# FY 1988
# ACCOMPLISHMENTS

## Office of Basic Energy Sciences

**January 13, 1989 (REV.)**

# Some Examples Of Accomplishments Under The Basic Energy Sciences Program During 1988

## JANUARY 13, 1989

The Basic Energy Sciences (BES) Program supports about 1,400 research projects. The following selection of accomplishments does not fully reflect the entire range of activities under the program. It does, however, provide some examples of how basic research can contribute to solving a wide variety of energy problems. The accomplishments identified are presented in four sections:



The following subprograms were managed and/or funded under Basic Energy Sciences during Fiscal Year 1988. The supporting subprogram is identified for each reported accomplishment at the beginning of each section.

Materials Sciences (MS)
Chemical Sciences (CS)
Engineering and Geosciences (EG)
Applied Mathematical Sciences (AMS)*
Energy Biosciences (EB)
Advanced Energy Projects (AEP)
Carbon Dioxide Research ($CO_2$)**
Small Business Innovation Research (SBIR)***

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* Managed by the Scientific Computing Staff of the Office of Energy Research

** Budgeted under the Biological and Environmental Research Program

*** Managed under Advanced Energy Projects

# SECTION 1

# Major Facilities Related Accomplishments During FY 1988*

1. **Residual Stresses in Composite Materials Uniquely Determined Using Neutron Diffraction Techniques**
   Intense Pulsed Neutron Source (IPNS), Argonne National Laboratory: J. Faber, Jr., D. Hitterman, D. Kupperman, K. Majumdar, J. Singh and S. MacEwen (MS)

2. **Polymer Film Characterization Using Neutron Beams**
   Intense Pulsed Neutron Source (IPNS), Argonne National Laboratory; IBM Almaden Research Center: T. Russel; and Northwestern University (MS)

3. **First Reported U.S. Production of Computer Chips Using X-Ray Lithography**
   National Synchrotron Light Source (NSLS), Brookhaven National Laboratory; and IBM (MS)

4. **New Method for Mapping Strain Fields Provided by Synchrotron X-Rays**
   National Synchrotron Light Source (NSLS), Brookhaven National Laboratory; and University of Illinois: H. Chen (MS)

5. **Spin-Polarized Photoemission: a New Tool to Measure Surface Magnetism**
   National Synchrotron Light Source (NSLS), Brookhaven National Laboratory: P. D. Johnson and L. Hulbert; University of Texas at Austin: A. Clarke and N. B. Brookes; and AT&T: B. Sinkovic and N. V. Smith (MS)

6. **Chemical States of Chromium in Protective Oxide Layers Determined Using Synchrotron X-rays**
   National Synchrotron Light Source (NSLS), Brookhaven National Laboratory: H. S. Isaacs, A. J. Davenport, S. M. Heald, and H. Chen; and University of Manchester Institute of Science and Technology: G. E. Thompson (MS)

7. **Protein Structure Solved Using New Synchrotron Radiation Based Technique**
   Stanford Synchrotron Radiation Laboratory: E. Merritt, R. Phizackerley, and B. Hedman; University of Sydney, (Australia): J. Guss, M. Murata,and H. Freeman; and Stanford University: K. Hodgson (CS)

8. **Technique for Imaging Transient Species in Flames**
   Combustion Research Facility (CRF), Sandia National Laboratory/Livermore: R. L. Schmitt and R. W. Schefer; Yale University: M. B. Long; and Altex Technologies Corporation, Los Gatos, California: M. Namazian (CS)

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* Also see item Nos 2. and 3. in Section 2.

# Section 1

# Major Facilities Related Accomplishments During FY 1988

### 1. Residual Stresses in Composite Materials Uniquely Determined Using Neutron Diffraction Techniques

Composite materials reinforced with fibers are being developed on a national scale for applications in the defense, aerospace, energy and transportation industries. Measuring and predicting the strength of these structural composites is critical in learning how to project their properties for safe and effective application. In the absence of obvious defects such as cracks, the mechanical properties of composites are related to the interaction of fiber stresses with those of the matrix in which they are embedded. The strain of the reinforcing fibers reflects the quality of the interfacial bond between the fiber and the dominant matrix material and can be used to calculate stresses. The Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory has provided the neutrons used as a probe to measure residual thermal strains in silicon carbide fibers -- usually called "whiskers" by materials scientists -- embedded in aluminum oxide. From the measured thermal strains, stresses have been calculated.

