FY 1991 Accomplishments

Office of Basic Energy Sciences

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Table of Contents

Technology Transfer; Small Business Innovation Research (SBIR); Awards and Recognitions

Introduction

The Office of Basic Energy Sciences (BES) annually funds over 1,300 research projects at about 200 U.S. universities, DOE laboratories, and industrial institutions. The other major function of the BES program is the design, construction, and operation of complex scientific facilities for use by the research community to conduct experiments in basic research in areas which underpin the Department's energy objectives. These activities provide support for about 4,300 professors, post-doctoral fellows, and graduate students at universities and about 1,800 full-time senior scientists at DOE laboratories. The BES subprograms listed below support research in basic energy sciences that results in over 11,000 published reports of scientific findings in peer-reviewed journals annually.

The following selection of accomplishments during FY 1991 does not reflect the full range of activities under the program. It does, however, provide examples of how basic research can contribute to solving a wide variety of energy problems. The accomplishments identified are presented in three sections:

The following subprograms were managed and/or funded under Basic Energy Sciences during Fiscal Year 1991.

Materials Sciences (MS)
Chemical Sciences (CS)
Engineering and Geosciences (EG)
Applied Mathematical Sciences (AMS)*
Energy Biosciences (EB)
Advanced Energy Projects (AEP)
Small Business Innovation Research (SBIR)**

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* Managed by the Scientific Computing Staff of the Office of Energy Research.
**Managed under Advanced Energy Projects.

Accomplishments

Major Facilities-Related Accomplishments

Advanced Light Source Achieves Important Milestone

The Advanced Light Source (ALS) presently under construction at the Lawrence Berkeley Laboratory (LBL) achieved a major milestone on February 20, 1991. On this date an important component of the ALS's accelerator system, the Linear Accelerator (LINAC) was successfully operated for the first time. The beam from the electron gun was accelerated through both LINAC accelerating guides to an energy of 30 MeV, subsequently transported through the LINAC-to-Booster line and beam switching magnet, and finally reached the Faraday cup at the end wall of the LINAC Cave. All subsystems such as the electron gun, accelerating guides, control system, interlocks, power supplies, instrumentation, and survey procedures were successfully operated at the same time.

First Beam in Advanced Light Source (ALS) Booster Synchrotron Achieved

After a year of careful installation, planning, and preparation, on May 3, 1991, ALS accelerator scientists and engineers succeeded in injecting electrons from the linear accelerator through a transfer line and into the booster synchrotron, where they circulated for more than 400 turns. After 7:15 p.m. on Friday, May 3, an electron beam was fired down the transfer line into the injection kicker magnetic that deflects electrons into the booster synchrotron. A radiation survey confirmed that there was no unexpected radiation, and beam monitors at the end of the transfer line yielded injection timing information. The booster magnets were then energized and adjusted, while the kicker was tuned to get the injection beam into the center of the first of the four retractable scintillation screens located around the booster. With the beam thus positioned in the middle of the vacuum chamber, the screen was removed and the current in the booster dipole magnets was scanned to look for beam further around the ring. The beam was seen making dozens of turns around the booster almost immediately. By 8:00 p.m., after additional tuning of the injection kicker and booster magnets, more than 400 turns were observed.

Stanford Synchrotron Radiation Laboratory (SSRL) Injector and Booster On-Line

At approximately 1:30 on the afternoon of April 14, 1991, the SPEAR storage ring accumulated 10 mA of electrons from the new SSRL injector and booster synchrotron thereby initiating the transition of SSRL to a self-contained, dedicated synchrotron radiation facility. On April 19th, an injection rate of 25 mA/minute was obtained at an injection energy of 2.3 GeV. Subsequently, SPEAR ramped the 2.3 GeV injection beam to 3.0 GeV for the first time with synchrotron radiation available at most of the beam lines. The ramping and injection tests are continuing. The performance of the system demonstrates a nearly perfect match between the injector and the SPEAR storage ring.

New "White Light" Capability at Stanford Synchrotron Radiation Laboratory (SSRL)

A modification to the SSRL 31-pole wiggler beam line improves the capability to perform protein crystallography. The first such experiment was carried out on Isocitrate Dehydrogenase on June 4,

1991. Using a low SPEAR current of 35-40 Ma very high quality diffraction patterns were obtained in only 60 milliseconds per exposure. The whole experiment required only 2 seconds! The establishment of this new facility for structural molecular biology research represents a significant increase in the national capability in this area.

Nano-Electronvolt Resolution X-ray Scattering Achieved Using Synchrotron Radiation

Scientists from Oak Ridge National Laboratory and Argonne National Laboratory have used the nano-electronvolt (neV) bandwidth X-rays from a nuclear Bragg reflection of $^{57}Fe_2O_3$, and obtained the first measurements of the elastic scattering properties of a crystal near a phase transition with the narrow angular resolution inherent in synchrotron radiation. These results were achieved using the high brightness and pulsed time structure during the recent undulator run at the Cornell High Energy Synchrotron Source (CHESS). The 002 reflection of $BaTiO_3$ was measured at temperatures a few degrees above and below the 120°C ferro-electric phase transition. These results clearly show that the Bragg reflection at the temperatures measured is purely elastic (on the 1 neV scale) exhibiting no sign of inelastic, coherent quasi-elastic, or incoherent quasi-elastic scattering. All previous measurements of samples with unknown elastic properties on this energy scale have been done using a radioactive Mossbauer source to produce the narrow band-width X-rays. However, these past experiments have suffered from the broad collimation required to get sufficient signal, and therefore measure both diffuse and Bragg scattering. Past measurements of $BaTiO_3$ using a radioactive source required days, whereas these synchrotron measurements were done in minutes. These shorter measurement times are needed for investigating transient phenomena. The tight collimation inherent in synchrotron-light sources, especially undulators, provides the narrow collimation of a few arcseconds (both horizontally and vertically) that enabled measurements with both narrow angular collimation and the narrow energy resolution of a Mossbauer line.

The dynamic aspects of materials (e.g., the mechanisms of phase transitions and solid state diffusion) are of both fundamental and technological importance, but are often poorly understood and difficult to measure. The ability to separate the inelastic scattering from the static structural effects, as well as to observe quasi-elastic scattering are two ways of directly obtaining X-ray information about the dynamics of a crystal. These methods have been of limited value due to the poor angular resolution available from radioactive Mossbauer sources as a result of their low brightness. This experiment demonstrates that we can now separate the inelastic scattering from the static structural effects, as well as look for quasi-elastic scattering close to a Bragg reflection with the narrow energy resolution inherent in the Mossbauer effect. Application of this technique will be significantly broadened by the hundred-fold increase in intensity provided by the new undulators planned for the Advanced Photon Source (APS).

Surface-Induced Ordering of a Polymer Film Detected by X-ray Scattering

The first successful effort to characterize the ordering induced in bulk polymers by the presence of a surface has been achieved at the National Synchrotron Light Source (NSLS). Grazing incidence X-ray scattering was used to assess the interchain and intrachain ordering of polymer molecules near the air or vacuum interface. The results demonstrate that the structure and conformation of the polymer near the surface is far different from the bulk morphology.

The polymer studied was an aromatic polyimide with the chemical acronym, PMDA-ODA. This material is in widespread use in the microelectronics industry and is used at storage ring sources as a window material (e.g., Kapton) because of its excellent thermal and radiation stability and the smooth surface of its films (surface roughness measured in these experiments was about 8Å). The grazing incidence X-ray scattering measurements show that the interface induces an essentially crystalline order at the polymer surface which persists only over short distances (about 90Å) before the normal liquid crystalline structure is observed. Because of the short range of this structure, no techniques have been available to characterize the atomic arrangements near a polymer surface until this synchrotron X-ray approach was perfected. Characterizing the behavior of polymers near surfaces is critical for understanding interfacial mixing, surface tension, and interdiffusion--factors often critical in determining mechanical, electronic, and optical properties of polymers. This work was performed at NSLS by researchers from IBM's Almaden Research Center, Stanford University, and SSRL with support from Materials Sciences.

New Sensor Improves Resolution of Atomic Force Microscope

A new electrostatic force-feedback sensor has been developed at Sandia National Laboratories, Albuquerque, to improve the atomic-scale resolution of the atomic force microscope. The sensor enables the stiffness of the force sensor to be dynamically adjusted by an electrostatic force which is controlled through an electronic feedback loop. Using this approach, the interfacial force is measured through the voltage on the feedback loop. The first prototype of the device was used to measure the force between the tungsten tip of the force sensor and a CuBe substrate. The improved atomic force microscope achieved an interfacial separation resolution of 0.5 nm, about 4 times the atomic radius of the copper (Cu) atoms. This improvement of the atomic force microscopic was developed as part of a Materials Sciences sponsored program in which state-of-the-art methods are required to study the process of adhesion of surfaces at the atomic level.

An understanding of adhesive forces between surfaces is important for understanding the strength and wear of materials and for improving manufacturing technologies. The atomic force microscope is an instrument which was developed in recent years which enables the experimentalist to study forces at an atomic level with atomic resolution. A major limitation in previous attempts to measure the interfacial force versus displacement relation is the instability that occurs when the interfacial force gradient is greater than the compliance of the force sensor. At the point of instability, the two surfaces catastrophically adhere and all information concerning the interfacial force displacement relation is lost. Using the electronic feedback loop to control the sensor displacement overcomes the instability and enables a full range of interfacial adhesive forces to be probed. This new capability will allow direct comparison between theoretical models for interfacial adhesive forces and experimental measurements of adhesion between well-characterized surfaces.

Advanced Neutron Source (ANS) Design Planning

The National Steering Committee for the Advanced Neutron Source (NSCANS) met on June 13, 1991, to review the progress of the Advanced Neutron Source (ANS). NSCANS is a peer group that was established in 1987 to serve as a forum for the user community to identify anticipated needs, to guide the design effort, and to weigh trade-offs associated with different research groups. The agenda included progress reports on the ANS project, cold source R&D, passive safety features of the ANS, instrumentation and neutron guide R&D, positron source, and a discussion of extended core life of the ANS. The extended core life was a significant issue. By decreasing the power from 362 MW to 300-330 MW, the core life could be extended to 17 days which would permit a 3-week operating cycle, improve operating margins, and reduce operating and construction costs. The main reason that the core life can be extended is that recent progress in the fuel design reduces the rate of oxide formation on the aluminum fuel plates which in previous designs limited core life because of reduced heat transfer across the oxide film. The ANS will still meet the criteria for neutron flux at the reduced power. NSCANS agreed with the extended core life provided that the materials irradiation and transuranium production design criteria are still met. Preliminary calculations indicate that these criteria can also be met. Observers from NSF, OMB, Japan, Canada, and Europe attended the meeting.

Basic Energy Research Advances

First-Ever Room Temperature Organic-Based Magnet

A scientific breakthrough in the decade long search for a plastic magnet was announced in the June 7, 1991 issue of the journal Science.

A DuPont-Ohio State University research team, supported by Materials Sciences, announced the discovery of a vanadium-containing organic polymer exhibiting magnetism at temperatures up to 350K (170F). The previous record critical temperature for an organic-based material (discovered by the same research group earlier this year) was 8.8K (-475F).

The new polymeric material was synthesized by reacting two non-magnetic organic compounds-a vanadium organometallic, bis(benzene)vanadium, and tetracyanoethylene (TCNE). The reaction product is an insoluble amorphous black solid which exhibits field-dependent magnetization and hysteresis demonstrating that it is a room temperature magnet. The critical temperature could not be estimated as it exceeds 350K (170F), the thermal decomposition temperature of the sample. The empirical composition of the reported material is $V(TCNE)_x \ y(CH_2Cl_2)$ with $x \sim 2$ and $y \sim 1/2$. This new magnet is stable when protected from the atmosphere. The magnetic strength is equal to about 1/60 of an equal mass of iron.

Possible uses of molecular/plastic magnets include the magnetic storage of information, mechanical devices (in particular, micromechanical devices) and electromagnetic interference shielding.

