoseconds) are an emerging area of research. Three developments at the ALS brought x-ray science into the femtosecond realm. First, researchers developed a high-speed x-ray detector (a streak camera) with a picosecond time resolution. Second, researchers showed how to use a femtosecond laser to "slice" tiny slivers from the circulating electron bunches in the storage ring and use them to produce pulses of synchrotron radiation lasting just 300 femtoseconds. Finally, accelerator physicists devised an arrangement of magnets that allow a narrow-gap undulator optimized for the production of femtosecond x rays to be installed in the storage ring.

Undulator has complete polarization control. The elliptically polarizing undulator (EPU) in the ALS is now in full user operation with a high-resolution beamline to provide state-of-the-art performance. This capability opens up many new experimental possibilities in polymer, biophysics, and magnetism research all without rotation of the sample.

Upgrades improve photoemission electron microscopy. By imaging the photoelectrons emitted from a sample with high spatial resolution, the photoemission electron microscope is an ideal tool for combining spectroscopy with variable polarization microscopy in the study of materials ranging from magnetic materials to polymers. The performance and sample-preparation facility of this instrument have been upgraded, making possible new experiments, such as probing the magnetic roles of the different elements in multilayer structures of the type under development for magnetic memory and data storage.

A facility for sub-micron x-ray diffraction developed. Many properties depend on behavior within individual grains and on the details of grain-to-grain interactions. The ALS has pioneered the technology needed for x-ray micro-diffraction and its application to thin-film stress analysis. The system is capable of measuring structural parameters from grains as small as 0.7 micron. The technique is starting to play a major role in many materials projects, from stress-induced cracking of indented high-strength materials to stress in magnetic thin films.

The Advanced Photon Source (APS) served 1,527 users in FY 2000 by delivering 4,724 operating hours to 34 beam lines at 93.6% reliability (delivered hours/scheduled hours). The APS is supported by the Materials Sciences subprogram.

3-D imaging in real time. A real-time, three-dimensional x-ray microtomography imaging system that can acquire, reconstruct, and interactively display rendered 3-D images of a sample at micrometer-scale resolution within minutes has been developed. This system could bring better understanding of an array of physical processes, ranging from failure in microelectronic devices to growth and depletion processes in medical samples.

Novel x-ray microprobe developed. The magnetic contribution to the cross section for x-ray scattering is of significant interest. A technique has been developed that combines microfocusing x-ray optics with Bragg-diffracting phase retarders to produce a circularly polarized x-ray microprobe. This will enable a wide variety of magnetic scattering experiments in applied fields like magnetic materials and superconducting compounds.

New beam chopper improves time-resolved experiments. A new beam chopper has been developed for time-resolved experiments. The time window of 10 nanoseconds enables time-resolved experiments in condensed-matter physics, atomic physics, and biological science.

Beam-position monitor improvements started. Significant upgrades have been made to the particle beam and x-ray beam position measurement systems. Further progress is expected when these changes are incorporated in all of the beamlines at the APS. This state-of-the-art improvement in beam stability will provide the APS users with more efficient beamlines and the capability of working with smaller samples and increased measurement resolution.

Storage-ring "top-up" operations developed. The APS is the first facility to implement "top-up" filling of the storage with electrons during normal operations. During 136 hours of top-up operation, the stored current was held constant to about two parts per thousand by injecting a pulse of electrons once every two minutes. This resulted in improvements in x-ray beam stability. Ultimately, top-up filling will be the routine operating mode of the APS.

Record FEL SASE achieved. Using the Low-Energy Undulator Test Line (LEUTL) and the injector linac, an experimental verification was obtained of the self-amplified spontaneous emission (SASE) process for 530 nm light. More recently, saturation of the SASE process at a power level 10,000,000 times higher than the light produced by a single undulator insertion device was verified. These experiments are viewed as necessary experimental milestones for achieving an x-ray free-electron lasers.

The National Synchrotron Light Source (NSLS) served 2,551 users in FY 2000 by delivering 5,620 operating hours to 90 beam lines at 112.9% reliability (delivered hours/scheduled hours). The NSLS is supported by the Materials Sciences subprogram and the Chemical Sciences subprogram.

New optical polarizer. A newly developed quadruple-reflector optical polarizer efficiently converts VUV light from linear to either left-circular or right-circular polarization. This polarizer expands the capability the U5UA beamline in the area of ultra-thin magnetic films.

High-resolution photoelectron spectrometer. A high resolution photoelectron spectrometer was installed on the U13UB beamline, and has already produced new physical insights into the electronic structure of high temperature superconductors.

Infrared beamlines revitalized. The 10 year-old infrared microspectrometer at U10B beamline was replaced with a state-of-the-art continuum microscope and advanced Fourier transform infrared spectrometer. The system has been used for the study of interplanetary materials, biological tissues, corrosion, and materials formed at high pressure. Also, the beam delivery optics for the U12IR beamline were rebuilt to provide infrared radiation to a new high-resolution spectrometer. This spectrometer will be used for magnetospectroscopy studies of materials such as $LaMnO_3$.

Fluorescence microscopy. For the first time, an infrared microscope has been modified such that fluorescence sample visualization and infrared microspectroscopic analysis can be performed simultaneously. This unique combination is a valuable analysis tool for probing the chemical composition of materials.

Advanced x-ray detector array enables study of trace elements. X-ray absorption spectroscopy of trace elements in samples poses a serious detection problem. The detector technology developed for high-energy physics applications was used to produce a 100-element energy-resolving detector array for use on an NSLS beamline.

Advanced x-ray detector system developed. One of the ways in which diffraction experiments can be made more efficient is to detect the entire diffraction pattern with high resolution. In order to accomplish this, a novel curved cylindrical detector was developed. In addition, a highly-parallel readout system was developed that is capable of processing events 10 times faster than before.

Low-cost monochromator, low-maintence spectrometer. A simple device that consists of a monolithic silicon diffracting element is near- zero maintenance and almost adjustment free. It is now used on five NSLS beamlines; several more such detectors will be installed at NSLS and at other facilities. The new device removes need for ultra-fine mechanisms that contribute to most of the cost of such an instrument and makes x-ray monochromators difficult to control.

Digital feedback system improves storage ring stability. Meeting the needs of the large population of NSLS users for high quality photon beams requires an extremely stable electron orbit. To that end, digital orbit feedback systems to replace the original analog ones were designed in both the VUV and the X-ray rings. The main advantage of switching to a digital architecture is the ability to use a higher number of beam position monitors to achieve a better match between disturbances on the beam and corrective action by the feedback system. The digital global orbit feedback system was put into operations in the VUV ring in August 2000. Implementation of the digital orbit feedback system on the X-ray ring is expected in FY 2001.