The bulk residual stresses determined by this method could not have been obtained any other way. This research is a unique application of neutron scattering techniques to provide strain measurements; the resulting stress estimates are important input for design and application of composite materials.

### 2. Polymer Film Characterization Using Neutron Beams

No longer regarded as cheap substitutes, polymers are versatile, high tech materials with complex chemical and physical properties. Scientists from several laboratories working together at the Intense Pulsed Neutron Source (IPNS) have developed a reflectometer using slow neutrons to investigate how two different polymers bond to each other, how a polymer sticks to a surface, which part of a polymer does the sticking, and how a melt made up of two different polymers wets a surface. The way neutron beams are reflected from the surface and from just below it provides information about the magnetic and atomic properties of both surface and near-surface polymer interfaces and compositions. By varying the neutron beam energy, profiles of the polymer composition and structure at varying depths below the surface can be reconstructed from their neutron energy dependent reflections. Measurements have been made on samples composed of two layers of different polymers to obtain a profile of the penetration of each polymer into the other one at the interface. Results indicate resolutions of 20 to 30 Angstroms (one Angstrom equals $10^{-8}$cm).

As a result of these and other experiments at IPNS using neutron reflectivity by thin polymer films, IBM has provided $150,000 to build a second reflectometer designed specifically to study polymer films. Dr. Russel of IBM found that he was able to resolve concentration profiles on a 20 Angstrom size scale which is much better resolution than available by any other technique available, and the neutron method has the added advantage of being non-destructive. IBM's interest is related to "resists" used to produce complex integrated circuits as well as for packaging; the general scientific interest, however, lies in broader areas such as polymer size, concentration profiles of polymers at polymer/polymer and polymer/substrate interfaces, and the behavior of polymers near a free surface. At least four other groups had submitted proposals to IPNS for research in this area during 1988.

3. **First Reported U.S. Production of Computer Chips Using X-ray Lithography**

In August 1988, IBM announced complete fabrication of the first computer chips ever made solely by X-ray lithography. These test chips were produced at the National Synchrotron Light Source, Brookhaven National Laboratory. Component spacings of 5,000 Angstroms have been attained with this method, providing two to three times the component density of present state-of-the- art mass-produced chips. By fabricating these fully scaled, working chips, IBM has demonstrated the applicability of synchrotron X-ray radiation for manufacturing devices with this higher line density -- a capability for smaller chips or more circuitry per chip. IBM was one of NSLS' earliest participating research teams and this research was carried out on the first U.S. beam line instrumented -- by IBM -- as a synchrotron-based X-ray lithography station. As a complement to this achievement, NSLS, initially with DOE funding, and now with DOD funding, is engaged in the development of a compact synchrotron expressly for use in X-ray lithographic production of electronic chips. Completion is expected in 1992.

4. **New Method for Mapping Strain Fields Provided by Synchrotron X-Rays**

A new synchrotron X-ray technique known as "absorption edge contour mapping" has been developed. It is being used to quantitatively measure the local strain in single crystals and to create "maps" showing the strain levels at different locations in a sample. These "maps" are not unlike weather maps or topographic maps with constant pressure or constant height above sea level connected by contour lines.

The new technique is superior to previous methods because it collects data faster and has a greater spatial resolution. It is non-destructive, providing an accurate mapping of the distribution of strain fields surrounding crack tips and inclusions under various loading situations. This new capability using synchrotron X-rays presents new possibilities for in situ strain field mapping well beyond the capability of the more traditional X-ray methods.

It is a new source for design information needed to reduce failure prob abilities, to more accurately predict service life, or even to maximize engineering service life. Strain mapping techniques are particularly important for quality improvement in the ever-increasing use of single- crystal materials in microelectronic and other high-tech industries.

This new technique requires a wide beam of highly parallel X-rays and a suitable filter which can be the specimen itself in some instances. The single crystal sample will only transmit X-rays of a single wave length. When the sample is correctly oriented with respect to the incident X-ray beam, it is possible to have one or more of the transmitted diffracted X-ray beams have a wave length that is extremely close to what is known as the "absorption edge" of the filter. This results in an abrupt change in the intensity of the diffracted X-ray beam and leads to the formation of what is known as an absorption edge contour on the film. Local strain affects the atomic "planes" in a crystal and can be followed through a change in the curvature of the absorption edge contours when the specimen is gradually rotated with respect to a given axis. This contour change can then be used to measure the local strain field in the specimen.