High-Accuracy Control of Industrial Semiconductor/Laser Process

On August 29, 1991, a group from AT&T Bell Labs and IBM Yorktown Heights using radiation from the SPEAR storage ring at SSRL recorded X-ray oscillations resulting from continuous layer-by-layer growth of GaAs on GaAs (001) substrates. These are the first measurements demonstrating this growth mode for an organometallic vapor phase epitaxy (OMVPE) reactor running at normal growth temperatures and pressures. OMVPE is widely used in industry for the manufacture of semiconductor devices and the manufacture of high performance lasers for optical communications systems and datalinks. These experiments used grazing incidence X-ray scattering and extended X-ray absorption fine structure measurements to perform an in-situ, real time analysis of the epitaxial growth of GaAs and InGaAs on InP and GaAs substrates using tertiarybutylarsine, trimethylgallium, and trimethylindium as source materials.

These experiments have revealed, for the first time, X-ray intensity oscillations from a continuously-growing film of GaAs. These oscillations occur because X-rays are scattered weakly from partially-filled layers and strongly from complete atomic layers. This ability to precisely measure the occupancy and lateral correlations of the top, growing layer is a powerful tool for the characterization of crystal growth. Using this tool and controlling process parameters such as temperature, pressure and stoichiometry, the group has been able to understand the microscopic growth mechanisms and to characterize and control the nucleation and growth behavior of these films. From this information, they were able to optimize the process parameters and to grow single monolayers (and even fractions of a monolayer) of high-quality epitaxial GaAs and InGaAs with precise control.

These results are the first of their kind in the world and demonstrate that, with the proper analysis tool, organometallic vapor phase epitaxy can be subjected to high accuracy process controls. Such process control will allow the optimization and extension of this powerful growth technique.

Phonons Modes Characterized in High Temperature Superconductors

In research support by the Division of Materials Sciences, triple-axis neutron spectrometry at HFIR has been used in conjunction with experiments at the Oak Ridge Electron Linear Accelerator to show that phonons are connected closely with superconductivity in the ceramic superconductors. The results show that the phonon modes for the copper atoms in the copper-oxygen planes soften dramatically to the transition temperature, while those modes propagating along the c-axis are unaffected. The neutron results have permitted the examination of individual phonon modes and showed that a number of inplane modes soften and broaden at the transition temperature, particularly near the zone boundary. The fact that some phonon modes decrease in energy at the transition temperature shows that there is a direct coupling between superconductivity and certain phonon modes, namely those propagating in the copper-oxygen planes. The change in width of the mode gives an estimate of the electron-phonon coupling constant which appears to be much larger than in conventional superconductors.

Designing Crystal Defects to Improve Superconductivity

Recent studies have demonstrated that properly tailored defects can greatly increase the current carrying capability of the high temperature superconductor $Y_1Ba_2Cu_3O_7$ ("1-2-3"). Specifically, scientists from ORNL supported by Materials Sciences in collaboration with scientists from the IBM Watson Research Center have irradiated single crystals of 1-2-3 with energetic (580 MeV) ions of tin using the Holifield Heavy Ion Accelerator at ORNL to produce linear columns of highly damaged material in the single crystal. These columns act as pinning centers for the magnetic flux or vortices and are particularly effective at inhibiting flux motion, since both the damage and the flux are linear structures. The effects are most striking at high temperatures in large magnetic fields. For example, the critical current (J_c) at 77K exceeded 10^5 Amp/cm^2 in a field of 4.5T in a heavy-ion irradiated crystal; which is a substantial improvement. These experiments demonstrate that the potential operating range of the "1-2-3" material can be extended to substantially higher fields and temperatures. Thus, one more barrier to technological applications of high temperature superconductors has been overcome.

First All High-T_c SQUID Magnetometer Developed

An all high-T_c thin-film SQUID magnetometer with unprecedented sensitivity has been fabricated and tested by a group of LBL investigators led by John Clark and supported by Materials Sciences. At a measurement frequency of 10Hz, its sensitivity is 3×10^{-12} tesla/Hz$^{1/2}$; the best performance yet reported for a thin-film, high-T_c magnetometer.

This work, for which two patents have been filed, is not only of significance for SQUIDs, but will be central to any future high-T_c electronics technology. The new magnetometer for example, is sufficiently sensitive for a number of SQUID applications including geophysics and nondestructive testing. A further improvement in sensitivity by one order of magnitude is believed to be possible in the near future; if achieved, the instrument would be adequate for certain types of magnetocardiology. This work was performed in conjunction with scientists from Conductus, Inc., with partial support from the State of California's Competitive Technology Program.

Chemistry Provides Clues to Avoiding Stress-Corrosion-Cracking of Pressurized Water Reactor (PWR) Cladding

An Ames chemist, Professor John Corbett, whose research is supported by Materials Sciences, predicted in a 1988 Journal of Nuclear Materials review article that it appeared possible that carbon would greatly reduce stress-corrosion-cracking in PWR cladding through the formation of very stable carbon-centered zirconium cluster iodides. Corbett had earlier synthesized for the first time some of these compounds and discovered their unusual stability. PWR fuel elements at the Chalk River nuclear research complex in Canada are composed of a graphite-UO_2 dispersion where the graphite is thought to act as a "lubricant" and, therefore, improve crack resistance. Corbett's suggestion was possibly another explanation. Scientists at Chalk River became very interested in Corbett's suggestion and initiated experiments to identify such crystals.

More than one year ago, Corbett provided the Chalk River scientists with samples of $Zr_6I_{12}C$, $Zr_6I_{14}C$, and $C_3Zr_6I_{14}C$ to use for identification and characterization purposes. The first results of the Chalk River experiments indicate that Corbett's predictions are correct. In initial experiments, large (5μ) crystals of $Zr_6I_{12}C$ were identified from a mixture of Zr, ZrI_4, and graphite at 230C, a representative innerwall temperature of a PWR fuel system in operation. These cluster carbides were also detected in a burned fuel rod. Experiments are just beginning to extend the observations to working systems (typically too radioactive to examine easily).

This work may lead to a new understanding of the role of the graphite dispersion in reducing stress-corrosion-cracking of the cladding in PWR fuel rods and, thus, to new rod designs.

Relativistic Effects First Measured via Resonant Transfer with Excitation (RTE) Experiments

A team of scientists has reported the first experimental test of Resonant Transfer with Excitation (RTE) where relativistic effects are clearly manifest. The team, led by scientists supported by the Division of Chemical Sciences, successfully measured the RTE cross sections of ninety-times ionized uranium ions (a uranium atom stripped of all but two of its electrons) in collision with hydrogen gas molecule targets. The experiments were performed using the LBL Bevalac, the only U.S. accelerator able to provide the necessary ion beam energies. Remarkably, the results were found to be in excellent agreement with theory on an absolute basis. RTE, referred to as the poor man's dielectronic recombination (DR) experiment, is the capture of an electron by a projectile ion with the simultaneous excitation of one of the projectile's electrons during a collision with a target atom. In RTE, the electron captured is initially captive of the target atom. In DR, the collision is with a free electron with the same result, simultaneous capture and excitation. DR experiments require use of a far more elaborate experimental end station. Scientists have been able to account for the difference between capture of a free and a captive electron and can translate RTE to DR cross sections. The technological interest in DR is that it involves an energy loss process in fusion energy plasmas since the collision energy can be lost by radiation and must be taken into account in energy balance calculations. The support of HENP is also acknowledged in this work.

Hysteresis Models Applied to Engineering Problems

Research supported by the Engineering Research Program has resulted in a monograph entitled "Mathematical Models of Hysteresis" by Professor J. Mayergoyz (University of Maryland). The book is the first treatment of methods for representing systems with memory (hysteresis) in real engineering situations. As such it will prove useful to electrical, mechanical, chemical, nuclear and civil engineers. The approach presented in the book prescribes the measurements on the systems needed to construct an operator representing the correct hysteresis loop. It can then be included in numerical simulations of the system behavior. Of course, for more theoretical studies, one can postulate the details of the operator, including piecewise continuous models of the hysteresis loop.

Fundamental Chemistry Applied to a Nuclear Scrap Waste Problem

Studies at Los Alamos National Laboratory in the Heavy Element Chemistry program on the fundamental chemical properties of uranium have provided the basis for safer, low temperature processing of uranium, neptunium, and plutonium metallic scrap for recycling. It was discovered that these metals are easily converted to a solution by oxidation with elemental iodine in common solvents such as alcohol. The actinides in the solution are readily converted to chemically stable oxides which are easily processed for recycle. This has attracted the attention of the LANL Waste Management Group which plans to expand this effort to the pilot plant scale in FY 1993. Handling of these nuclear materials generates metric ton quantities of hazardous scrap which are stored in dry oil due to the extreme chemical reactivity of the metal. Present methods for converting this scrap into a form for recycle involve cleaning off the oil and burning the pyrophoric metal to the oxide or dissolving it in acid. The former route is dangerous because of the possibility of uncontrolled oxidation or explosion and the latter results in an acid waste stream.

Antibody Catalyst Discovered for First "Non-Biological" Reaction

Scientists at the Lawrence Berkeley Laboratory, supported jointly by Materials Sciences and Energy Biosciences, have developed a "catalytic antibody" that catalyzes one of the two most important reactions in organic synthesis, a two substrate Diels-Alder addition.

The use of biological catalysts in the synthesis of novel compounds and materials had, until now, been thought to be restricted to the synthesis of products commonly thought of as "biological," including unusual variants of polyamides, lipids, and polysaccharides. Important as these new materials will be, the attractive properties of biological catalysts for materials synthesis--their high rates of reaction, extraordinary specificity for starting material and product, absence of toxic by-products, and low energy requirements--make it desirable to identify enzyme activities that can catalyze reactions leading to "non-biological" substances as well. The new catalytic antibody reported here is the first of this kind to be discovered. Although there exist over 1500 known enzymes, there are no documented examples of any that catalyze the Diels-Alder reaction. Not only does this achievement illustrate the power of the catalytic antibody approach for generating tailor-made enzyme-like catalysts, it also proves the claim that catalysts can be created for the synthesis of complex new, "non-biological" molecules. Continuing work involves investigating the use of such antibodies to synthesize novel polymeric materials.

Ultra-Sensitive Mass Spectroscopy Yields New Information on Volcanic Eruptions

Newly developed mass spectrometric techniques at LANL have been used to investigate both the processes and timescales of magma formation prior to eruption. Studying uranium-series isotopic abundances in minerals erupted in major volcanic eruptions whose dates are accurately known, A.M.

Volpe and M.T. Murrell have been able to show on the basis of disequilibrium between the radioactive isotopes in the series 238U-226Ra that the time for crystal formation within crustal magma chambers may be relatively short prior to eruption. Measurements on minerals from three strato-volcanoes (those often displaying conical shapes), Mounts Shasta (CA), St. Helens (WA), and Erebus (Antarctica), indicate that the entire process of forming melts at depth, through chemical fractionation, crystal growth, and eruption occurred in much less than 10,000 years. Measurements of the type needed to date the minerals requires precise measurements of 226Ra at femtogram abundance level (one part in a million-billion), and this is made possible using the solid source mass spectrometric methods developed at LANL. Beyond providing basic information of how magmas form, these techniques may have practical applications in geologic hazard risk assessment. Shasta and St. Helens are characteristic of volcanic arcs, such as found in the Circum-Pacific belt. Mount Unzen in Japan and Mount Pinatubo in the Philippines, two currently destructive volcanoes in the news, typify this potentially explosive and very hazardous volcano type.

New Catalyst for the Conversion of Carbon Monoxide

A new catalyst for the conversion of carbon monoxide to carbon dioxide has been discovered by a Chemical Sciences researcher at the University of Pennsylvania. This new catalyst exceeds by a factor of four the best commercial catalysts known for this reaction. Carbon monoxide conversion is essential for air quality in automobiles or in tightly enclosed spaces such as the space shuttle or highly insulated homes and offices.

This discovery came as a serendipitous observation while attempting to understand titania support effects on metal catalyzed hydrogenations. The catalyst consists of metallic gold on a titania support, which has not heretofore been recognized for its catalytic activity. The extent of improved activity should be of considerable commercial interest, since this catalyst is completely compatible with the existing commercial practices for carbon monoxide conversion in tightly enclosed spaces.

First "Magnetocardiograms" of the Human Heart

An all high T_c thin-film SQUID magnetometer with unprecedented sensitivity has been used to record the faint magnetic fields produced by the human heart--the first "magnetocardiograms" to come out of this new technology. The technology and the instrument were developed by a team of LBL researchers (headed by John Clarke) in collaboration with a small California company (Conductus, Inc.). The project is being supported by the Division of Materials Sciences and the California Competitive Technology Program.