The Stanford Synchrotron Radiation Laboratory (SSRL) served 895 users in FY 2000 by delivering 4,143 operating hours to 26 beam lines at 96.8% reliability (delivered hours/scheduled hours). The SSRL is supported by Materials Sciences subprogram and the Chemical Sciences subprogram.

Reliability of SPEAR improved. The reliability of the injector was improved by rebuilding the regulation of power supplies in the beam transport line. This contributed to shorter filling times, and, consequently, to longer beam times available to the users.

Quality of the photon beam enhanced. Stable photon beam intensity is one of the requirements for performing demanding synchrotron radiation experiments. Accelerator physics studies determined that one type of beam noise was due to the excitation of high order electro-magnetic modes in the accelerating cavities. To alleviate this problem, waveguide dampers were installed in the radio-frequency accelerating system. As a consequence, SPEAR operates more reliably and the beam stability is improved.

SSRL beam line systems modernized. Six beam line stations were upgraded to the SSRL standard data acquisition system and control software. This greatly increases reliability while reducing user training time, spares requirements, and staff support requirements.

High magnetic field x-ray scattering station commissioned. A new high magnetic field end station incorporating a 13 Tesla superconducting magnet was constructed and commissioned on SSRL's premiere x-ray scattering beam line, BL7-2. This facility is one of the few facilities in the world that enable state-of-the-art x-ray scattering experiments in high field environments. The unique matching of a versatile, high-field magnet with an intense synchrotron x-ray source allows scientists to unravel the properties of these new materials. Eventually, the fundamental understanding that will be derived from this research will lead to higher performance sensors and magnetic storage devices.

Photoemission beamline improved for higher throughput and resolution. The high-resolution angle resolved photoemission beam line station 5-4 has been used to study the fundamental mechanisms of high temperature superconductivity and improvements in FY2000 have brought the station to new levels of performance. The upgrades include a new primary focusing mirror and an angle mode option to the photoelectron energy analyzer greatly improving throughput.

Molecular environmental science facility commissioned. The importance of molecular based research in the environmental area is increasing in importance due to the emergence problems ranging from environmental remediation at the DOE weapons labs, to long term storage of nuclear waste, to basic questions concerning molecular interactions of pollutants at the surfaces of soils. Beam line station 11-2 has been optimized for x-ray absorption studies of samples in a variety of states and under dilute field conditions. The station also includes capabilities for small spot analysis as well as specialized facilities for the safe handling and analysis of radioactive materials such as soils contaminated with actinides or wastes from nuclear storage sites.

New research and training gateway program initiated. A Gateway pilot program involving SSRL and the University of Texas at El Paso (UTEP) is providing training and research opportunities targeted toward Mexican and Mexican American students. In FY 2000, a group of 16 UTEP students and staff underwent training and carried out experiments on four separate beam lines.

The Intense Pulsed Neutron Source (IPNS) served 230 users in FY 2000 by delivering 3,842 operating hours to 15 beam lines at 101.6% reliability (delivered hours/scheduled hours). The IPNS is supported by the Materials Sciences subprogram.

Upgrade of QENS instrument. The quasielastic neutron scattering (QENS) instrument was compleely upgraded. This instrument is used for measurements that determine the diffusion rates of both molecular rotation and translation on the typical time-scales of simple liquids, adsorbates etc. QENS is also capable of measuring vibrational excitations up to a few hundred meV, providing access to both external and internal vibrational modes for hydrogenous systems.

IPNS hosts second National Neutron and X-Ray Scattering School. During the two-week period of August 14-26, 2000, Argonne National Laboratory once again hosted the National School on Neutron and X-Ray Scattering. The success of the previous year was so overwhelming that additional funds were provided by BES to increase the size of the school from 48 to 60 graduate students. Funding was also provided by the National Science Foundation. This school fulfills a continuing need for training graduate students in the utilization of national user facilities. The formal program included 32 hours of lectures given by an internationally known group of scientists recruited from universities, national laboratories and industry.

The Manuel Lujan Jr. Neutron Scattering Center at the Los Alamos Neutron Science Center LANSCE served 25 users in FY 2000 by delivering 736 operating hours to 7 beam lines at 78.8% reliability (delivered hours/scheduled hours). LANSCE was down for installation of upgrades and safety shutdowns in FY 2000. The Lujan Center is supported by the Materials Sciences subprogram.

Neutron flux increased. The Lujan Center is the first spallation neutron source to exploit the increased neutron flux provided by coupled moderators. A new coupled liquid-hydrogen moderator provides an increase of approximately 2.5 times over the previous decoupled moderator. Both the small-angle diffractometer, LQD, and the Surface Profile Analysis Reflectometer, SPEAR, benefits from this increased flux at Lujan. The increase in flux is a result of the interaction of the moderator, the reflector surrounding the moderator, and the lack of decouplers.

The High Flux Isotope Reactor (HFIR) served 269 users in FY 2000 by delivering 5,817 operating hours to 12 beam lines at 92.9% reliability (delivered hours/scheduled hours). The HFIR is supported by the Materials Sciences subprogram and the Chemical Sciences subprogram.

Cold source progress. Work continues on the development of the nation's highest-intensity cold neutron source. This cold source, which will be comparable in intensity to the world's best at the Institut Laue–Langevin (ILL) in Grenoble, France, will support four neutron guides and instruments. The cold source building and refrigeration plant have been completed, and the guides and cold-source moderator vessel are in fabrication.

The Combustion Research Facility (CRF) is supported by the Chemical Sciences subprogram.

New capabilities brought on line. The CRF provides a primary interface for the integration of BES programs with those of DOE’s Office of Energy Efficiency and Renewable Energy and Office of Fossil Energy related to combustion by collocating basic and applied research at one facility. Phase II of the CRF more than doubled the laboratory floor space to 37,000 square feet, increasing the number of labs to 37. The new wing houses unique instruments, such as picosecond lasers for diagnosing molecular energy transfer. The turbulent flame diagnostics laboratory, which has become an international standard, has been expanded to accommodate two simultaneous and independent experimental stations for visitors. The new laser-imaging laboratory has also been expanded to include several flame geometries with controlled, reproducible flow structures. New staff members have been or are being hired in theoretical chemistry, computer science, and experimental chemical dynamics.