5. **Spin-Polarized Photoemission: a New Tool to Measure Surface Magnetism**

Surface magnetism is a phenomenon with technological implications, both in the field of magnetic film technology where contamination on a surface may influence the properties of the film in an unpredictable way, and in the chemical industry where the influence of magnetism on catalytic reactions is still unknown.

Information about surface magnetism can be obtained directly from the measurement of certain properties of electrons emitted from the surface when it is bombarded by relatively low energy, high intensity photons. The properties to be measured are the energy, momentum, and spin-polarization of the photoemitted electrons. Until recently, the resolution and intensity needed to make these measurements were unattainable.

Now, these measurements are possible using the new facility for performing spin-polarized photoemission experiments commissioned in 1988 at the National Synchrotron Light Source. The first experiment has already provided new insights into the role of contaminant atoms on surface magnetism. The results indicate that when oxygen and sulfur atoms are placed on an iron surface, electrons with different spins have different energies. The observation of this effect provides the first direct evidence of the presence of a "magnetic moment" on the adsorbed atoms and this indicates that these atoms do influence the magnetic properties of the surface, and that it is possible to measure and understand this influence.

### 6. Chemical States of Chromium in Protective Oxide Layers Determined Using Synchrotron X-rays

The role of chromates and their chemical changes in inhibiting corrosion has been studied at the National Synchrotron Light Source. X-rays have been used to determine the distribution and chemical states of chromium ions incorporated in oxide layers grown by anodizing aluminum in a chromate solution. The measurements were made by reflecting a grazing beam of single wave length X-rays off a very smooth anodized aluminum surface. The X-rays penetrate to a very small depth, so only the chromium ions very close to the surface are caused to fluoresce by the X-rays. As the incident angle is increased, the penetration depth increases giving information about the distribution and oxidation states of the chromium ions within the oxide. Depth analysis of the different oxidation states of chromium has not been obtained using any other technique.

Chromates are excellent corrosion inhibitors. However, their use is limited due to environmental concern about their carcinogenic nature. Understanding the mechanisms whereby chromates improve the corrosion resistance of passive oxide films on metals is an important aspect of the search to find alternative inhibitors. The development of this new technique for monitoring the chemical changes which chromates undergo as they are incorporated in passive oxide layers will contribute to the search for, and development of, new inhibitors.

### 7. Protein Structure Solved Using New Synchrotron Radiation Based Technique

A new X-ray technique was developed to determine the molecular structure of proteins using synchrotron radiation. The technique is based on varying the X-ray wavelength over a specific X-ray region in the continuous spectrum of the synchrotron radiation. A continuous X-ray spectrum is a unique property of synchrotron radiation produced using high energy electron storage rings. In applying the technique, the scattering power of a heavy atom -- scattering of X-rays from it -- in the protein molecule is measured at several different wavelengths and scattering powers compared. These data allow a parameter, "phase of reflection", that has evaded routine measurement before, to be determined. When this new information is added to other routinely obtained data, solution of a complex structure is possible.

The technique was demonstrated by determining the structure of the Cucumber Basic Protein, a complex structure with a molecular weight of nearly 10,000. In this case, the scattering power of the copper atom contained in the protein's chemical structure was determined at four different wavelengths. In contrast to the weight of the molecule, the copper atom has a weight of 63. Because the weight of copper is concentrated over the atom's size while the remaining weight of the molecule is distributed over a much larger region, the denser metal atom gave rise to strong, easily detected, scattering. A comparison of how the scattering varied over four different, but close, wavelengths allowed determination of the reflection phases. In the typical X-ray scattering experiment, only one fixed wavelength is used and does not provide sufficient data to determine phases, only intensities.