The noninvasive detection of magnetic signals from the human heart and brain (normal by-products of the electrical activity of these organs) has extraordinary diagnostic potential. The magnetocardiograms are not new in themselves; many groups around the world have made similar measurements using SQUIDs based on low-temperature superconductors for more than a decade. However, these instruments are cumbersome, expensive, and require liquid helium. The LBL group, "to make a point," used a $15 thermos purchased from a local drugstore to hold the liquid nitrogen in which the SQUID is operated.

Sponge for Mercury Spills Discovered

Scientists from the Manuel Lujan, Jr. Neutron Scattering Center (LANSCE) facility at Los Alamos National Laboratory have discovered recently that mercury can be intercalated into titanium disulfide (TiS_2) at ambient temperatures. Mercury can also be regenerated quantitatively upon heating the resulting compound, Hg_xTiS_2, to temperatures above 250°C. The regenerated host showed no signs of structural or compositional deterioration. These findings suggest that titanium disulfide may be a prototype material for a class of recyclable "sponges" for use in mercury clean-ups. It has been found that TiS_2 can absorb up to twice its own weight in mercury, resulting in a compound with the stoichiometry of $Hg_{1.3}TiS_2$.

From the point of view of basic science, this reaction is also intriguing. Unlike other metals, mercury was found to be intercalated into the host primarily as the neutral species. For other metals intercalated, electron transfer from the metal to the host conduction band is the primary driving force for the intercalation. Furthermore, a reversible thermal event near 195°C associated with the intercalated mercury in the host, likely due to Hg_x clusters, was observed prior to mercury deintercalation above 250°C.

This new compound has been characterized by neutron and X-ray powder diffraction, X-ray photoelectron spectroscopy, thermogravimetric analysis, differential scanning calorimetry, ion-exchange/X-ray fluorescence spectroscopy, and incoherent inelastic neutron scattering.

Catalytic Activity Probed Under Actual Industrial Process Conditions

Among the major problems in understanding catalysis are the difficulties found in real-time analyses of reactive intermediates under actual in situ industrial process conditions where elevated temperatures and pressures preclude the observation of elusive species by the usual techniques.

For the first time, chemists at ANL have directly observed catalytically important reaction intermediates in situ. The new technique uses a toroid detector as part of a high pressure NMR probe. The probe is unique in that being highly sensitive, direct observations of nuclei with low NMR receptivities such as may be present in homogeneous catalysis are now made possible.

The new detector probes use toroids in which optimum magnetic flux is confined to internal regions of the coil, thus solving the problem of sensitivity losses through magnetic coupling with metal pressure vessels. Six times greater sensitivities than with conventional NMR detectors have been demonstrated, and the new toroid probes have been granted a U. S. Patent. The catalytically important but extremely insensitive ^{103}Rh species has now been detected in a high-pressure probe and the steady-state concentrations of catalytic cobalt species in the Oxo reaction have been directly observed for the first time. These observations of important nuclei should allow for in situ scrutiny of more important catalytic reaction intermediates in the future, thus enhancing our basic knowledge of how chemical reactions occur.

Coal Micropores Analyzed by Xenon-129 NMR

Coals are thought to be cross-linked, 3-dimensional networks whose irregular building units enclose extensive pore structures. Understanding this porosity is of great significance since it influences coal behavior during mining, preparation, and coal utilization processes such as liquefaction and gasification.

Now, through the efforts of chemists at ANL, the structural properties of these micropores are being probed using ^{129}Xe NMR spectroscopy. Pore structures in three Argonne Premium coal samples have been characterized. Chemically inert gaseous Xenon, with a relatively large van der Waals radius (2.2 Å), readily penetrates the micropores in coal creating small perturbations in the Xenon atom's large, polarizable electron cloud. The polarized atom may be detected in the 20 Å diameter micropores through NMR spectroscopy. Two pore structures of similar size were found and tentatively assigned to aliphatic and aromatic regions in the coals.

Many techniques have been employed to characterize coal porosity, but the properties of the micropores have been very difficult to ascertain. The ^{129}Xe NMR results are helping to develop a more accurate theoretical model of coal that will describe its reactivity and swelling characteristics, the understanding of which is so necessary for the efficient utilization of an important indigenous resource.

Control of Crust Growth and Gas Retention in Synthetic Hanford Wastes

Scientists at DOE's Pacific Northwest Laboratory (PNL) have shown that crust growth and retention of flammable gases which are problems in Hanford double-shell radwaste tanks are controlled by adsorption of organic components onto the surfaces of inorganic particles in the wastes. The Hanford double-shell tanks contain large quantities of chemical and radioactive wastes from past defense activities and are of considerable concern because of their perceived high risk. Tank 241-SY-101, for example, periodically releases hydrogen and nitrous oxide gases in flammable concentrations. In laboratory tests conducted on synthetic Hanford double-shell wastes, adsorbed organic components made the solid particles less easily wetted by the liquids in which they were immersed and provided a surface more likely to adhere to gas bubbles that were generated in the liquid. Gas bubbles provided ample buoyancy to float some of the solids to the surface of the liquid. The solid particles aggregated into a solid crust. Gases also were retained at the bottom of the container in sold/gas bubble combinations that were insufficiently buoyant to float to the surface. Stable crusts could also be grown through synthetic waste slurries containing surface-active organic components, similar that which occurs in mineral flotation widely utilized by the mining industry. Floating crusts could not be formed from synthetic waste components containing no organic components. Development of a fundamental understanding of the physical and chemical phenomena responsible for the behavior of the Hanford waste tanks is important for the development of approaches to mitigating the release of flammable gases. This work was carried out by L. R. Pederson and S. A. Bryan under a program supported by the Division of Materials Sciences.

Thin-Film Temperature Sensors Developed

Scientists at DOE's Pacific Northwest Laboratory (PNL) have developed a novel technique, based on fluorescence lifetime measurements, for the in-situ determination of thin-film temperatures during high-temperature characterization and testing. Homogeneous thin films (less than 100 nanometers thick) of either ruby (chromium-doped alumina) or Sm:YAG (Samarium-doped yttrium aluminum garnet) are deposited from solution on various substrates as sensors for determining the temperature of a second material, subsequently deposited, that is the subject of study. The red fluorescence, which can be excited in both of these sensor materials, exhibits a temperature-dependent lifetime that provides an optical method for the in-situ determination of thin-film temperatures to within $\pm$ 1 K. The ruby sensor can be used to measure temperatures up to 700 K and is currently employed in ongoing studies of the transformation kinetics and transient film stresses during laser-induced crystallization of sol-gel films. The Sm:YAG sensor, which is the subject of a PNL patent application and is undergoing additional development, will extend the measurement range to much higher temperatures (greater than 700 K). These materials can also be used to coat the end of an optical fiber to produce a flexible temperature probe of any environment or material that comes in contact with the fiber tip. This research was carried out at the Pacific Northwest Laboratory by G. J. Exarhos and N. J. Hess under support from the Division of Materials Sciences, Office of Basic Energy Sciences.

Non-Imaging Optics Utilized in Automobile Tail-Lights

The principles of non-imaging optics studied by Professor R. Winston (University of Chicago) have been incorporated in a new design of automobile tail-lights. That design, reduced to practice by Hewlett-Packard, uses instead of incandescent lights a bank of 20 light emitting diodes on each side of the car. The 1992 Ford Thunderbird will be the first model to use this new technology. While there have been other examples of commercialization, as far as it is known, this is the first instance of technology transfer to a consumer product based on long-term engineering research.

Atmospheric Measurements on Effects of Kuwait Oil Field Fires

Pacific Northwest Laboratory has been requested to provide instrumentation in support of the Kuwait Oil Field Fire Experiment (KOFFE) in Saudi Arabia. This is a multiagency program involving NSF, DNA, and DOE (OHER) and will evaluate the plume migration as it passes over Saudi Arabia. The experiment involves a number of aircraft observations and deployment of land-based sensors. PNL has been requested to supply four of the rotating shadow-band radiometers (RSR) to determine atmospheric aerosol concentrations, and investigators at PNL will be involved with the data analysis and interpretation. The instruments will be deployed to complement instrumentation set out by SAIC under DNA auspices, and will be used to provide long-term, ground-based base-line data for correlation with the airborne sensors. This instrumentation, to be used in the DOE ARM Program (Global Climate Change), SERI, NOAA, and by University researchers, in addition to those at PNL, was developed in the BES/Geosciences program to acquire needed troposphere and stratosphere. It was the centerpiece in the cover illustration of "The Futurist" (May-June, 1991 issue) and as the logo for the article, "The Greening of High Tech," in that issue. The Futurist (ISSN 0016-3317) is the bimonthly journal of the World Future Society.

Tracer Experiments Map Underground Water Flow

At the Annual Meeting of the Geological Society of America, in November 1990, David Janecky of the Isotope Geochemistry Group at Los Alamos reported on a field experiment to trace the flow of ground water at the Mammoth Hot Springs area in Yellowstone National Park. The test, conducted in cooperation with the U.S. Geological Survey and the National Park Service, was designed to determine whether a geothermal area north of the park is connected with the Mammoth Terraces system and to monitor the flow from the terraces into the Yellowstone River. The tracers, consisting of a suite of stable isotopically labeled, naturally occurring, organic compounds such as amino acids and organic acids, were detected in all sampled outflow areas as far as several kilometers from the source. The nine different tracers were detected by gas chromatography/mass spectrometry. The method is highly sensitive and requires only small samples. A portable version of the instrument that will enable investigators to run analyses in the field is under development at Los Alamos. The suite of organic molecules and stable isotopically labeled organic compounds have chemical and physical properties identical to naturally occurring compounds but retain extremely low natural backgrounds. Further experiments are being designed to trace flow paths in oil and geothermal reservoirs and in environmental systems. The development of this technique was supported by BES/ Geosciences.

Improvements in Superconducting Microcomposites Produced from Metallic Precursors

Research at MIT by John Vander Sande and Wei Gao, funded by OBES/DMS, has recently led to considerable improvements in the critical current density obtained in high temperature superconducting wires. The process begins with melt spun metallic precursor ribbons of Bi-Pb-Sr-Ca-Cu-Ag which are then oxidized, leading to a microcomposite of $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$-Ag. The process then continues with a mechanical pressing step. Superconducting ribbons with superconducting transition temperature, $T_{R=0}$ = ~105K and critical current densities, J_c(77,OT) as high as 4000 A/cm^2 have been achieved to-date. This is only a factor of ~5 lower than the highest J_c values presently quoted for a continuous wire processing methodology. The process has also been applied to multiple stacks of ribbons clad with a thin metallic sheet with comparable results. The total process has a high potential manufacturability inasmuch as the combination of melt spinning and rolling can lead to a high production of very long wires or ribbons. The formability of the ribbons or wires is very good and the size and thickness of the superconducting composite can be accurately controlled throughout the processing steps. The wires are strengthened by the cladding and the deformation steps. This method can also be used to join superconducting wires to each other or to normal metal wires. The superconducting wires produced with this method have good environmental stability; the electrical transport properties do not degrade even after an immersion in water for 30 days.

New Source of Yttrium-90 for Cancer Treatment

A new process for the removal of strontium-90 (^{90}Sr) from nuclear waste has been adapted to the preparation of yttrium-90 (^{90}Y) in high yield and with purity required for regio-specific cancer treatment. The separation is accomplished by chromatographic adaptation of the SREX and TRUEX processes developed for extraction of Sr and transuranic elements, respectively, from nuclear waste. The source material consists of the fission product ^{90}Sr separated from nuclear waste. The ^{90}Y isotope accumulates as a result of beta decay of ^{90}Sr. Sr is therefore always present in the source material but, for medical applications, its concentration must be reduced to a level below 100 parts per billion (ppb). This level is achieved with three chromatographic stages. The first two employ columns based on the SREX process to remove Sr. The third stage uses a column based on the TRUEX process to sequester the remaining ^{90}Y.

The ^{90}Y is recovered by treating the stationary phase from the TRUEX column with water. Because of the specificity of the TRUEX process, all other metallic impurities are reduced to tolerable levels. An extraordinary separation factor of 10^{14} for the yttrium is achieved. The process uses only nitric acid and water as reagents and is simple and inexpensive.