Selected FY 1999 Scientific Highlights/Accomplishments

Serendipitous Applications of Research in the Physical Sciences to the Life Sciences. It has long been recognized that tools and concepts developed in the physical sciences can revolutionize the life sciences. One need only consider the impact of x-ray synchrotron radiation and MAD (multiple wavelength anomalous diffraction) phasing on macromolecular crystallography; both were developed within the BES program. In FY 1999, many of the annual BES program highlights illustrate the rapidity with which advances in the physical sciences are impacting the life sciences. Two examples are given here. First, new techniques of nuclear magnetic resonance (NMR) are being used to study the molecular structures of solid protein deposits implicated in brain diseases such as Alzheimer's Disease and BSE (Mad Cow Disease); both diseases involve the transformation of normal, soluble proteins in the brain (whose structure is known) into fibers of insoluble plaque (whose structure is largely unknown). Second, a nano-laser device has been shown to have the potential to quickly identify a cell population that has begun the rapid protein synthesis and mitosis characteristic of cancerous cell proliferation. Pathologists currently rely on microscopic examination of cell morphology using century-old staining methods that are labor-intensive, time-consuming, and frequently in error.

Materials Sciences Subprogram

Seashell Provides Key to Strong Composites. Mollusk shells have evolved over millions of years to provide hard, strong, tough shelters for fragile occupants. These outstanding mechanical properties derive from a laminated construction of alternating layers of biopolymer – a biologically produced rubber – and calcium carbonate, commonly known as chalk. It has been recognized for decades that materials with alternating hard and soft layers absorb energy and impede cracking. Unfortunately, it has proven difficult to transcribe seashell-like designs into manufacturable materials. Now, a rapid, efficient self-assembly process has been developed for making "nanocomposite" materials that mimic the construction of seashells. This process can be generalized and should lead to materials with unprecedented mechanical properties.

Imaging Fluid Distribution and Flow in Materials. Dramatic pictures of the distribution and flow of fluids inside intact objects and porous solid materials have been obtained by magnetic resonance imaging (MRI) and nuclear magnetic resonance (NMR). The ability to observe such images and spectra results from the use of noble gases, particularly xenon, magnetically polarized by means of a laser. This advance makes possible the observation of MRI pictures and NMR spectra in ultralow magnetic fields. The technique produces brilliant pictures (up to a millionfold increase in brightness) and provides a new capability for noninvasive investigation of flow and transport. The images and spectra allow the characterization of atomic distribution and flow from the smallest scale of nanotubes to the largest scale of macroscopic samples. The flow of fluids through solid materials is a crucial component of many industrial processes from the catalytic conversion of petroleum to the containment of toxic environmental agents. These advances will eliminate the need for high magnetic fields in some applications of MRI and NMR, a welcomed event given the cost, bulk, hazard, and lack of portability of the magnets used in contemporary instrumentation.

New Fullerene Species Synthesized - Stickyball, C_{36}. A new fullerene species, C_{36}, has been synthesized and produced in bulk quantities for the first time. Fullerenes or "buckyballs" are hollow clusters of carbon atoms. They have been studied extensively since the Nobel prize-winning discovery of C_{60} in 1985 (supported by BES). C_{36} is the smallest fullerene discovered to date and is characterized by unusual and potentially very useful properties. For example, in contrast to C60 molecules, which interact only very weakly with one another, C_{36} molecules stick together – hence the nickname "stickyballs." The lower fullerenes, such as C_{36} are predicted to have more highly strained carbon bonds, resulting in exciting properties for those molecules such as very high chemical reactivity and high temperature superconductivity. The synthesis of C_{36} is particularly significant, because previously it was believed that any fullerene smaller than C_{60} would be too unstable to isolate in bulk.

Seeing Clearly Now. Using a new imaging technique called Z-contrast imaging, researchers have achieved the highest resolution electron microscope image of a crystal structure ever recorded, resolving adjacent columns of silicon atoms separated by a scant 0.78 angstroms (3 billionths of an inch). Better resolution enables scientists to see and understand important details they had not been able to see before. This technique also offers both high spatial resolution and the ability to distinguish different kinds of atoms. The precise atomic-scale structure of a material controls the performance of materials for semiconductor devices, superconductors, and a host of other applications. Combined with improved electron imaging optics currently under development, this result promises to revolutionize the atomic-scale understanding of materials.

New Family of Bulk Ferromagnetic Metallic Glasses for Energy Efficient Motors and Transformers. New rules for designing alloys have been developed that enable the creation of a family of bulk metallic glass alloys. These alloys exhibit outstanding ferromagnetic behavior with virtually no energy loss. These new alloys are at least 65 percent iron plus contain up to seven other elements. Until now, such alloys could only be produced as thin foils. Commercial transformers based on the thin foil ferromagnetic metallic glasses are in service, but their size and application are limited due to difficulties in thin foil assembly and manufacturing processes. The new bulk glasses can be cast into exact shapes and substituted into the standard assembly processes now in use for traditional crystalline materials. It is expected that the availability of bulk ferromagnetic glasses will decrease the energy losses of transformers by about 2/3 compared to today's transformers made from crystalline ferromagnetic materials. That's good news for electric utility customers, since it is estimated that power-distribution transformer losses cost about $4 billion annually.

Universal Magnetic Behavior in High-Temperature Superconductors. Understanding high temperature superconductors remains one of the most significant research issues in condensed matter physics. The observed properties of two major classes of high temperature superconductors initially appeared to be significantly different from one other, leading scientists to believe that the fundamental interactions responsible for the superconducting behavior were quite different in the two materials. However, recent neutron scattering results have shown that the superconducting behavior of both major classes of superconductors is connected to excitations of the magnetic spin system in each material. The new results offer insight on high-temperature superconductivity including the promise that a single physical mechanism can account for this phenomenon.

Chemical Sciences Subprogram

Measuring Chemical Processes in Combustion One Molecule at a Time. A powerful new experimental instrument just completed at the Combustion Research Facility promises to provide new information about how molecules dissociate when given enough internal energy. Understanding such processes is critically important for combustion, because, at the high temperatures of combustion, dissociation occurs in a variety of ways that are difficult to observe, model, and predict. In the experiment, pulses of laser light a few femtoseconds in duration pump enough energy into a molecule to cause it to dissociate. (One femtosecond is one millionth of a billionth of a second.) A second femtosecond laser pulse ionizes the molecular fragment during the dissociation process. From the simultaneous measurements of the fragments produced by the second laser, the details of the dissociation process can be extracted. These measurements are made one molecule at a time. This new experimental facility promises to be a tool of unrivaled power for the validation of predictive models and theories of chemical reactions.