## 8. Technique for Imaging Transient Species in Flames

The design, optimization, and control of combustion systems requires accurate predictive models to relate system performance to the structure and chemical properties of the flame. Predictive models require spatially resolved data on temperature, chemical composition, and component velocities for testing and calibration. Of particular importance to the testing and calibration of predictive models are so-called free radicals, highly reactive species of transitory existence such as CH and OH, to which the models are highly sensitive. In a collaboration between industry, Yale University, and the Combustion Research Facility, Sandia National Laboratory/Livermore, a technique has been developed that allows the simultaneous measurement of the concentration of CH radicals and methane molecules in a turbulent flame, producing a two-dimensional, time resolved image. To accomplish the simultaneous measurement of CH and methane, the flame is rastered with a laser simultaneously operating at two different wavelengths. One wavelength stimulates fluorescence emission from the CH radicals and Raman scattering from the methane whereas the other wavelength stimulates only Raman scattering from the methane. The emitted light is measured by two vidicon detectors located on opposite sides of the flame tuned to different wavelengths and computer analyzed to produce color-coded, two-dimensional images of the CH and methane concentration profiles. The technique has been demonstrated on a methane diffusion flame allowing scientists to study directly how turbulence influences flame structure and properties.

## SECTION 2

## Superconductivity Related Accomplishments During FY 1988

1. **Atomic-Level Studies of Superconducting $YBa_2Cu_3O_{7-x}$**
   Sandia National Laboratory/Albuquerque: G. Kellogg and S. Brenner (MS)

2. **Intrinsic Critical Current Density Measured for High $T_c$ Superconductors**
   Argonne National Laboratory: G. Crabtree, D. Lam and J. Z. Liu (MS)

3. **Superconducting Properties of $YBa_2(Cu_{3-x}Fe_x)O_{7-y}$**
   Argonne National Laboratory: B. Veal, A. Paulikas, L. Nowicki, H. Claus and K Van der Voort (MS)

4. **Superconductivity at 110° K in the Bi-Sr-Ca-Cu-O System Attained by Phase Purification**
   Argonne National Laboratory: B. Veal and D. Lam (MS)

5. **Superconductor Thin Films by Laser Ablation**
   Oak Ridge National Laboratory: D. Lowndes, D. Geohegan D. Mashburn, D. Eres, L. Boatner, and B. Sales (MS)

6. **Single Crystals of High $T_c$ Superconductor Grown**
   Los Alamos National Laboratory: D. Peterson, et al. (MS)

7. **First Superconducting Thin Films from Thallium Compound**
   Sandia National Laboratory/Albuquerque: D. S. Ginley, J. F. Kwak, R. Hellmer, R. Baughman, E. Venturini, and B. Morosin (MS)

8. **Absence of a "Linear Term" in the Specific Heat of Superconducting Bi- Ca-Sr-Cu Oxide**
   Lawrence Berkeley Laboratory: R. Fisher, S. Kim, S. lacy, N. Phillips, D. Morris, A. Markelz, and J. Wei; and Sandia National Laboratory/Albuquerque: D. Ginley (MS)

9. **The Valence State of Copper in High $T_c$ Superconductors**
   University of Illinois: C. Slichter, et al. (MS)

10. **New Defect Model of a High-Temperature Superconductor**
    Argonne National Laboratory: C. Smedskjaer, S. J. Rothman and J. L. Routbort (MS)

11. ***Positron Experiments and the Fermion Surface in $YBa_2Cu_3O_7$**
    Northeastern University: A. Bansil, R. Prasad and W. Dlugosz; Tampere University of Technology: R. Pankaluoto and R. S. Rao; Netherlands Energy Research Foundation: P. E. Mijnarends; and Argonne National Laboratory: L. C. Smedskjaer (MS & AMS)

12. **Grain Boundary Engineering Key to Improved Ceramic Superconductors**
    Lawrence Berkeley Laboratory: G. Thomas; and University of California, San Diego: S. M. Green and H. L. Luo (MS)

* This research was directly dependent on the availability of the Energy Research Supercomputers.