New Methods for Hardening and Improved-Wear of Aluminum Discovered

A Materials Sciences sponsored study at Sandia National Laboratories has shown that oxygen-ions implanted into aluminum produce near-surface hardness comparable to that of high-strength steel, reduces sliding friction by more than 60 percent and suppresses catastrophic galling wear. Microindentation of one-half micrometer implanted layers revealed flow stresses near three gigapascals, several times greater than previously achieved for any aluminum alloy. This strength results from the unique implantation-produced microstructure. The aluminum matrix contains twenty volume percent of nanometer-size aluminum oxide precipitates, and these strongly impede dislocation motion. The large improvements in friction and wear were observed in unlubricated sliding tests where the implanted aluminum disc moved against a steel pin.

Aluminum alloys are widely used where weight is important, as in aerospace and ground-based transportation systems. Compared to steel, however, the strength of conventional aluminum-based materials is modest, ranging up to about one-half gigapascals. Moreover, the friction and wear behavior of aluminum is notorious for exhibiting pronounced stick-slip galling and adhesion which inhibits bearing-surface applications. The above technical achievement affects these limitations in two ways. First, it established a new microstructure which, if successfully reproduced in bulk aluminum, would greatly enhance the strength of structural components. Second, it identifies oxygen-ion implantation as a promising treatment for the fabrication of technologically viable aluminum sliding surfaces.

Improved Method for Strontium Extraction from Nuclear Waste

Chemical Sciences researchers at Argonne National Laboratory have developed a separation process for reducing the strontium content of nuclear wastes by a factor of over 100,000. Strontium-90 is a major hazard in nuclear waste because of its 30 year half-life which necessitates long term storage. The new process is based on research leading to an understanding of the molecular coordination chemistry of the Sr^{2+} cation and its extraction from nitric acid solutions. A crown ether complexing agent, dicyclohexano-18-crown-6, binds to the Sr^{2+} and removes it from the acid solution, while at the same time the dissolved water in the octanol diluent removes the hydrated NO_3^- anions. Both the complexing agent and the octanol diluent are commercially available materials. The ^{90}Sr extraction process called SREX (pronounced sir-ex) is operated in conjunction with the earlier developed process for removal of transuranic elements from radioactive waste, called TRUEX, and further reduces the volume of waste which must be isolated in deep storage. Dr. E. Philip Horwitz, ANL, is leader of the team which developed this process and TRUEX.

Solar Energy Conversion Mechanisms Better Understood in the Bacteriorhodopsin Photosynthetic System

Significant advances have been made over the past few years in understanding the initial steps of the energy conversion process in bacteriorhodopsin (bR), one of only two natural photosynthetic systems; the other is the chlorophyll (Chl) system. While the molecular mechanisms are different in the two systems, the fundamentals are quite comparable. In work at UCLA supported by the Chemical Sciences Division rapid time resolved spectroscopies have been used to show that bacteriorhodopsin does not have a separate antenna molecule to absorb solar energy. Rather a retinal molecule itself captures the solar energy and undergoes a chemical isomerization. Rapid time resolved Raman spectroscopy has been used to prove that the structural changes in retinal are the first step in the solar energy to electrical energy conversion in bR. The isomerization leads to the separation of a positively charged atom on the retinal from a neighboring negatively charged group. The charge separation leads to a proton gradient which drives subsequent chemical changes. Once these mechanisms are fully understood an artificial solar energy converter, based upon that derived by nature, might be built.

Synthesis of Smallest Ring Molecule Containing a Carbon-Carbon Triple Bond

Compounds with carbon-carbon triple bonds, acetylenes, are normally linear due to the electronic orbitals bonding the two carbon atoms. For many years chemists have attempted to disturb this linearity by incorporating the triple bond into a cyclic structure, with the limit being apparently reached in 1972 with the isolation and characterization of a 7-membered ring acetylene.

Basic Energy Sciences-supported researchers at the Ames Laboratory have now synthesized the first 6-membered ring molecule containing a carbon-carbon triple bond. As part of a program of synthesis of silicon-acetylene polymers as preceramic materials, it was serendipitously discovered that condensation of dilithioacetylene and 1,4-dichlorotetrasilane does not produce the expected linear polymer but rather cyclizes to afford a 6-membered ring containing 4 silicon atoms and the pair of triply-bonded carbon atoms. The reaction scheme is a simple, high yield (75%) synthesis. The structure of the new molecule was confirmed by single crystal X-ray diffraction and the Si-C-C bond angle was found to be 146.8°, a remarkable 33.2° deviation from the normal 180° angle.

Method Developed to Understand 3-D Structure of Proteins

The July 12, 1991, issue of **Science** carries as its features research article a paper entitled "A Method to Identify Protein Sequences that Fold into a Known Three-Dimensional Structure". The first author is Dr. James U. Bowie, an Energy Biosciences post-doctoral fellow supported through the Life Sciences Research Foundation (LSRF). The work was performed in the laboratory of Dr. David Eisenberg of the Department of Chemistry and Biochemistry at UCLA. The research is important in gaining a better understanding of the mechanism of protein folding so that ultimately insights into protein activity, such as enzymatic reactions, may be gained. Dr. Bowie is now in his third year as an Energy Biosciences LSRF fellow.

Breakthrough on Atomic Ordering in Thin Films

Researchers at the University of Utah have made a significant breakthrough on the ordering of III/V semiconducting alloys. The main advance is the development of a model for the formation of ordered structures that involves the motion of atomic steps on the surface. Based on this model, which has been confirmed by experimental results, a procedure was developed for the controlled formation of ordered domains using grooves etched in the surface to control the motion of the surface steps. This unique process has resulted in the first controlled growth of very large domains (several square microns) in thin films of III/V compounds. This breakthrough may lead to the accelerated use of these advanced materials in improved electronic and photonic devices. This work was carried out at the University of Utah by Professor G. B. Stringfellow, G. S. Chen, and D. H. Jaw under a grant from Materials Sciences.

High-Temperature Crack Growth Measured in Ceramic Matrix Composites

Scientists at DOE's Pacific Northwest Laboratory (PNL) have made the first measurements of high-temperature crack growth in ceramic matrix composites. Subcritical crack growth in SiC composites reinforced with SiC fibers has been measured at 1100°C in atmospheres of both pure argon and argon plus 2000 ppm O_2 utilizing PNL's High-Temperature Mechanical Properties Laboratory (a new state-of-the-art facility). The measurements indicate that the high-temperature behavior of these SiC composites is similar to that of ductile metals, in agreement with a recent model for crack growth developed at PNL. There is a stress intensity threshold for crack growth followed by three distinct stages of crack growth. Preliminary results indicate that the presence of a slight oxygen environment causes a more rapid crack growth at low stress intensities. This research was carried out by C. H. Henager, Jr., R. H. Jones, and J. L. Humason of Pacific Northwest Laboratory under support from the Division of Materials Sciences, Office of Basic Energy Sciences.

Molecular-Scale Images of Monolayers at Metal-Liquid Interfaces Produced

Chemical Sciences researcher Marc Porter and his group at Ames Laboratory are the first to report the use of scanning tunneling microscopy (STM) to produce molecular scale images of monolayers formed at the metal-liquid interface. Images have been obtained for monolayers of ethanethiolate (ET) and *n*-octa-decanethiolate (OT) spontaneously adsorbed on gold films epitaxially grown on mica substrates. For both ET and OT, the image corresponds to that expected for a hexagonally packed adsorbate overlayer with nearest-neighbor spacings of 0.5 (±0.02) nm and 0.87 (±0.04) nm, respectively. As Porter's work seeks to use principles of molecular recognition to control processes at the metal-liquid interface, the molecular-scale characterization made possible by such images are of great value to the work. Prior methodology permitted only macroscopic measurements, such as electrochemical desorption to determine coverages and characterization of the surface layer by infrared reflection spectroscopy. The work was featured in the June 3, 1991, issue of Chemical and Engineering News.

Further Advances in Methane Conversion to Higher Hydrocarbons

The catalytic oxidative coupling of methane to ethylene has been the subject of substantial research in recent years. About two years ago it was discovered by a chemical sciences supported researcher that the reaction occurred in two phases, one on the surface of the catalyst and one in the gas phase. Determining the extent to which the reaction occurs in the gas phase has been a major concern of all researchers because the gas phase portion of the reaction cannot be controlled by the catalyst and thus is not subject to potential selectivity improvements.

Further work by this same researcher has shown that the gas phase reaction only contributes 10% of the total ethylene. Furthermore, he was able to determine that the undesired reaction of the methyl radicals with oxygen to ultimately form carbon dioxide was largely due to reabsorption of gas phase methyl radicals on the surface and subsequent reaction with surface oxygen. This result means that advances in catalyst design can increase the ethylene yield, and also decrease undesired products.

Improved Synthesis of Superconducting Alkali-Metal-Doped C_{60}

A new solution-phase technique has been devised for the synthesis of the novel superconducting C_{60} buckminsterfullerene compounds, K_xC_{60} and Rb_xC_{60}, where x represents a presently unknown stoichiometry. This technique, which consists of refluxing a mixture of the alkali metal and purified C_{60} in an organic solvent, is much simpler, more reproducible and easier to control than the vapor-transport technique employed in the initial work from AT&T Bell Laboratories.

This work is a collaborative program supported by Materials Sciences in the Chemistry Division and the Materials Science Division at ANL and at the SNL, Albuquerque. The K- and Rb- doped compounds prepared by this technique were confirmed to be bulk superconductors with T_c=18.0 $\pm$ 0.1K and 28.6 $\pm$ 0.1K, respectively, using low-field dc magnetization measurements. The magnetization studies indicated that the superconducting phase occurs as only a small volume fraction (~1% and 5% respectively) of the synthesized product by either synthetic technique. Mass spectrometric studies suggest the superconducting phase may consist of a simple 1:1 salt, MC_{60}, where M is K or Rb. Pressure studies carried out at Sandia National Laboratories on the Argonne-synthesized K_xC_{60} material yielded a negative pressure dependence for T_c, which is consistent with the increase in T_c on replacing K^+ with the larger Rb^+ ion.

Novel FT-EPR Method Developed to Study Mechanisms of Photochemical Reactions

A new experimental technique, Fast Fourier Electron Paramagnetic Resonance, FT-EPR, spectroscopy has been developed by Chemical Sciences-supported researchers at the University of Massachusetts-Boston. In conventional direct-detected EPR, free radicals, and the interaction of their unpaired electrons with nearby nuclei which have nuclear spin, are detected by absorption of microwave radiation as a function of applied magnetic field. EPR is particularly useful when species having unpaired electrons (free radicals) are present in low concentration. The new FT-EPR technique, which involves the Fourier transform of the magnetization induced in the plane perpendicular to the magnetic field applied at various delay times following laser-pulse generation of the free radicals, makes it possible to study their formation and decay with nanosecond time resolution. The instrumentation provides a valuable new spectroscopic tool for kinetic studies of photochemically generated free radicals (such as porphyrins) and their application to biomimetic solar energy conversion.

New Combustion Measurements Improve the Rate Constant Values for Methane Dissociation

Scientists at Brookhaven National Laboratory have made careful measurements of the rate of the thermal dissociation of methane, CH_4 CH_3 + H, over the combustion relevant temperature range of 1700K to 2150K and found the reaction to be four times slower than previously believed. The measurements were made by monitoring the time dependence of the hydrogen atom formation in a shock tube using atomic resonance absorption. The new rate constant will not only affect predictive combustion models, it will also have a strong ripple effect on many other rate constants important to combustion. In the field of chemical kinetics, most chemical reaction rate measurements are relative measurements. The previous measurement of the methane decomposition rate constant was thought to be sufficiently reliable that it could serve as a basis of comparison. As a result of the Brookhaven measurement, many relative rate constants may have to be revised.

Novel Technique Allows Study of the Alkyl Radical Reactions Involved in Hydrocarbon Conversion

Organic radicals are uncharged hydrocarbon fragments which contain an unpaired electron. As a result, they are highly reactive and short-lived in solution. While they are well known to be important as reactive intermediates in organic and organometallic reactions, little is known about the details of these reaction pathways. This is largely due to the lack of a general method for generating the radicals.