New Designs for Molecular Wires Help Mimic Photosynthesis. One way to capture and store the sun's energy is to design systems that mimic photosynthesis. In nature, biological systems use charge separation to store energy. This charge separation occurs by transfer of an electron from a photoexcited donor molecule through a bridge molecule to an acceptor molecule. Researchers have recently constructed donor-bridge-acceptor systems in which the bridge – or molecular wire – is a conjugated organic molecule analogous to natural carotenes that transfer charge over long distances. This research may lead to new molecular devices for efficient charge separation and storage.

New Insights into Surface Catalysis. One of the oldest problems in surface-catalyzed reactions is understanding how the molecules actually come together on a metal surface. Researchers studying the hydrogenation of acetylene on crystalline nickel using sophisticated atomic and molecular beam preparations and subsequent thermal desorption spectroscopy demonstrated that this simple reaction proceeds via hydrogen absorbed into the bulk of the metal rather than adsorbed on its surface, as previously thought. This startling discovery has changed the way we think about industrial hydrogenation catalysts such as Raney nickel and palladium, and may have general implications for heterogeneous catalysts presently used in energy-intensive industries such as ammonia production (the Haber Process).

First Observation of Relativistic Thomson Scattering – 60 Years After its Prediction. British physicist J. J. Thomson, who identified the electron in 1897, showed in 1906 that light could cause electrons to oscillate up and down and reemit at the same frequency in a dipole pattern; this phenomenon was subsequently termed Thomson scattering. Nearly a century later, researchers have demonstrated a new phenomena – relativistic Thomson scattering – in which electrons oscillate in a more complex figure-8 pattern and emit light at both the exciting laser frequency and multiples of that frequency, each emitted in a different direction. The more complex pattern results from the electron interacting simultaneously with both the electric and magnetic fields of the laser light. To observe this phenomena, the research team built a tabletop neodymium-glass laser and compressed its billionth-of-a-second pulses by a factor of about 1,000, boosting their power to 4 trillion watts of very high-quality beam. This experiment is an important milestone in the study of nonlinear optics with electrons unbound to atoms. Furthermore, this work may lead to new laboratory tabletop x-ray sources producing very short x-ray pulses useful, for example, for probing molecular motion during reactions.

Engineering and Geosciences Subprogram

Making Waves. Unfortunately, many facets of nature exhibit chaotic changes, driven by external forces, never settling down to a predictable state. Progress has been made in understanding one kind of chaos in which information travels from one point to another by means of traveling waves. Examples include the ripples on a wind-blown lake, light in a laser, weather patterns, and even the fibrillation of a human heart. In order to understand this kind of chaos, scientists studied the flow patterns in a thin layer of fluid heated from below. In certain fluid mixtures, the patterns move laterally like waves on a pond. The key discovery is that these patterns can be understood in terms of so-called phase defects, which are places where the waves circle around a point in a pinwheel-like motion. Looking at only the defects to understand the entire pattern is much like keeping track of traffic jams and accidents to understand the operation of a freeway system. The next step will be to predict how the patterns change with time. If present ideas are confirmed, they could be useful controlling such important phenomena as heart fibrillation, and controlling lasers used in communications, cutting and welding.

Changes in Seismic Properties of Rocks Detects Damage. Seismology uses the reflection and transmission of elastic waves to locate subsurface features of interest. Various types of rocks respond differently to different kinds and frequencies of waves. The theoretical geophysics program has developed new techniques to study these phenomena. The research examines rock behavior through ultrasonic resonance experiments, which show that rock has both a rapid resonance response and a slow resonance response. The resonance between the vibrational modes gives the rock a memory of the shaking it has been through. The resonance behavior has implications for accurately locating subsurface features, and for understanding strong ground motion damage patterns during earthquakes when the resonant modes of regions of different ground properties couple with those of man-made structures. A similar resonance response is also characteristic of damaged man-made materials such as metals, ceramics and composites. Thus the nonlinear elastic wave studies can contribute to understanding and testing the characteristics of most man-made materials as well as rock or concrete.

Energy Biosciences Subprogram

Orienting Molecular Syntheses. A component of plant cell walls that severely restricts the use of the carbohydrates in plant biomass is lignin. Lignins are aromatic polymers that make up a significant fraction of the earth's renewable carbon resources. Research has provided evidence that the biosynthesis of these large polymers from smaller lignol units does not proceed in a random fashion, as was previously thought. Novel plant genes have been discovered that encode proteins that serve as a scaffold, helping to hold the lignol units in the right orientation as they are joined together by other biosynthetic enzymes. These results have broad implications for the efficient use of plant biomass as well as offering new strategies for enzyme catalysis in an industrial setting.

Plant Cell Walls. The characteristics of plant cell walls – the major energy component of renewable biological resources – vary to meet the structural, metabolic, and developmental needs of different plant cell types. The biosynthesis of the plant cell wall is precisely regulated to conform to these constraints; however, relatively little is known about how such variation is achieved during cell wall formation. Researchers recently identified an enzyme responsible for modifying the xyloglucan polymer backbone, an important factor in determining cell wall strength. This discovery offers the potential to isolate similar enzymes that modify cell wall properties. A better understanding of plant cell wall biosynthesis can eventually improve the properties of wood and other biomass materials through the efficient design of specific complex carbohydrates and other renewable carbon resources.

Designer Enzymes. Research on fatty acid desaturases and hydroxylases has deciphered the mechanism that controls how these two types of enzymes introduce a double bond (desaturase) or a hydroxyl group (hydroxylase) at specific sites along the carbon atom backbone of long-chain fatty acids. This knowledge of the active site of the two enzymes has enabled the modification of the gene that encodes the desaturase for a specific fatty acid to change it into the hydroxylase and vice versa. Both enzymes perform important tasks in altering the melting response of the fatty acid to heat. This pioneering work lays the groundwork for future advances in designing vegetable oils—which have hundreds of potential uses from heart-healthy margarine to lubricants and nylon.

Selected FY 1998 Scientific Highlights/Accomplishments

Materials Sciences Subprogram

Helping to Solve the Mystery of High-Temperature Superconductivity. Understanding high-temperature superconductivity, discovered in 1987, remains the outstanding problem in modern condensed matter physics. Recent neutron scattering experiments suggest that the electric current in high temperature superconductors may be like "stripes" of flowing current separated by stripes where current does not flow. These stripes can be static or dynamic (like the stripes on our flags, waving in the wind). These and other experiments point to a very different electron pairing mechanism than that seen in low-temperature superconductors. Once the pairing mechanism is understood, it will be easier to find materials with higher critical superconducting temperatures and better mechanical properties.