13. **Point Defect Clusters Critical in Oxide Superconductor Processing**
Northwestern University: T. O. Mason (MS)

14. **Processing Ceramic Superconductors for Maximum Current Carrying Capability**
Massachusetts Institute of Technology: Y.-M. Chiang, A. Roshko, and J.A.S. Ikeda (MS)

# Section 2

## Superconductivity Related Accomplishments During FY 1988

There are several superconductor ceramic materials ~~discussed~~ in the follow ing items and they are identified by their chemical compositions. Item 1, for example, is about $YBa_2Cu_3O_{7-x}$; its molecular composition is 1 atom of yttrium, 2 atoms of barium, 3 of copper and 7-x atoms of oxygen. The expression "x" is a deviation from stoichiometry (a perfect molecule with no "vacancies"), typically around .1 in the materials being studied. The ex pression "y" also appears and reflects the substitution of one metal-atom-for-another. Thus "$Cu_{3-y}Fe_y$" denotes iron being substituted for copper as y increases. Another term that arises is "1-2-3 compound" which refers to the ratio of the principal metal atoms in the system, e.g., 1 yttrium, 2 barium and 3 copper atoms in the example above. ~~Transition Tempera-ture~~ and Critical Temperature, ~~$T_c$~~, mean the temperature at and below which a material is superconducting.

In FY 1988, Basic Energy Sciences supported about $16.5 million in super conducting research.

1. **Atomic-Level Studies of Superconducting $YBa_2Cu_3O_{7-x}$**

In studies designed to examine the structure and composition of high-$T_c$ superconductors at the atomic level, the techniques of field ion microscopy and atom-probe mass spectroscopy were applied to the superconducting ceramic $YBa_2Cu_3O_{7-x}$ in work at Sandia National Laboratory/Albuquerque. The goals of this research were to determine the variations in local microscopic structure of this material and to identify compositional fluctuations on an atomic scale.

The sharply-pointed needles (tips) required for the field ion microscopy work were high-quality, strong, hot-pressed samples prepared by electro chemical polishing procedures. Field ion microscope images of high $T_c$ superconductors were obtained for the first time in this study and the atomic layers of the material were clearly evident. These layers could be removed using a high-electric field evaporation technique in a controlled manner. It was then possible to analyze the composition of the evaporated layer using time-of-flight mass spectroscopy. All of the constituent elements were present in the mass spectrum.

2. **Intrinsic Critical Current Density Measured for High $T_c$ Superconductors**

Researchers at Argonne National Laboratory have shown that the amount of current that a single crystal yttrium-barium-copper oxide high-temperature (95° K) superconductor can carry is as high as $1 \times 10^7$ amps/cm$^2$ at 11° K, in agreement with earlier results on oriented thin films of the material. Most applications of bulk superconductors would require critical current densities of between $10^4$ and $10^5$ amps/cm$^2$. These measurements on the single crystals are inferred from magnetic studies. These measurements showed that critical currents of $7 \times 10^4$ amps/cm$^2$ could be obtained at 45° K in a magnetic field of 1 Tesla. This value was increased to above $1.3 \times 10^5$ amps/cm$^2$ by the deliberate introduction of additional defects using fast neutron irradiation at the Intense Pulsed Neutron Source. The single crystal results indicate intrinsic current densities in excess of that required for many applications and demonstrate the effectiveness of defects to increase the current density.

3. **Superconducting Properties of $YBa_2(Cu_{3-y}Fe_y)O_{7-x}$**

A recent study using a 1-2-3 high-$T_c$ superconductor with some of the copper (Cu) atoms replaced by iron (Fe) atoms led to the conclusion that the superconducting properties of the 1-2-3 type superconductors are primarily affected by the concentration of oxygen (O) vacancies in the copper-oxygen chains rather than directly by the oxygen stoichiometry. Researchers at Argonne National Laboratory combined transition temperature measurements with neutron diffraction studies on a series of 1-2-3 compounds containing between 0 and 15 percent Fe substituted for Cu (y ranged from 0 to .15). Neutron investigations of the structure had shown that the Fe substitutes exclusively on the Cu sites in the Cu-O chains. It was concluded that the Fe ions in the chains force O ions into certain sites in the crystal increasing the O vacancy concentration correspondingly in the chains. The superconducting transition temperature was correlated with this vacancy concentration. The work also strengthens the argument that the superconductivity is connected to the Cu-O planes, rather than the Cu-O chains which are significantly modified by the Fe substitution.