Chemical Science sponsored researchers have now developed such a method. The program at AMES Laboratory uses a laser flash photolysis technique to generate an instantaneous burst of nearly any type of alkyl radical by photohomolysis of organometallic complexes. The method has been applied to determining rate constants for oxygen addition to different types of benzyl radicals. Fundamental data derived from these studies are providing support for some models of alkane reactions, as well as some new hypotheses and insights into the important chemical reactions involved in hydrocarbon conversion.

A New Efficient Alkane Functionalization Reaction Studied

Alkanes are generally unreactive molecules and their efficient conversion into olefins and other important petrochemicals remains a major, yet elusive goal in energy research. Much interest has, therefore, been directed to activating or cleaving the alkane carbon-hydrogen bond by the intermediacy of low valent transition metal complexes, but progress has been limited.

Catalysts and mild conditions have recently been observed that permit these conversions. Using a rhodium complex in solution Professor Goldman at Rutgers University has achieved the thermal dehydrogenation of alkanes in the presence of a hydrogen acceptor, under hydrogen pressure at moderate temperatures. Extremely high catalytic turnover rates and yields are obtained. Previous examples have utilized photochemical activation or required severe reaction conditions and had limited efficiencies.

These extremely reactive catalytic systems and mild conditions may lead the way to developing new routes to organic compounds from alkanes which are an abundant potential resource.

Critical Point Opalescence of Electron Gas Measured

Professor Gordon Kino (Stanford University) has reported the direct observation of critical point opalescence of electrons undergoing normal-to-superconducting (and reverse) transition in high T_c

superconductors. The opalescence, evidenced by a sudden increase in the scattering of light, is associated universally with the increase of the level of fluctuations at the critical point. The experiment is non-trivial because the light photons are more energetic than the binding energy of the paired superconducting electrons. Therefore, very low incident light levels must be maintained, or else the measurement itself will destroy the superconducting state by disrupting the electron-pairs.

This is the first measurement of its kind, and steps are being taken to determine if the technique can be used in other cases where electrons in solids appear to undergo a phase change, e.g., space-charge waves.

Direct Observation of Turing Bifurcation

About forty years ago A. M. Turing noted the possibility that a particular type of symmetry-breaking bifurcation in a reaction-diffusion system might lead to the formation of stable, stationary characteristic patterns. Since then, theoretical considerations published in the biological literature have suggested that Turing bifurcation may be at the root of many patterns seen in living systems.

H. Swinney and Q. Ouyang (University of Texas), working on a project supported by the Engineering Research Program, reported in Nature on a new experimental technique. It allowed them to verify for the first time that a recently studied reaction-diffusion process is indeed subject to Turing bifurcation. The key aspect established by the technique in the process under study is that, unlike other chemically induced patterns, here the pattern is stationary as predicted by Turing.

Novel Mixed-Halide Chain Solids Found to Have Potential as Solar Cells

It has recently been shown that photoexcitation of mixed-halide MX chain solids, such as platinum chlorides and bromides, above the band gap leads to long-lived electron-hole pair separation. The electron and hole defects created upon photoexcitation separate into differing chain segments and are stable for long times (>hrs) at low temperature. Spectral and theoretical studies show the existence of edge states (junctions between differing halide segments) with absorption above the band gap ("ultragap" edge states). The driving force for the electron-hole pair separation is not yet known, although it may be related to direct excitation of the "ultragap" edge states. The excitation dependence of the photodynamics are currently being explored.

The central question in solar energy conversion and in photosynthesis is the separation of the electron and hole following photoexcitation. While photosynthetic bacteria perform this electron-hole pair separation efficiently, it has been difficult to tailor synthetic molecules and materials to optimize this critical step. The mixed-halide MX solids, which contain novel heterojunctions between quasi-1-dimensional chain semiconductors, show efficient electron-hole pair separation upon photoexcitation. The MX bulk crystalline solids themselves have no real potential in solar energy conversion applications. However, if thin films of the MX chains can be prepared directly on a conducting substrate under conditions where the heterojunctions are controlled and fine-tuned to optimize their optical and physical properties, they may be useful. Detailed experimental and theoretical understanding of these novel quasi-one-dimensional heterojunction materials could help in the better understanding of solar energy conversion and the development of other solar cell materials.

This work is being conducted at the Los Alamos National Laboratory under Materials Sciences support.

Solid State NMR Reveals New Information on Supported Pd Catalysts

A ^{13}C nuclear magnetic resonance (NMR) study of 99% ^{13}C-enriched carbon monoxide adsorbed on supported Pd clusters shows that the ^{13}C NMR spectrum consists of two lines. Each line reflects a particular phase of the CO monolayer differing in the arrangement of the CO molecules on the Pd surface. It was found that the transition from one phase to the other depends on temperature and cluster size. The transition appears in the NMR spectrum as a change in shape and position of the line. Supported Pd clusters are used in industrial catalysts for the hydrocracking of petroleum distillates, automotive exhaust treatment, and other catalytic processes.

It was found that the surface diffusion rate for CO is much higher in one phase than in the other. The CO molecules shows little surface mobility until the surface phase transition occurs, at which point it becomes highly mobile. The surface diffusion rates also depend on cluster size, being larger when CO is adsorbed on large clusters. It was also observed that CO bonds differently to small Pd clusters than to large ones. On small clusters, CO seems to stick mainly to one surface atom in a linear configuration, whereas it occupies a bridge site bonding to two surface atoms on large clusters.

The use of CO to study fundamental aspects of surface interactions is well established and thought to be fairly well-understood. These findings contrast with previous concepts describing CO behavior on Pd clusters. It had been assumed that the bonding was not dependent on cluster size and that a single CO diffusion rate on the Pd surface was assumed. Both of these assumptions have been shown to be incorrect by the present results.

This work was done in Professor C. P. Slichter's group at the Materials Research Laboratory of the University of Illinois and was supported by the Materials Sciences Division.

Puckered Porphyrins Offer Way to Tailor Electron Transfer Rates

Conformational variations in porphyrin molecules provide an attractively simple mechanism for controlling their chemical reactivity. Porphyrins, which are similar to chlorophyll molecules, absorb light in the visible region and can effect solar photochemical energy conversion by photoinduced electron transfer. They have long been considered by chemists to be essentially flat molecules. The conformational variations, changes in the shape of the skeletal ring system from planar to puckered, are introduced by steric crowding of substituents attached to the rings. Combined experimental and theoretical studies under the direction of Dr. Jack Fajer at Brookhaven National Laboratory have correlated conformational parameters, obtained by x-ray crystallographic structure determinations, with light absorbing properties and chemical reactivities of planar and deliberately distorted porphyrins. The work has shown that the substituents and their effect on conformation can alter the distribution of electrons in a predictable manner and thereby influence electron transfer rates and mechanistic pathways in biomimetic solar energy conversion.

New Uranium Extraction Agent Discovered

A new extractant for uranium when it is present as the uranyl ion, UO_2^{2+}, has been developed that depends on the linear structure of the ion for its specificity. The new extractant molecule is a tripodal tertiary amine carboxylate. This agent is well-suited to the extraction of uranium from neutral aqueous solutions. The complexing molecule encircles the uranium at the midplane or girdle as well as bonding with the apical oxygen atom. It may be possible to use this agent to extract uranium from sea water, the location of most of the earth's uranium. This discovery stems from the research of Dr. Kenneth Raymond, a Chemical Sciences investigator at the Lawrence Berkeley Laboratory and Professor of Chemistry at the University of California at Berkeley. A patent has been applied for.

Acoustically Driven Coherent Light Source Identified

Professor S. Putterman (UCLA) has observed a stable, repetitive emission of photon bursts driven by a source of sound at the upper limit of the hearing range (approximately 25kHz). In the present experiment, sonoluminescent pulses, each containing about 10^6 photons, are emitted at a rate coinciding with the driving sound frequency. The medium is a 25% water solution of glycerine. The light, visible with the naked eye, is blue-green (about .5 m) and emerges from a well-defined region in space, less than 10 m in diameter. The pulse length is probably less than the time resolution of the measuring instruments, i.e. less than 0.6 nanoseconds, or about 100 times shorter than spontaneous emission time. Although there are other possible explanations, the small size of the emitting region, and the short pulse length suggest the possibility of coherent emission. While sonoluminescence is not entirely new, this appears to be the first time that the phenomenon has been produced in a reproducible, controllable fashion, permitting it to be characterized in some detail. Possible patents are under consideration. The Washington Post of August 12, 1991, carried an extensive story about Professor Putterman's sonoluminescence experiments.

Atomic Physics Project Tackles Mysteries of Highly Charged Ions

In the article, "Hollow Excitement Energizes Atomic Physics," the February 16, 1991, issue of Science News reported on an atomic physics project supported by the Division of Chemical Sciences at ORNL. It is a new basic research effort made possible with the advent of stabilized sources of highly charged ions, stripped of nearly all of their electrons, in this case an ECR source. To our knowledge, this study is the only one of its kind in the U.S. and provides information on the behavior of highly charged ions useful to fusion energy development. The project is still in the exploratory stage but the preliminary results have already challenged our fundamental understanding of how these ions are able to attach many electrons at once and how these electrons once captured release excess energy to form a stable atom. In the initial process, the electrons attach themselves to the ion forming a neutral excited atom, i.e., they occupy the atom's higher energy levels leaving the lower levels unfilled. Thus, their designation as "hollow" atoms.

Chemical Reaction Rate Theory Employed to Understand Formaldehyde Decomposition

Scientists at the Lawrence Berkeley Laboratory have recently developed a new approach for characterizing chemical reactions typical of combustion environments. The ability to predict chemical reaction rates, or for that matter, extrapolate measured reaction rates, is greatly hampered by the extraordinary complexity of states in which energy-rich reactants find themselves. "Quantum chaos" is the rather imprecise buzz-word currently used to describe strongly mixed quantum states such as the highly vibrationally excited states of polyatomic molecules. Properties of these states such as chemical reactivity typically show erratic, random-like fluctuations. For example, recent experiments on the decomposition of formaldehyde, H_2CO $H_2 + CO$, show rates that vary by up to a factor of 100 for different individual quantum states, all of which have essentially the same energy and angular momentum. The recent theoretical research has shown, however, that one can understand and calculate the *statistical* properties of such states. For the case of chemical decomposition, ideas from random matrix theory, developed by Eugene Wigner in the 1950's to describe the statistical properties of excited nuclei, have been combined with transition state theory, developed in the 1930's, also by Wigner, to predict the probability distribution of reaction rates for a set of chaotic states. The theory has been applied to the chemical decomposition of formaldehyde and compared with the experimental data with encouraging success.

Enhanced Anharmonicity Observed in Surface Phonons of Copper Metal

Anharmonicity of an unreconstructed surface has been directly measured for the first time in a joint project between ORNL and the University of Pennsylvania supported by the Division of Materials Sciences. An examination of the temperature dependence of surface phonons on Cu(110) using high-resolution electron energy loss spectroscopy gave the energy and lifetime of the surface phonons. In both cases, at the surface where the adjacent atoms move collectively and at the zone edge, where adjacent atoms move out of phase, the phonon energies decreased and linewidths increased as the sample temperature was raised. These effects were larger at higher temperatures - a signature of anharmonic effects. The surface anharmonicity was found to be approximately four times higher than for bulk copper. Anharmonicity in bulk materials is responsible for a number of properties including aspects of thermal expansion, thermal conductivity and specific heat. The results of this discovery imply that anharmonicity is even more important at metal surfaces; certainly much more than previously thought. The enhanced surface anharmonicity has implications for processes such as energy transfer, gas adsorption, vibrational relaxation and surface structure. The latter influences phase transitions, surface melting, diffraction, and thin-film growth. Work is now underway to model the results.

Helium as an Indicator of Large-Scale Fluid Migration in the Crust

Researchers in the Department of Physics, UC Berkeley, in collaboration with workers at LANL have found evidence to support the hypothesis that some mineral deposits in sedimentary basins are related to the injection of "fertile fluids" into basinal areas by pressure gradients resulting from ancient plate collisions and concomitant magmatic activity. Their studies of $^{3}He/^{4}He$ ratios in hydrocarbon gases from the Canadian Alberta Basin reveal an anomalous enrichment of ^{3}He relative to ^{4}He, which is derived from the radiodecay of U - Th in crustal rocks. Having ruled out other possible sources of ^{3}He, they have concluded that the ^{3}He was derived from the earth's mantle and must have been transported over great distances to explain its occurrence in areas of no apparent recent volcanism. The occurrence and magnitude of excess ^{3}He in sedimentary basins may eventually prove to be a reliable tracer for tracking the movement of ore fluids originating from tectono-magmatic processes.