Magnetic Resonance Imaging (MRI) Without Magnets. Striking, high resolution MRI images have been obtained without the need for high field magnets or high frequency detectors normally required for MRI. The breakthrough involves MRI enhancement by noble gases magnetically polarized (100,000 fold) through laser treatment. A new ultra-low-field MRI instrument now makes it possible to obtain extremely bright MRI pictures of polarized samples in the earth's natural magnetic field, which is thousands of times weaker than fields obtained from traditional MRI magnets (which are bulky, expensive, and often hazardous). The new instrument has been used with localized injection of polarized xenon solutions into human blood to provide the first observations of the real-time process of xenon penetrating red blood cells. (Xenon is an inert gas and an FDA-approved anaesthetic.) This combination of techniques opens the way to provide high resolution MRI images of localized areas in animal and human subjects.

Discovery of New Materials Using LEGO. Of the enormous number of combinations of elements in the periodic table, only a very small fraction are used in real materials. It is quite certain that materials with optimum properties for various applications have not yet been discovered. For example, high-temperature superconductivity occurs in ceramic compounds with a most unlikely combination of elements. A new strategy using fast computers and concepts from quantum mechanics has been developed to search for "winning combinations" of atoms to produce materials with improved physical properties. This approach -- Linear Expansion in Geometric Objects (LEGO) -- recognizes that even complex crystal structures can be viewed as a collection of simple geometric objects such as dumbbells, triangles, etc. By assigning each geometric object an energy value, computers can rapidly scan hundreds of thousands of candidates looking for the lowest overall energy and, therefore, the most stable structures. LEGO has already predicted several new intermetallic compounds missed through conventional approaches.

Electrically Conducting Nanoscale Ropes. Incredibly light synthetic metals with a potential electrical conductivity 50-100 times better than copper per weight are being made from carbon nanotubes doped with metals. First discovered in 1991, nanotubes are a new class of materials formed from graphite-like sheets of carbon rolled into exquisitely small cylinders. They self organize in the vapor phase during growth to form well ordered crystalline bundles of individual nanotubes. The introduction of dopant atoms, such as potassium or lithium, into the open spaces between adjacent tubes within a rope can increase electrical conductivity significantly at room temperature. Doped nanotube ropes are also attracting increased interest as constituents of novel nanoscale device structures and as replacements for pure lithium metal in Li ion batteries.

Molecular Bricks for Nanotechnology. Lightweight materials are commonly composed of polymers, which are long chains of atoms. The chains are difficult to order completely, which limits their functionality and durability. Researchers have recently demonstrated new possibilities for the design of polymers using nano-objects, which can be regarded as molecular bricks. These bricks, which might have shapes as diverse as those of nature's proteins, create a toolbox for the design of lightweight materials that could self assemble into structures with surprising functionality. Using the first elements of this toolbox, a spherical nanostructure has been created that has internally continuous channels; some channels transport water and ions, while others block water but accept organic substances. These nano-sponges could trap toxic metals from water streams.

What Makes Stainless Steel Stainless? Corrosion damage is estimated to cost the U.S. 4.2 percent of the Gross National Product each year. Metals can be used in industrial and technological applications only when appropriately protected. In the case of stainless steel and many other metals, protection is provided by a thin oxide film that prevents further corrosion. However, the structure of these oxide films has remained a mystery despite decades of study. Recent research using surface-sensitive synchrotron x-ray diffraction with a combination of electrochemical experiments has now unambiguously determined that the oxide film on pure iron has a very fine-grained, nanocrystalline structure. Results for iron-chromium alloys (e.g., stainless steel) have shown that the oxide films are also nanocrystalline. This overturns the long accepted belief that stainless steel is corrosion resistant because its oxide film is non-crystalline. These surprising results provide a more realistic basis for understanding corrosion resistance and for the development of better corrosion protection coatings.

Do Cracks "Melt" Their Way through Solids? Predicting and explaining why, how, and when solids fracture is a significant scientific challenge. The driving force for fracture is intensification of the local stress at a crack tip, yet the mechanism by which local strain is dissipated during crack propagation is not well understood. Can strain energy be dissipated via “local melting” around the crack tip? Recent computer simulations of crack formation predict this intriguing possibility. Simulations indicated that the melting in front of a crack tip can lead to catastrophic fracture. Using high-voltage electron microscopy, observations of moving crack tips in an intermetallic compound confirmed the prediction of the computer simulations and showed the development of melted and rapidly re-solidified regions adjacent to the crack tip. This new picture of fracture as a stress-induced melting process may lead to new approaches to stress-corrosion cracking in the automotive, aerospace, power generation, and ship building industries.

Smart Filters. New materials with tailored pore sizes and pore chemistry can selectively remove deadly heavy metals -- such as mercury, lead, and silver -- from water. Researchers discovered that precise control over the amount of water in the pores of porous silica enabled the insertion of useful organic molecules on the walls of the pores. Using this knowledge, monolayers of organic sulfur compounds were bound to the internal surfaces of porous silica to prepare selective filter materials. The high surface area of the porous silica (a few grams have as much surface area as a football field) coupled with the bonding characteristics of the organic compounds results in high filtering capacity and high selectivity for specific contaminants. In addition, pore openings in the silica are designed to be too small for microbes to enter and digest the contaminants, later causing human illness from, for example, mercury contamination. The filter materials can purify highly contaminated water in a single treatment to a level that exceeds drinking water standards. The filters can also be recovered and reused after removing the contaminants.

A Line in the Sand. Granular materials like gravel, salt, or dry chemicals are ubiquitous in our daily lives and central to many industrial processes, yet controlling their motion is both surprisingly difficult and not well understood. For example, granular material subjected to a driving force remains at rest until a minimum "critical force" is applied; then it moves in uncontrollable events like avalanches. Inefficiency in handling granular materials may result in the loss of up to 40 percent of the design capacity of industrial plants. In its retrospective of the last 50 years, Physics Today highlighted the emerging science of granular materials as a notable event of the last decade. Scientists have recently developed a theoretical approach to describe the motion of granular materials in a vibrating environment. This theory correctly describes the unexpected formation of stripe, square, and hexagon patterns on the surface of vibrated granular media and the formation of localized excitations called "oscillons." The theory also predicted how to control aspects of granular motion -- a prediction that was confirmed by experiment. The new theory brings the description and control of granular motion to a higher level of understanding and shows promise of substantial advances in basic granular science, which can lead to industrial applications that exploit the controlled motion of granular materials.