4. **Superconductivity at 110° K in the Bi-Sr-Ca-Cu-O System attained by Phase Purification**

Scientists at Argonne National Laboratory have successfully fabricated a bulk quantity of a superconductor with a transition temperature -- the temperature at which a material exhibits zero electrical resistance -- of 110° K. The superconductor is a Bi-Sr-Ca-Cu-O system. This system had previously been found to be superconducting at 85° K. The increase in the superconducting transition temperature from 85 to 110° K is attributed to the increase in phase purity which resulted from careful study of the composition range and heat treatments needed to prepare a pure single phase oxide superconductor. The 110° K transition temperature was verified by both resistivity and magnetization measurements.

Since the discovery of superconductivity in $YBa_2Cu_3O_{7-x}$ at temperatures exceeding that of boiling liquid nitrogen, new superconducting materials have been sought and a number of new ones found. The Bi-Sr-Ca-Cu-O system was previously known to have two superconducting phases with critical temperatures of 85 and 110° K. The higher-$T_c$ phase had been observed only as one constituent in multicomponent samples. Because of the peculiar layered nature of the material, with the tendency for lower-$T_c$ material to form interpenetrating layered regions, previously reported materials do not show zero resistance until cooled to about 85° K. Substantial phase purity is needed before this residual resistive behavior can be overcome. The improved processing is responsible for eliminating the phase with the lower $T_c$.

The new, single-phase Bi-Sr-Ca-Cu-O superconductor which results from controlled processing has the highest $T_c$ of any material except the oxide superconductor which contains thallium, which may have practical limitations because of toxicity problems. Thus, single-phase Bi-Sr-Ca-Cu-O is an important material to study extensively for clues to the nature of high $T_c$ superconductivity and to explore for technological applications. With its high $T_c$, potentially high current-carrying capacity and low toxicity, this material could play an important role in the developing superconductivity technology.

5. **Superconductor Thin Films by Laser Ablation**

Scientists at Oak Ridge National Laboratory have fabricated thin films of the high temperature superconductors $YBa_2Cu_3O_7$ and $HoBa_2Cu_3O_7$ using a technique known as laser ablation. Pulses of light from a KrF excimer laser are focused onto bulk pellets causing some of the material to be ablated and deposited onto a nearby substrate. The films formed have the same atomic composition as the starting material. Oxygen annealing yields films with transition temperatures near those of the bulk materials, although at this time the transition widths are somewhat broader. The researchers have been successful in depositing the films on a variety of surfaces. High quality films can be used for a range of superconducting device applications such as electronics, detectors and computers.

6. **Single Crystals of High $T_c$ Superconductor Grown**

At Los Alamos National Laboratory, scientists have succeeded in growing what may be the largest single crystals to date of the high $T_c$ superconductor $YBa_2Cu_3O_7$. The crystals are grown by heating the precursors to approximately 1600° Fahrenheit where the crystals form.

The larger crystals are produced by repetitive heatings; the crystals grow in size each cycle. Growth of large single crystals is considered one of the key steps in the characterization of these materials which is necessary before they can be successfully exploited.

7. **First Superconducting Thin Films from Thallium Compound**

Researchers at Sandia National Laboratories/Albuquerque have made the first thin films out of the new thallium-based superconducting materials. The polycrystalline film of $Tl_2CaBa_2Cu_2O_y$ is 7000 Angstroms (1 Angstrom equals $10^{-8}$ cm) thick and has a zero resistance at 97° K, the highest critical temperature for any thin film yet made. The film is deposited on single- crystal substrates of yttrium-stabilized cubic zirconia. The new films can carry current densities of 1.1 x $10^5$ amps/cm$^2$ at 77° K and is only weakly dependent on the magnetic field.

8. **Absence of a "Linear Term" in the Specific Heat of Superconducting Bi-Ca-Sr-Cu Oxide**

Lawrence Berkeley Laboratory and Sandia National Laboratory scientists have shown that the "linear term," which has been observed in all previous superconductors, does not occur in the recently discovered Bi-Ca-Sr-Cu example of these materials. A linear term (a contribution to the specific heat that is proportional to temperature) is generally found only in normal metals, and its appearance in the new superconductors has been interpreted as evidence that their superconductivity is fundamentally different from that of "conventional" superconductors. The measurements on Bi-Ca-Sr-Cu oxide show that the linear term is not a general property of the superconducting state of the oxide superconductors, and suggest that its observation in earlier measurements on other oxide superconductors has another explanation, probably the presence of an impurity phase.