Research on Transport in Random Media Contributes to Cloud-Radiation Models

Professor G. Pomraning's (UCLA) research supported by the BES Engineering Research Program has found an unexpected application of his results, namely cloud-radiation interaction in general circulation models. The current rough models of that interaction correspond to two limiting cases in Dr. Pomraning's theory of particle and energy transport in random media. It is widely recognized that those models are not realistic, but they have been used by default. Experts supported by DOE's Atmospheric and Climate Research Division feel that the new method offers a natural way to treat radiative transfer in a cloudy atmosphere.

New Molecular Models Constructed for Photosynthesis

A series of structurally rigid, three-part molecules have been synthesized and found to duplicate for the first time the high ion pair yield, the charge separation lifetime, and the structural characteristics of the light-energy conversion apparatus of photosynthesis in the solid state. Up until now, no such model system has been made to function in the solid state at any temperature. The research is led by Dr. Michael Wasielewski at ANL. Illumination of the model system with visible light initiates electron transfer reactions which causes charge separation that lasts for 4 milliseconds, more than ten times longer than in previously reported models. The new molecules represent an important step forward in "tuning" the geometry of model systems to the highly efficient natural photosynthetic apparatus and to the development of the concepts needed for efficient solar photochemical energy conversion.

NMR Technique Characterizes Surface Hydrocarbon Intermediates on Catalysts

Determination of the intermediates in catalytic surface reactions has been a longstanding problem. While a number of techniques provide some information on the nature of the possible intermediates, they generally provide little information on the molecular size. Chemical Sciences supported researchers at Ames Laboratory have developed a Solid State NMR technique which determines the maximum number of hydrogens associated with an intermediate. The technique is known as multiple quantum coherence spectroscopy. In this technique a single-quantum propagator is developed that in effect filters out all the hydrogens associated with the support and the small fragments (which normally dominate a spectrum); thus, providing a means to detect and count hydrogens on the large, chemically interesting, fragments.

Electron Orbital Chemistry Sheds Light on Principle of Superconductivity

The mechanism that accounts for high T_c superconductivity is not entirely understood. The chemical series, $RBa_2Cu_3O_7$ (R = lanthanide) all are superconductors except for the praseodymium (Pr) compound. Heavy element chemists at Argonne National Laboratory have, for the first time, substituted an actinide, curium (Cm), for the chemically similar lanthanide (Pr), into the series. The curium-containing compound also is not superconductive. The suppression of superconductive behavior has been attributed to the large radius of magnetic interaction of the 4f and 5f electrons in Pr and Cm with the conduction electrons. In the higher lanthanides above Pr, the radius of the 4f electron orbits is reduced (the so-called "lanthanide contraction"). The parallel behavior between the Pr and Cm compounds lends credence to the postulated suppression mechanism and provides valuable insights into the mechanism of superconductivity. The Cm-248 used in these experiments is a long-lived isotope produced by the HFIR-REDC complex at ORNL.

Temperature and Velocity Measurements in Process Plasma Jets

Researchers supported by the Engineering Research Program at the Idaho National Engineering Laboratory (INEL) have been successful in directly measuring gas temperatures and flow velocities in thermal plasma jets using high resolution scattered laser light lineshape analysis. Using a scanning tandem Fabry-Perot interferometer with sub-milliangstrom resolution, the lineshape of pulsed laser light scattered by the plasma was determined. Gas temperature is directly and unambiguously related to the width of the lineshape, while the flow velocity is directly determined by the Doppler shift of the lineshape relative to the incident laser light. Since the results do not rely on assumptions of local thermodynamical equilibrium (LTE), they can be used to test various LTE models and compared with results obtained by other techniques.

New Theory Predicts Properties of High-Temperature Superconductors

Since the recent discovery of a new class of high temperature superconducting oxides an intensive research has been undertaken to both understand and predict the properties of these materials. An important part of this work is the development of sophisticated computer codes to properly model the relevant physical processes that occur. In a recent development, Drs. W. Shelton, M. Stocks, and F. Pinski, materials scientists at ORNL, working in conjunction with Dr. A. Geist, a computer scientist, devised an algorithm based on the Korringa-Kohn-Rostoker coherent potential approximation theory of magnetism which is showing great promise. The power of the approach resides in the new physical insight that was brought to bear on the problem. Initial computer experiments have been performed on some perovskite high T_c superconductors, and have already revealed interesting effects related to alloy softening of the density of states and Fermi nesting. These experiments were performed on the 8 processor Cray Y-MP8/864 at the Ohio Supercomputer Center, and the 128 processor Intel iPSC/860 at ORNL, using innovative coding procedures to take advantage of parallel processing capability of the multi-processor machines.

Self-Segregation of Multicomponent Sand Piles During Processing Studied

Scientists at the Oak Ridge National Laboratory have obtained results pertinent to the processing of mixtures of granular materials. They have shown that when a random mixture of two different granular materials have sufficiently different sizes, shapes or other physical properties such that the critical angles of repose for the materials are different, segregation of the components can occur during certain types of processing. The critical angle of repose is the maximum slope that any point on a pile of the material can sustain. If the random mixture is poured into another container, the nonlinear dynamics of the granular flow leads to the almost total segregation of the two constituents. The material with the higher critical angle of repose needs a greater slope to induce motion. As a result, it tends to bunch up around the site at which it is poured while the more mobile granules with the lower critical slope tend to move more freely. The final distribution of the granules in the new container shows a concentration of the more mobile constituents at the bottom and the periphery of the pile with the less mobile species near the center and top. The flow of granular material composed of more than one type of constituent is common in material preparation. Typically, various materials are mixed in one container and then poured into another for sintering. Self-segregation under such conditions can significantly affect the final form of the treated material. In fact, such self-segregation, experimentally observed, led to the modeling effort and subsequent explanation of the phenomenon.

NMR Technique Utilized to Determine Bond Distances in Organic Solids

A nuclear magnetic resonance (NMR) technique for solids, double cross polarization-magic angle spinning (DCP-MAS), has been shown to provide selected structural information such as internuclear separations in homogeneous organic compounds. The key observation, was that the measured cross polarization oscillation frequency was proportional to the dipolar coupling, and a proportionality constant for the dipolar coupling was determined. With this methodology, a value of 0.270 + 0.015 nm was found for the ^{13}C-^{31}P internuclear distance in a methoxyphenyl diphenyl phosphine compound. This value is in excellent agreement with the value of 0.275 + 0.001 nm which was obtained from an x-ray crystal structure. The general principles for using these dipolar coupling interactions for quantitatively determining bond distances in amorphous or microcrystalline solids may provide similar invaluable information on complex, heterogeneous organic materials such as fossil fuels and blends of organic polymers.

Tin Alloys Found on Surface of Bimetallic Reforming Catalysts

Bimetallic reforming catalysts with tin added to platinum are currently being used for high octane gasoline production. It is known that tin makes the catalyst more resistant to deactivation; however, the role of the tin is not understood. Recent results by Chemical Science researchers have shown for the first time that Sn is actually incorporated into the platinum surface as a surface alloy. Two surface alloy structures were found using the low angle ion scattering technique developed for these studies at ORNL.

These two alloys were first thought to be simple overlayers, which have the Sn sitting on top of the Pt atoms. One of the alloy structures is similar to a known bulk phase, while the second is a new surface phase alloy. Work is continuing on understanding the role of each of these alloys in the catalytic reforming process.

This study supports the current thinking that alloys, rather then surface overlayers, play the dominant role in commercial reforming catalysis.

New Insights into Biological Nitrogen Fixation Mechanisms

Another couple of pieces of information have been discovered about the complicated puzzle defining the manner in which nodulation occurs in plant roots during nitrogen fixation. Dr. Sharon Long of Stanford University and coworkers have found that one of the genes involved in nodulation (nodPQ) encodes information for the synthesis of the enzyme ATP sulfurylase. One aspect of this is the first demonstration of in vitro activity of any of the nodulation gene products so far studied. In another case the nodulation gene (nodC) shows homology to chitin synthase, an enzyme involved in polymerization of N-acetylglucosamine. The significance of the research is in accruing a better appreciation of the component activities of biological nitrogen fixation, a critical segment of the global nitrogen cycle as well as a major energy saving activity in agriculture.

Seismologists Find Important Constraint on Crustal Evolution

Seismologists at LLNL have found experimental evidence that the mid-crustal velocity anomaly at a depth of 15 km beneath the Death Valley region is consistent with a crustal model containing multiple, thin low-velocity layers of magma. By analyzing seismic records taken 130 to 160 km from a large chemical explosion at the China Lake Naval Weapons Center on seismologists found that waves reflected upward from the base of the crust were being affected on both their downward and upward travel by the low-velocity zones. If the seismic interpretation is correct, it explains how the extreme crustal extension at the surface (300 to 400%) over the last 10 to 15 million years was isostatically compensated. This amount of extension requires that the crust had to be uplifted 3 to 5 km over a broad area. Intracrustal intrusion of magma had been proposed as a possible mechanism for the uplift, and the seismic experiment has provided a strong constraint on the evolution of the crust and the nature of heat sources beneath the western Basin and Range province.

New Catalysts Discovered for the Production of Fuels from Synthesis Gas

Professor Wolfgang Sachtler at Northwestern University has developed a catalyst which can be tuned to produce either methanol and Fisher-Tropsch products from reaction of CO and H_2 or, by modifying the pretreatment it will produce non Fisher-Tropsch hydrocarbon products which range in size from C_1 to C_8. The quantity of lighter products decreases with increased reaction time, showing that the gasoline range material increases as the catalyst ages. The product distribution of the latter reaction does not follow the Schulz-Flory distribution and has a higher iso to normal ratio than equilibrium, indicating high octane numbers for the gasoline fraction of the product.

Conversion of synthesis gas (CO and H_2) to fuels typically follows a Schulz-Flory product distribution which is high in C_1 to C_3 and decays with increasing carbon number. Additionally, the isomeric products approach equilibrium by starting from low iso/normal ratios. With the new catalyst the product distribution peaks in the gasoline range (with the exception of the C_1 product in the early stages of reaction) and the isomeric equilibrium is approached from the high ratio side of equilibrium. The discovery was made with support from the Chemical Sciences Division of BES, in a program to develop fundamental understanding of the formation of small metal particles within zeolite matrices and their role in catalytic reaction selectivity.

New Insight into Combustion Intermediates Obtained from the Argonne Molecular Beam Machine

Argonne National Laboratory's molecular beam machine for the detailed study of chemical reactions of importance in combustion was employed to study the chemical reaction of the free radical CH with molecular hydrogen. This research is producing exciting new information on the dynamics of this chemical reaction and on the potential energy function that governs those dynamics. In this study, CH molecules in precisely known energy states are reacted with the deuterium analog of the hydrogen molecule. The observed processes include inelastic collisions of D_2 with CH and chemical reactions in which the final reaction products are CD and HD. A new phenomenon of rotational locking was observed in which the rotational motions of the products for both inelastic and reactive collisions tend to rotate in a synchronous manner as they recede from each other. As a result, their rotational frequencies prefer to be the same. This is in contrast with conventional wisdom in which the rotational energy would be expected to be randomly distributed. Phenomena such as this have practical implications in that they determine how energy is distributed and transferred in complex systems such as combustion. They also have important scientific implications in that theories of chemical reactions must be able to predict in detail such departures from random behavior if those theories are to be trusted and used. The experimentalists at Argonne are working closely with theoreticians at Argonne engaged in advanced theoretical and computational calculations of the same chemical reactions.

Conclusive Structural Analysis of a Coal Elucidated

The study of fossilized resins found in coals has been the object of many programs aimed at understanding coal structures, and how these coals may have been formed from plant debris under early coalification conditions. However, until now, the chemical structures of coal products could only be described in "statistical" or "average" terms due to the highly complex nature of coal. Analysis of resinite structures by a combination of spectroscopic techniques, has now shown conclusively that Class I resinites consist of (poly)communic acid, the natural polymer of diterpenoid carboxylic acids. This abundant class had been the subject of considerable controversy in the literature.