Vortex Matter -- A New Understanding of Magnetism in Superconductors. Magnetic fields in superconductors are carried by "vortices." Each vortex consists of a tube of magnetic field surrounded by a circulating flow of electrons that move without resistance. It is this free flow of electrons that gives superconducting materials their special property. Recently, it has been shown that the system of magnetic vortices can take many forms analogous to the solid, liquid, and gaseous forms of ordinary matter. The analogy between the behavior of vortices and ordinary matter is so strong that a new term has entered the scientific vocabulary -- vortex matter. Vortex matter melts from a crystalline to a liquid state in much the same way that ice melts to water. The properties of vortex matter can be controlled over a wide range. For example, the density of vortices can be varied by a factor of 10,000 simply by changing the applied magnetic field. This remarkable control enables the study of many types of phenomena in vortex matter whose analogies in ordinary matter are difficult or impossible to observe. Thus, the identification and characterization of the melting transition in vortex matter has significant implications for phase transitions in ordinary matter, for understanding the electromagnetic properties of superconductors, and for developing applications of superconductivity.

Chemical Sciences Subprogram

Landmark Experiment Challenges Combustion Models. Combustion is perhaps the oldest technology in human experience, yet its complexity limits predictions of combustion processes in devices ranging from simple laboratory burners to automobile engines. The challenge is characterizing the influence of chemistry and fluid dynamics on one another. A simple experiment recently has demonstrated a major error in current models for combustion processes. The experiment allows the interaction of chemistry and turbulence to be examined in quantitative detail for the first time. A planar flame sheet is deformed by a puff of air generated by a small loudspeaker. Spectroscopic techniques are used to determine the concentrations of reaction intermediates as the flame sheet deforms. Comparisons of these experiments with computational simulations showed that the widely accepted chemical reaction mechanism for simple methane combustion is in error, thus, requiring a fundamental change in our models for combustion.

Fishing for Radioactive Actinides with Molecular Hooks. The selection, separation, and removal of radioactive actinide ions from complex aqueous waste stream mixtures remain vexing technical issues. The development of new, improved separation approaches will result in significant cost savings for nuclear waste treatments as well as improve environmental safety and materials safeguard security. A new family of chelate agents or "chemical fish hooks" suitable for the reversible "catch and release" of trivalent actinide ions in highly acidic solutions has been designed, prepared, and characterized. The latest chelate derivatives show separation characteristics that are especially suited to practical, batch type waste treatments.

First Isolation of a Catalytic Oxidation Intermediate. Despite worldwide efforts over the last 15 years on catalytic olefin oxidation, little progress has been made in extrapolating from ethylene (the smallest olefin) to larger olefins such as propylene. The key question -- the molecular mechanism of ethylene epoxidation (which gives us anti-freeze and polyester fibers) -- remains unresolved. Now, a combined experimental and theoretical tour de force has yielded the first definitive isolation and spectroscopic characterization of a stable intermediate in the catalytic process -- an oxametallacycle. Calculations were employed to determine the structure for the oxametallacycle on silver and to predict the infrared spectrum and molecular motions for that structure. Conclusive identification was provided by the excellent agreement between the predicted infrared spectrum and the experimental electron energy loss spectrum.

Liquid Crystalline Organic Semiconductors Discovered. Liquid crystals change their optical properties as they transition between distinctive geometric states. Digital watch displays, for example, cycle between transparent and opaque forms. They, like other technologically important liquid crystals, are electrically insulating. Semiconducting crystals could have much broader application than insulating crystals, but large single crystals of these materials are difficult and expensive to produce. In a recent breakthrough, a family of liquid crystalline derivatives of perylene diimide was discovered that has semiconductor properties. The films of one compound self organize from a red, polycrystalline phase with randomly oriented crystallites into a black phase with highly ordered ribbon-like structure. The fluorescence intensity increases seven-fold during the transformation. This spontaneous change in photophysical properties makes this class of organic liquid crystals look very promising for future photoconversion applications.

Diode Lasers Detect Radiotoxic Isotopes. Solid-state diode lasers, similar to those used in compact disc players, have been used in a new approach to detect the toxic radioisotope strontium-90, which received attention because of high levels found in milk after atomic weapons tests and the Chernobyl reactor accident. Diode lasers excite and efficiently ionize the strontium atoms; the resulting ions are detected using a mass spectrometer. The high efficiency allows the detection of less than one femtogram (femto = 10-15, e.g., a single postage stamp compared to the area of Texas) of strontium 90. Furthermore, it is possible to selectively ionize the strontium 90 even in the presence of large excesses of the stable, naturally-occurring isotopes of strontium. Measurements can be performed in a few minutes as compared to the several weeks required previously for conventional radiochemical decay counting methods. Thus, this new approach should significantly improve the capabilities for near real-time monitoring of environmental restoration activities, nuclear weapons tests, reactor accidents, and the processing of nuclear fuels.

Photochemical Studies on the Light-Activated Drug Hypericin. The popular herbal remedy St. John's wort contains the compound hypericin, which upon exposure to light is toxic to tumors and HIV, the human AIDS virus. Now, the fundamental photochemistry of hypericin has been elucidated. A novel laser spectroscopic technique, fluorescence upconversion, was used to show definitively that the primary photochemical process is excited-state intramolecular proton or hydrogen transfer. Any incomplete proton or hydrogen atom transfers would acidfy the aqueous solution immediately surrounding hypericin, which may be of importance in its toxicity to viruses. The study is yet another example of the role that the physical sciences play in providing fundamental information relevant to a wide variety of subject areas.

Engineering and Geosciences Subprogram

Remote Sensing of Fractures and Prediction of Failure in Rocks. Long before catastrophic fracturing and failure of a material, sound waves transmitted through the material show a dramatic frequency shift. This shift has been documented before in fractured materials, but the observation of the shift before the formation of a continuous crack is a new discovery. Monitoring for the frequency shift can therefore be used to provide a warning of failure. The sound shifts to a lower frequency because the high-frequency sound (with shorter wavelengths) is preferentially absorbed or scattered. Because the frequency shift occurs prior to creation of a single fracture, there should be a network of oriented, disconnected features appearing prior to a crack that absorb or scatter the high-frequency sound in the same way as do observable cracks. Connected cracks in rocks provide pathways for water, oil, or pollutant flow. The growth of cracks can improve fluid flow or cause failure of well-bores, reservoirs, and tunnels or engineered structures; therefore, it is very important to understand how and when cracks form.