With these new analyses of resinites, an accurate and detailed chemical structure of this important maceral can be drawn without the averaging or statistical approaches previously taken. The identification of the maturation products of communic acid may now allow the development of the first reliable, chemically defined maturity indices applicable to coal and other terrestrial sediments. Equivalent maturity indices developed for crude oils have had significant impact in oil exploration. The chemical nature of fossil resins could provide a measure of the conditions under which organic matter was converted from plant debris to coals.

Analogy Made Between Dense Colloidal Suspensions and Atomic Liquids

There are many important instances where it is necessary to estimate the transport properties (viscosity, diffusion, and thermal conductivity) of dense colloidal suspensions. A notable example is the flow of slurries consisting of very fine powders mixed with larger particles. Recent research at Rockefeller University supported by the Engineering Research Program has shown that to a very good approximation, a dense suspension of either electrically charged or neutral colloids behaves very much like an atomic liquid, e.g. liquid argon. Over the years enormous experimental, theoretical and computational effort has been expended in the study of such relatively simple liquids. The newly discovered analogy will permit the use of simple scalings of the available results of that basic research for predicting accurately the transport properties of colloidal suspensions encountered in practical engineering situations.

Photoacoustics Found to Characterize Droplets and Small Particles

A new method to determine the dimensions, geometry, and acoustic properties of small fluid and solid bodies has recently been discovered as a result of fundamental research on the origins of the photoacoustic effect. Temporal profiles of acoustic waves generated as a consequence of the absorption of pulsed laser radiation by a single small drop or particle suspended in a transparent liquid are valuable indicators of geometry and physical properties. The body's temperature rises as a result of light absorption and the attendant thermal effects cause sound waves, a series of compressions and rarefactions, to be transmitted into the fluid. Sound waves thus created are detected by an ultrasonic transducer and their temporal profiles recorded. Though the photoacoustic effect has received much attention in the analytical community, the temporal profile of the acoustic wave generated by small bodies had not before been extensively investigated. Chemical Sciences researcher Gerald J. Diebold, Brown University, has performed detailed theoretical analyses based on monopole radiation of acoustic energy from small absorptive bodies suspended in a transparent fluid. He finds that the time domain expressions for photoacoustic waveforms can be written in terms of Fourier integrals. Predicted profiles for drops, cylinders, and sheets have been experimentally verified.

Major Advance Made on Measurement of Electron Electric Dipole Moment

Scientists at the Lawrence Berkeley Laboratory supported by the Division of Chemical Sciences, the Division of Nuclear Physics and the Division of High Energy Physics have placed a new experimental limit on the value of the electron electric dipole moment. Using an arrangement where an atomic beam of thallium is crossed with laser beams, the scientists measured the energy of an atomic transition subject to a strong electric field. The electron dipole moment derived from this measurement was found to be a factor of at least seven less than that derived from any previous measurement. The new result is a test for the existence of new physics beyond the Standard Model of strong, weak and electromagnetic interactions and, in particular, the origin of CP violation. The new upper limit provided by the LBL group is consistent with there being no electron electric dipole moment and is a value approaching those predicted by Higgs boson models of CP violation. The result also verifies that atomic physics experiments are in a position to provide stringent tests of the fundamental tenants of particle physics at a fraction of the cost of other types of experiments designed to provide similar information.

Improved Procedure for Preparation of Spherical Titania Particles

The Materials Research Laboratory at the University of Illinois at Urbana-Champaign recently reported an improved procedure for formation of uniform, microscopic-size, spherical titania (titanium dioxide) particles. Previously reported procedures for the precipitation these spherical particles were found to be unreliable. Contrary to conventional wisdom it was found that high mixing rates induced aggregation. Control of colloid stability was demonstrated to be critical to achieving particle uniformity. Increasing the charge on the ultrafine particles (sols) in the liquid did not change the kinetics of precipitation but did allow control of particle size and uniformity. Increasing the short-range repulsive forces between the particles through solvation or hydration forces provided control of the final particle size distribution. By indicating the control variables responsible for the maintenance of uniformity, these results open the possibility of scaling-up precipitation reactions such that large quantities of uniform particles can be prepared. Controlled precipitation of ceramic precursor powders are a means of producing high-quality powders needed for the subsequent fabrication of high-strength, tough ceramics as well as other applications as filter-beds, catalysts, fillers, pigments, etc. This work was carried out by C. Zukoski as part of a program supported by BES/DMS.

New Hydrogen-Defect Center Discovered in Gallium Arsenide

Sandia National Laboratories, Albuquerque, has reported the discovery of a defect center in gallium arsenide (GaAs) due to the bonding of an arsenic atom to a hydrogen (H) atom. This defect center is referred to as an As-H center. The center was observed by infrared vibrational spectroscopy following hydrogen-ion implantation at cryogenic temperatures. The hydrogen bonding was demonstrated through a shift in the absorption frequency upon isotopic substitution of deuterium for hydrogen, whereas the role of arsenic was deduced from observation of a similar As-H center in indium arsenide. The As-H center becomes unstable at temperatures above 250 K (-23 C), giving way to previously known Ga-H center. This study is part of a Materials Sciences sponsored program to investigate the effects of ion implantation on materials.

Hydrogen is widely used in silicon technology to neutralize electrically active defects, and a large body of new research suggests that this highly mobile and reactive element will serve the same purposes in devices based on gallium arsenide. Moreover, hydrogen-ion bombardment is currently used to produce electrical and optical isolation in gallium-arsenide integrated circuits. It is important in such applications to understand hydrogen bonding at defects. The above achievement represents a key step in this direction. The earlier observation of Ga-H, but not As-H, bonding contained a serious gap in understanding. This gap is now closed by the observation of modest stability of the As-H center which dissociates below room temperature.

A New Approach to Optical Storage of Information

A new method of information storage with potential to significantly increase the capacity of optical storage media was recently demonstrated by Chemical Sciences researchers at Oak Ridge National Laboratory. The approach relies on the modification of the fluorescence spectrum from a distribution of small particles which have been treated with fluorescent dye. Only when the wavelength of the illuminating light is resonant with the circumference of the particle can the intensity reach levels sufficient to photolyze the dye molecules. Selective photolysis of the dye causes a reduced intensity, or spectral "hole," in a narrow region of the broadened fluorescence spectrum from the collection of particles, with the position of the "hole" determined by particle diameter. These spectrally localized "holes" constitute information storage. Photolysis is the "write" cycle for the memory, while spectral analysis of the fluorescence is the "read." If the dye were photolyzed at ten different wavelengths, the amount of information which could be stored on optical media would be increased ten-fold. These spectral "holes" have previously been observed only at extremely low temperatures, but the fact that the above process occurs at room temperature makes this approach practical. The method could also be used to characterize the size distribution of a random array of spherical particles, like those produced on space flights. The concept is due to Professor S. Arnold, Polytechnic University in Brooklyn, and was demonstrated by a collaborative effort with Drs. W. Whitten and M. Ramsey, ORNL, while Professor Arnold served a temporary appointment to Chemical Sciences Programs at Oak Ridge National Laboratory.

Technology Transfer; Small Business Innovation Research (SBIR); Awards and Recognitions

X-Ray Technology Transferred to Small Firm

The technology associated with a high repetition rate plasma focus source for X-ray lithography has been transferred from Lawrence Livermore National Laboratory (LLNL) to Science Research Laboratory, a small business located in Somerville, Massachusetts. A prototype X-ray source was developed by Dr. Louis Reginato at LLNL with funding from the Division of Advanced Energy Projects (AEP). The key technology studied with AEP funds was the development of an ultra-low inductance, magnetically switched driver for a plasma focus X-ray source. The low inductance allows peak currents of up to 360kA to be delivered to the plasma focus. Such high currents from a relatively low total energy drive could lead to an efficient plasma focus, with perhaps as much as 20J of the stored energy converted into useful X-rays for sub-micron lithography. A one percent efficient, compact, reliable point source of X-rays would mark a major milestone in the development of modular alternatives to synchrotrons, for X-ray lithography. Science Research Laboratory will develop the source under a three-year contract with DARPA.

Nonimaging Optics Technology Used for Jamming Missiles

Lockheed/Sanders has revealed recently the application of R. Winston's (University of Chicago) ideas in non-imaging optics to devise counter measures against heat-seeking missiles. The newly designed jamming devices present to the incoming missile an apparent large heat emitting area, rather than a small spatially limited target. The system can be used to protect aircraft, ships, and ground vehicles.

Separately, the Board of Directors of the Optical Society of America has honored Professor Winston by elevating him to a fellowship of the society. He is cited for founding the field of non-imaging optics, and for contributing to its development.

Argonne Spins-Off Advanced Ceramics Firm

Inexpensive, formable ceramics stronger than steel will be manufactured and marketed by a new company, Nanophase Technologies Corporation of Darien, Illinois, that is based on research carried out by and scientists working at Argonne National Laboratory. The company's initial products will be fiber-optic connector components, high-temperature engine seals, and gas filters that help control quality during semiconductor manufacturing and are anticipated to be on the market in about a year according to their President and Chief Executive Officer James E. Moore. Dr. Richard W. Siegel, one of the Argonne scientists associated with Nanophase Technologies Corporation and whose research has been supported by Materials Sciences, said the new materials are stronger as well as easier to form than the conventional ceramics. Objects are formed by combining grains less than 50 nanometers in diameter, which are made by vaporizing a source material in the presence of a gas, then condensing the vapor. Siegel's nanophase research at ANL has shown that nanophase ceramics are more formable and less brittle with smaller grain size, and also become easier to machine without cracking or breaking. Sintering temperatures for ceramics can be reduced by 500°C and shrinkage during sintering is greatly reduced, resulting in an object that is close to "near net shape" thus requiring less machining.

Nanophase Technologies Corporation was founded in 1989 with funding from ARCH Venture Fund L.P., a venture capital fund operated by the ARCH Development Corp., Chicago, which is a technology marketing arm of ANL and the University of Chicago. The firm has received $475,000 from the state of Illinois Technology Grants to scale-up and commercialize Argonne's technology.

Chromatographic Materials Marketed for Environmental Analysis

A new company has been formed to market products based on patents issued to the Chemical Separations Sciences Group of the Chemistry Division, Argonne National Laboratory. EIChroM Industries, Inc., Evanston IL, which derives its name from Extraction, Ion Exchange Chromatographic Materials, offers products it calls TRU.Spec, Sr.Spec, and U.Spec for chromatographic analysis for transuranic elements, strontium, and uranium, respectively. TRU.Spec is currently used for a range of environmental analytical and bio assay applications. The product Sr.Spec is used for environmental and geochemical determination of strontium and for removal of strontium contamination, while U.Spec is intended for the determination and extraction of uranium in environmental and biological samples. These products constitute the first and only commercially available extraction chromatographic materials with such specificity. Each of the extractants is based on fundamental research on the design and synthesis of molecules by the Chemical Separations Sciences Group at Argonne National Laboratory.

Basic NMR Research Results in Licensing Agreements for Advanced NMR Technology

Bruker Instruments, Doty Scientific and Chemagnetics-Otsuka have each completed or are close to completing licensing agreements to incorporate advanced nuclear magnetic resonance (NMR) technology developed at Lawrence Berkeley Laboratory into their product lines. The impact of the availability of these enhanced instruments on studies of ceramics, catalysis, geophysics and high temperature superconductivity are expected to be profound. The basis for the advanced technology lies in a Division of Materials Sciences-supported program led by Alex Pines.

Earlier results of the work led to studies of the concept and theory of NMR spectra of solid materials. Spectra of liquids can be obtained with high resolution; the normal motion of the molecules in the liquid averages out non-symmetric atomic interactions that would otherwise broaden the "lines" of the observed spectrum, and make interpretation impossible. Molecules in solids do not have such motion, thus the spectra obtained show broad uninterpretable peaks. "Magic angle" spinning (MAS) of the solid sample container, a technique developed in the 1950's, does effectively average these unwanted signals but only for atoms with spherical nuclei. MAS spectra for non-spherical atoms such as oxygen-17, sodium-23 and aluminum-27, which have quadrupolar spins, are still too poorly resolved for intensive study.