Energy Biosciences Subprogram

Building Doors into Cells. Before any molecule can enter a cell, it must first pass through the cell membrane—the thin, fat-containing film that covers all cells. The passage of most molecules through biological membranes is controlled by pores, defined openings made with specific proteins. The composition and structure of pore proteins can now be altered through genetic engineering. Changes in the size of the pore, the selectivity of the pore for letting different molecules pass through, and the pore's ability to open and close are three properties currently being studied by bioengineering new pore proteins. Successful attempts to engineer modified pore opening and closing properties have provided insight on how these processes can occur mechanistically as well as for developing new biotechnological applications. Among the potential products of this research are chemical triggers or molecular switches that can be used to create new sensors to detect harmful chemicals or viruses. Other potential applications are the development of small light switches and new drug delivery systems.

Selected FY 1997 Scientific Highlights/Accomplishments

The Advanced Photon Source (APS) Completes Its First Year of Operation. As the floor of the APS became crowded with experimental hutches, new results emerged that took advantage of the very high brightness of this new light source and that could not have been done elsewhere. While much of the work at the APS and the other BES synchrotron radiation light sources has been and will continue to be in the area of materials sciences and condensed matter physics, many studies are also being done in the areas of biological, plant, environmental, and geosciences. For example,

- A new structural determination and biochemical analysis of the human fragile histidine triad (FHIT) protein has been performed. The FHIT protein derives from a fragile site on human chromosome 3 that is commonly disrupted in association with cancers. The understanding of this tumor suppressor protein will focus on a diverse human HIT family member in search of their in vivo function throughout biology.

- The first experiments were conducted with a newly constructed beamline for geosciences/soil/environmental research. Molecular-scale observations (made possible by the high brightness of the APS) enable new understanding of local structural and chemical changes that govern the mechanisms of mineral-fluid interactions. For example, the molecular form or speciation of environmental contaminants, such as chromium, arsenic, lead, uranium or plutonium, determines their toxicity and bioavailability.

- Over 90% of the world's plants, including essentially all crops, make use of symbiotic associations with fungi. X-ray imaging studies performed on these systems using an x-ray microprobe have provided detailed information on the elemental distribution in plant roots and associated fungi. These images, with unprecedented spatial resolution, will be a key to understanding the symbiosis between the plant roots and fungi.

Materials Sciences Subprogram

Breakthrough in Processing of Aerogel Films. A breakthrough in the processing of ceramic aerogel films won a prestigious award of the American Chemical Society and was cited as an important discovery by the Wall Street Journal. This breakthrough overcame the sixty year barrier to the large scale commercial utilization of these films. Aerogel films have a foam-like structure, exceptional lightness and transparency, and are ideal insulating materials for double-paned windows and other uses. When freshly formed from a liquid, the film can be easy torn until it has been hardened. Older processes required a toxic liquid and high pressure and temperature to dry the films. Employing a new understanding of film drying and chemical treatment of the surfaces of the pores in the film, a non-toxic, low-pressure and temperature process was developed to keep the film flexible and resilient as it formed.

Cool Sounds. Air conditioning from your favorite music? Not quite yet. However, sound, or acoustic energy, has now been used to make refrigerating and heating units. These devices, called thermoacoustic refrigerators, or thermoacoustic engines when operated in a heating mode, have no moving parts and use sound waves in air or helium to transfer heat. Operation of these devices has been based upon a standing acoustic wave in a closed system, limiting their usage. Now, a radically new concept has been devised in which the air or helium would flow slowly through the device during operation. This concept would allow for heating and cooling of buildings and for other industrial air conditioning applications with an economic advantage over current technology through the elimination of the bulky heat exchangers on building roofs. First results from a test system operating as a refrigerator using helium or air have confirmed the concept. Further developments of this concept are under way.

Slick and Sticky. Pencil-shaped organic molecules called "rod-coils," designed and synthesized to have half of the molecule rigid and the other half flexible, were discovered to exhibit unusual and important clustering mechanisms on several size scales. Aggregates of these molecules self-assemble into mushroom-shaped clusters with the rigid ends forming the stems and the flexible coils forming the caps. At the next level of organization, the mushroom clusters pack side by side into layered sheets to form, ultimately, a thick film. Because the building-block molecules are all oriented in the same direction, the film's properties mirror those of the individual molecules, resulting in a film whose bottom surface is sticky and top surface is slippery. Such a film has many potential applications, for example as an anti-ice coating on an airplane wing or an anti-blood-clot lining for artificial blood vessels. This new molecular organizational technique is being explored to make films with other properties by replacing the slippery and sticky groups capping the rodcoils with compounds that perform other functions, such as conducting electricity or changing their size in response to an electrical pulse.

Materials Failure in a Radiation Environment. The safe storage of nuclear materials and radioactive wastes is a major challenge for the post cold-war generation. The long term effects of radiation on the physical integrity of these materials and their containers is still poorly understood. Recent work using simultaneous electron microscopy and ion irradiation experiments shows that the impact of just a single high energy ion on the surface of a material has a much greater effect than previously realized and disrupts tens of thousands of atoms near the surface of the material. The impact causes local melting, displacement of many atoms beneath the surface, and the formation of surface craters and holes. This work should lead to a correct understanding of how materials are damaged by radiation and will help explain and predict the behavior of materials used for waste storage and other applications.

Powder Process Produces Cheaper Stronger Permanent Magnets. A collaborative team from two laboratories is a recipient of a prestigious R&D 100 Award for the processing of nanocrystalline composite powder for high-strength, permanent magnets. The permanent magnet industry is a very large global industry worth 3.2 billion dollars in 1995 and is predicted to reach 10 billion dollars by 2010. The high magnetic strength of the prize-winning neodymium-iron-boron 'super magnets' results from matching the crystallite size formed on cooling the alloy from the melt to the size of the magnetic domains. The previously used rapid cooling process that creates the fine-grained polycrystalline material is too expensive for many commercial magnet applications. It was discovered that adding titanium and carbon to the molten alloy allows a spray atomization process to create appropriately sized particles that can be consolidated into magnetic compacts.

New Process Forms Diamond-Like Boron Nitride Films. A process to grow diamond-like boron nitride films, the second hardest material known, has been discovered based on a new understanding of how hard nitride films are formed. Like diamond, films of boron nitride can be grown from hot gases and plasmas without the use of high pressures. However, it was recently discovered that irradiation of boron nitride films with low-energy ion beams will produce films of boron nitride that contain the hard, diamond-like form rather than the soft graphite-like form. This new process to form ultra-hard boron nitride films could revolutionize the tool industry, because, unlike diamond, boron nitride does not react with iron or steel; therefore, boron nitride is an ideal material for cutting tools.

A Microscopic Understanding of Materials Joining Enables the Intelligent Processing of Materials. Welding is a critical fabrication technology used extensively in a wide variety of industries such as energy, automotive, construction, aerospace, shipbuilding, and electronics. Weld failures are among the most common reason for unscheduled outages in power plants with the cost of replacement power often exceeding $1,000,000 per day. Recent advances in materials joining science have improved our understanding of the welding process and welded materials. With the help of massively parallel computers, complex physical models that link both macro- and microscopic scale phenomena during the melting and solidification of a weld have been developed. Using such models it is now possible to visualize directly the solidified weld microstructure for a given set of processing conditions. The resulting knowledge has been transferred to industry thereby allowing the intelligent processing of defect-free, structurally sound and reliable welds.

Magnetic Refrigeration to Eliminate Harmful Freon. Conventional air conditioning of domestic and commercial buildings, and cooling in food processing and other industrial plants requires enormous quantities of electricity and uses huge amounts of environmentally harmful chlorofluorocarbons (CFCs). Magnetic refrigeration uses the magneto-caloric effect, the ability of a magnetic material to raise its temperature upon application of a magnetic field and to lower it upon removal of that field. For many years the alloys showing this effect operated only at impracticably low temperatures. New understanding of thermal and magnetic behavior uncovered a gadolinium-silicon-germanium alloy that cools efficiently near room temperature. Refrigerator devices based on magneto-caloric material could cut energy costs and eliminate ozone-depleting CFCs.

Chemical Sciences Subprogram

"Green" Separation Process for Hanford Wastes. The radioactive components in the Hanford waste tanks comprise a mere 1/100th of a percent of the millions of gallons of contaminated waste in storage. Thus, highly selective removal of the radioactive components could significantly reduce the volume of waste, which will require very costly processing and long-term storage. Fundamental studies of technetium extraction in the 1980s, followed by more recent investigations of the structural and thermodynamic aspects of the extraction of alkali metal salts with crown ethers has led to a new technetium extraction process. The crown ether binds sodium ions already present in the waste, and then extracts technetium as much as four orders of magnitude better than others ions in the waste, such as nitrate, which are present at much higher concentrations. The crown ether complex is readily decomposed by contact with water to release the extracted technetium thereby affording a convenient, safe, and economical stripping method. The crown ether is then recycled thus minimizing secondary waste production.

New Metallocene Catalysts Lead to Commercial Applications. The new family of metallocene polymerization catalysts, in which polymerization occurs principally at a single type of metal center with a well-defined coordination environment, are a substantial advance over the prior heterogeneous polymerization catalysts. Recent advances on two fronts -- strained early transition metals and non-coordinating counterions -- have resulted in new commercial applications by Dow Chemical and by Exxon Chemical. The remarkable stereospecificity features of these new catalysts have not only led to a variety of new, advanced polymer products over a wide range of densities, but they also provide the ability to "turn a microscope on" the underlying molecular mechanisms, thus leading to continually improved catalysts and products. The new polymers produced from these catalysts are found in wide-ranging applications from food wrapping to the plastic front end front bumper combinations on automobiles. The impact of these new products can be imagined from the Dow Insite process, which produces plastics with a market of about $2,000,000,000 per year at Dow's Texas plant.

Joint Program Results in a New "Smart" Window. Windows with reduced transmission have been shown to be energy savers by reflecting some of the heat from solar radiation. However, such windows have fixed transmission that also reduces visible light. On a cloudy day a building or home equipped with such windows may not have adequate natural lighting. Research jointly supported by BES and the Department's Energy Efficiency program has led to the initial development of a self-powered "smart" window that can control its own transparency. Integration of two technologies, electrochromic windows and dye-sensitized solar cells, yields a smart window that darkens, reversibly, when exposed to sunlight.

Engineering and Geosciences Subprogram

Fast-Transport Predicted in Subsurface Fluids. Underground flow properties of fluids containing two or more components (oil(s)/water) are a major issue for environmental remediation. New experimental work documents how upward and downward flow of different fluids can be driven by differences in their density and their tendency to diffuse. Such transport occurs much more rapidly than has been predicted by earlier models. This new research developed innovative experimental methods to test the earlier predictions, and successfully measured and modeled the effects of multiphase flow in simple porous materials. This work is a significant step towards developing improved models to make better predictions for complex and highly variable natural subsurface environments.

Energy Biosciences Subprogram

New Sensor Provides Instant Litmus Test for Pathogens. A new class of colorimetric sensor materials has been invented that makes it possible to instantaneously and inexpensively detect a wide range of biological toxins and common disease-causing organisms. Building on earlier discoveries, researchers have developed a thin film consisting of receptor molecules attached to a film of linked diacetylene molecules.

The film transmits blue light. The surface receptor molecules are designed to very selectively bind specific pathogens causing the film molecules to reorganize and the film to turn red. Pathogens thus far detected with good sensitivity include an influenza virus, cholera toxin, botulism toxin, and the toxin produced by the bacteria responsible for 200 deaths per year in the US alone, as noted by the recent contamination of fruit drinks and fast food hamburgers. Existing tests for all of these pathogens require at least a 24 hour culture. After further development, the sensors can be placed on plastic, paper, or glass and incorporated into inexpensive packaging and portable detection devices.

Silicon in Biology. Silicon is an element that is a principal component of glass, computer chips, coatings and numerous consumer products. There are only a few biological systems that metabolize this element. Silicon is metabolized by some simple animals, by algae to make the equivalent of glass houses, and by some higher plants (the rough feel of corn leaves comes from shards of silicates in the leaves). Recently a gene was identified that encodes a protein that is involved in binding and transporting silicon into a cell. This discovery will extend our understanding of how silicon is taken up and processed by biological systems which may lead to applications such as the mining of silicon from seawater and the manufacture of silicon-containing products.

Bioproduction of Natural Gas. The few microorganisms that possess the ability to produce methane (natural gas) have been studied for a number of years in the hope of using these organisms to produce a renewable energy source. Last year the genome of a methane-producing bacterium was sequenced which showed the uniqueness of these organisms. It is now thought that these bacteria are among the first life forms ever developed on earth. Recently, procedures have been developed which will permit the genes of methane-producing bacteria to be manipulated. This development will allow scientists to determine the nature and properties of these organisms and their unusual metabolism.

Controlling Natural Energy Resources through Plant Genetic Engineering. Cellulose is the most prevalent biological compound on earth. It is the principal component of all plants, wood, paper and cotton. When considered globally, cellulose constitutes an enormous supply of chemical energy, all of it renewable. Recently, several plants have been manipulated to make significantly less cellulose. This modification is important because it may now permit identification of the factors that control the synthesis and deposition of cellulose and related compounds. This development may permit the genetic engineering of plants to produce either more cellulose, or plants that produce larger amounts of other chemicals such as liquid fuels and plastics.