The Pines group, noting that the quadrupolar problem could be resolved by spinning the sample around not one but two mathematically defined axes, developed two techniques to achieve this (cf Biweekly March 27, 1990). In the first, dynamic-angle spinning (DAS), the sample is spun first in one direction and then, within 40 milliseconds, in the other direction. In the second technique, double rotation (DOR), the sample is spun in both directions simultaneously using an ingenious rotor within a rotor (rotation speeds of the two rotors are 60,000 and 300,000 rpm). As a result, critically important classes of materials in the billion dollar petrochemical, pharmaceutical and microelectronics industries, can be analyzed in 100 times greater detail than before.

This analysis can provide information about the structure and function of molecules and, in the case of zeolite catalysts for example, lead directly to the production of additional useful products from crude oil.

Doty Scientific of Columbia, South Carolina has already commercialized DAS technology. Bruker Instruments (a German company) is now advertising instruments using DOR and Chemagnetics-Otsuka (a Japanese owned U.S. company) is also undertaking a full-scale venture to commercialize these techniques.

Technology Transfer in Engineering Research

Several years ago J. Kestin (Brown University), in work supported by the Engineering Research Program, pointed out that in theory the onset of choking in steady-state gas-liquid flows is analogous to the transition to sonic flow analyzed exhaustively in gas dynamics. That analogy persists no matter how complex is the interaction between the gas and the liquid. As reported earlier, the theoretical result could have an important impact on the current practices in modeling of loss-of-coolant accidents in nuclear reactors. Now at the forthcoming 27th National Heat Transfer Conference, a French team will report on their experiments carried out at Grenoble, France, showing unequivocally the correctness of Kestin's theory. In particular the latest results confirm Kestin's explanation of unexpected results from previous experiments, e.g. "Super Moby Dick", meant to duplicate certain conditions arising in loss-of-coolant accidents. The new experiments and their interpretation in the light of Kestin's work will influence the structure of nuclear reactor safety codes, as well as related calculations for liquefied gas storage facilities and runaway reactions in chemical plants.

SBIR Program

Fifty-six people from 48 companies with SBIR Phase II projects attended the Kick-Off Meeting on May 29, 1991, in the Germantown auditorium for this year's Commercialization Assistance Project. The primary purpose of the project is to provide individual assistance to Phase II awardees in development of a business plan for commercialization. The objectives of the meeting were to (1) explain in detail the effort that will be required of each SBIR awardee in the business plan development phase and (2) answer questions from the companies concerning the project. A workbook, entitled "Business Planning for Scientists and Engineers," was presented to each awardee at the meeting. This document was prepared by Dawnbreaker of Rochester, NY, the grantee for the project.

Companies that produce the best 20 business plans will be invited to participate in the following two phases of the project: (1) A Sponsor Presentation Workshop, in which awardees will develop presentation materials for use with potential funding sources (October 11-15 in Washington, D.C.). (2) A Commercialization Opportunity Forum, in which awardees will present business plans to a group of about 30 investors from Fortune 500 Companies and Venture Capital Firms (October 16-17 in Tysons Corner, VA).

Publication Cited as "Citation Classic"

A paper written by Alex Pines (LBL and UC/Berkeley) and two co-authors in 1973 and published in the Journal of Chemical Physics has been designated a Citation Classic by the Institute for Scientific Information. A Citation Classic is a publication which has been highly cited in the scientific literature. The Science Citation Index indicates that the Pines' paper has been cited over 1000 times. In recognition of this achievement the August 12, 1991, issue of Current Contents, a widely read magazine which lists the tables of contents of current scientific journals, will publish an abstract of the paper and a commentary by Pines emphasizing the human side of the research.

This paper introduced the concept, the technique, and the theory of "cross-polarization" which expanded the use of nuclear magnetic resonance (NMR) to solids especially organic solids. Today, cross-polarization coupled with magic-angle spinning is widely used on commercial NMR instruments to study structure, dynamics, diffusion and other aspects of organic and inorganic solids.

Fortune Magazine Cites BES Researcher as One of "America's Hot Young Scientists"

LBL chemist, Peter Schultz, has been recognized by Fortune magazine as one of "12 brilliant thinkers" whose research "will change our lives, and perhaps lead to some entirely new industries." The cover story in the October 8, 1990 issue recognizes twelve scientists whose basic research has made important breakthroughs in fields of astronomy, biology, chemistry, computer science, mathematics, and physics. The twelve were chosen from a large number nominated by senior scientists at universities, corporations, and federal labs. Fortune is one of America's leading business magazines with a focus on business management and a biweekly circulation: national 665,000, international 115,000. This is only the second time Fortune has highlighted the importance of basic scientific research in enhancing the economic well-being of the nation. The first time, (June, 1954), the magazine identified twenty promising young scientists. Five have since won Nobel Prizes.

Schultz, who is a senior scientist at LBL and a Professor of Chemistry at the University of California at Berkeley, was cited for his research, supported by Materials Sciences, in the use of molecular biology to make novel compounds and materials. Schultz has pioneered the process by which living organisms are induced to produce antibodies (normally disease fighting molecules) that have enzyme activity. In recent months Schultz and his group have announced the development of an antibody with enzyme activity that can catalyze a chemical reaction not found in biology. The reaction catalyzed, the Diels Alder addition, is one of the most important reactions in organic synthesis. It leads to the formation of carbon-carbon bonds, the backbone of most molecules of interest, from proteins to polyethylene. However, although there exist over 1500 known enzymes there are no documented examples of any that catalyze this reaction and there are no known organisms capable of performing it. As a result, the use of enzyme catalysis in the synthesis of novel compounds and materials need no longer be thought of as restricted to "biological" products such as proteins, lipids, and polysaccharides. All of chemistry is now a potential target.

R&D 100 Award for Ceramics Research

Ceramatec, Inc. of Salt Lake City, Utah has recently received one of the prestigious R&D 100 awards for its work on low thermal expansion structural ceramics. The work was funded in a Phase II SBIR project managed by the Division of Materials Sciences and has resulted in substantial follow-on industrial funding. To date, this funding totals approximately $360,000 and includes support to investigate applications as exhaust port liners, diesel particulate traps, catalytic combustors, refractories, assorted instruments and selected aerospace components. The ceramics composition developed, known as LE-1500, has two unusual characteristics which make it suitable for these applications: it can survive large thermal gradients and shock without fracture - this fracture resistance is due to a near-zero dimensional change in the material between room temperature and 2500 degrees F; and it has a much lower thermal conductivity than metals, making it a good thermal insulator. For example, LE-1500 can be heated to 2500 degrees F then plunged into ice water without breaking; in addition, a two inch rod can be held at one end by hand and heated on the other end to melting - ca. 3000 degrees F - without discomfort to the fingers.

High Honor for Engineering Researcher

One of the highest honors of the American Society of Mechanical Engineering, Honorary Membership, was conferred upon Dr. George Herrmann, Professor of Applied Mechanics, Stanford University, Stanford, California at its 1990 Winter Annual Meeting in Dallas, Texas. The citation for this high honor, conferred at the Honors Assembly, stated that the Award was "for leadership in the solid mechanics community for educating many successful graduate students, and for pioneering research contributions in structural and continuum mechanics."

Dr. Herrmann was founder and editor-in-chief of the International Journal of Solids and Structures from its beginning in 1965 through 1985, and he is a member of the editorial boards of several other scientific and engineering journals. He was Associate Editor of Applied Mechanics Reviews from 1958 to 1962. He was elected to the National Academy of Engineering in 1981.

Among his many distinguished awards are the 1980 von Karman Medal of the American Society of Civil Engineers; the Humboldt Foundation Award in 1984; the Silver Anniversary Medal of the Society of Engineering Science, and the 1989 Distinguished Service Award of the American Academy of Mechanics.

Dr. Herrmann is currently the principal investigator on a BES/Engineering Program research project.

Biological and Biomimetic Ceramics Recognized in American Ceramic Society's Orton Memorial Lecture

In his Edward Orton Jr. Memorial Lecture to the American Ceramic Society, on April 29, 1991, A. H. Heuer described highly innovative studies of natural hard tissues - shells, bones and teeth - and a "second frontier" of biomimetic processing of novel ceramic/polymer composites. Biologically produced hard tissues are composites of mineral and polymer (protein), with exceptionally high mineral contents. The process of tissue formation occurs at ambient-conditions, with molecular control, and results in a material with strengths which exceed that of the bulk minerals. When comparable ceramic composites are produced at high temperatures, very little process control is possible to optimize the structure formation and materials strength and toughness. Thus, much may be learned from the study of the properties of natural hard tissue and the manner in which it is formed to improve the design and processing of manufactured composite ceramics. Processing which mimics biological processes (biomimetic processing) may include adaptation of aqueous processing techniques, use of macromolecules to enclose precipitation reactions and for microstructure organization, and cell-mediated processing on mineral-producing organisms.

The Orton Memorial Lecture is one of the significant annual events of the American Ceramic Society, and the honor is awarded to recognize important and innovative research. The study of biomimetic processing offers an innovative approach to understanding and controlling at a molecular level the formation of new and improved ceramic composites. DOE's Division of Materials Sciences is supporting the research at Case Western Reserve University through a collaborative program at Battelle Pacific Northwest Laboratory.

U.S. Patent Number 5,000,000 Awarded to Energy Biosciences Invention

Dr. Lonnie Ingram of the University of Florida was awarded the Patent Office s five millionth patent covering work that was partially sponsored by the Energy Biosciences program. The press release follows:

Patent Number 5,000,000, entitled Ethanol Production by Escherichia coli Strains Co-Expressing Zymomonas PDC and ADH Genes , is being granted to the University of Florida for a genetically engineered bacteria which can convert almost all types of sugars found in plant material into ethanol. The invention is the product of research by Dr. Lonnie O. Ingram, Dr. Tyrell Conway, and Dr. Flavio Alterthum conducted at the University of Florida s Institute of Food and Agricultural Sciences.

Today, only a small number of naturally occurring bacteria are capable of making ethanol. These bacteria are able to produce ethanol from only a limited number of relatively expensive starting materials such as starch and cane sugar.

The newly patented bacteria allows other plentiful materials such as agricultural wastes, wood and garbage to be converted to fuel grade ethanol. What the inventors have done is transferred two genes from an ethanol producing bacterium (Zymomonas mobilis) into another bacterium (Escherichia coli) to enable the transformed bacteria to produce ethanol. With the new genetically engineered bacteria, many more starting materials may be used to produce ethanol.

The principal investigator has stated that the basis of this patent was basic research that was performed under Energy Biosciences auspices without which the work would never have been done. The USDA provided additional support for the performance of the applied aspects of the problem. Dr. Ingram s former post-doc, Dr. Tyrell Conway, now at the University of Nebraska, is also an Energy Biosciences grantee.

Critically Needed Accelerator Physicists Trained in Graduate Program

Since joining the Stanford Synchrotron Research Laboratory (SSRL) in 1983, Professor Helmut Wiedemann has developed a training program in accelerator physics, with support from the Division of Materials Sciences, which is now producing critically needed graduates who are finding a very eager reception at the various DOE accelerator-based research facilities across the country. The training of the students entails becoming familiar with and contributing to computer programs that help design accelerator components and simulate accelerator beam stability. And hands-on experience is gained, whenever it is possible, by conducting machine physics shifts of the Stanford accelerators (SPEAR, PEP and SLC). The 3 GeV SPEAR injector project afforded a unique experience for a number of students to gain an intensive taste for real accelerator physics. Each of the students has covered a significant part of the accelerator design including beam transport lines and all are actively involved in the commissioning of the injector. Louis Emery has completed his thesis and in September joined the APS project at Argonne. Michael Borland will be the next student to finish his thesis which concentrated on the theoretical and experimental understanding of an RF-gun. His design was used to build an RF-gun which is now routinely used at the SPEAR injector. James Safranek who is now the backbone of the injector commissioning will finish in 1991 has already received a firm offer from a research group at Stanford and has been invited to visit Brookhaven, SSC, Fermilab and Argonne (APS). Professor Wiedemann plans to teach an accelerator physics course again this year and a text book in accelerator physics, the first of its kind, will appear in early 1991.