The linear term was one of the most striking properties of the new high-$T_c$ superconductors, and one of the most fundamental ways in which they appear to differ from conventional superconductors. A successful theory of the new superconductors will have to account for this new experi-mental result, which will therefore play a role in distinguishing between presently competing theories.

9. **The Valence State of Copper in High $T_c$ Superconductors**

Magnetic resonance measurements, made on a superconducting single crystal of Y-Ba-Cu oxide (one of the new high temperature superconductors) show that <u>all</u> of the copper atoms, those in the copper oxide planes and those in the chains between planes, have the same valence state. Some prominent theories of the mechanism of high temperature superconductivity require the presence of two copper charge states. These measurements cast considerable doubt on the validity of such theories but, at the same time, give theorists an important piece of information to use in the search for the explanation of superconductivity in these oxides.

Two independent measures of the charge state of the copper atoms were made and it was concluded that the copper atoms are in the same charge state regardless of location in the crystal.

10. **New Defect Model of a High-Temperature Superconductor**

The defect structure of one of the new classes of high $T_c$ oxide superconductors, $La_{2-x}Sr_xCuO_4$, has been determined by transport studies. Oxygen tracer diffusion measurements were successfully performed as a function of strontium concentration, lanthanum concentration, and temperature. The oxygen mobility was found to decrease as the amount of strontium increases. A sharp increase in oxygen vacancy concentration and activation energy occur at the same strontium concentration as the maximum in the critical temperature for superconductivity. A model to explain this correlation has been proposed. As the strontium concentration increases up to $x = 0.15$, $Cu^{+3}$ ions are introduced to compensate for the lesser positive charge of the $Sr^{+2}$ ion vis-a-vis the $La^{+3}$; hence $T_c$ increases. Above about $x = 0.15$, the charge compensation is carried out by oxygen ion vacancies; hence $T_c$ falls. The oxygen ion vacancies form clusters with the $Sr^{+2}$ ions and these clusters impede the motion of the oxygen ions.

The superconducting behavior of this new and important class of materials depends on the concentration of oxygen. These unique measurements and the resulting defect model are, therefore, the prerequisite to unraveling some of the structural aspects of the origin of superconductivity. The results will also be essential for successful commercial fabrication of these materials.

### 11. *Positron Experiments and the Fermion Surface in $YBa_2Cu_3O_7$

Two dimensional angular correlation of annihilation radiation (2D-ACAR) positron experiments have recently been completed at Argonne National Laboratory on one of the new high temperature superconductor materials, $YBa_2Cu_3O_7$. These measurements are of considerable interest because they are sensitive to the Fermi surface of the material, an important feature in any understanding of superconductivity. Though the measurements are dependent on the Fermi surface in a complex manner, 2D-ACAR is one of the few experimental techniques capable of displaying any knowledge of the Fermi surface. The ground state electronic structure was calculated utilizing the local-density-approximation (LDA) band theory and the derivative two-photon momentum density to compare with the 2D-ACAR measurements using the Energy Research CRAY computers at Livermore National laboratory. The results are in semiquantitative accord with the measurements indicating that the LDA framework provides a reasonable description of the Fermi surface and ground state of $YBa_2Cu_3O_7$.

Reasonable agreement between a LDA band theory calculation for an important high temperature superconductor, $YBa_2Cu_3O_7$, and 2D-ACAR measurements has been achieved. This may be a significant step in understanding the mechanisms of superconductivity in these materials.

### 12. Grain Boundary Engineering Key to Improved Ceramic Superconductors

Recently, critical temperatures above 100° K have been found for superconductivity in Bi-Ca-Sr-Cu oxide and Tl-Ba-Ca-Cu oxide. These ceramic oxides are prepared by conventional sintering processes of the precursor oxides. It has, however, been observed that, in the case of the bismuth compounds, steps in the resistivity vs temperature curve appear such that the $T_{c,0}$ the critical temperature for zero resistivity is only 75-80° K although the onset of superconductivity transition temperature is around 110° K.

Detailed microstructural analysis using advanced transmission electron microscopy techniques has shown that a lower $T_c$ phase forms near the grain boundaries than in the interior of the grain. Thus, it is now known why the polycrystalline samples do not have superconducting connectivity near the grain boundaries. Structural-compositional differences at grain boundaries have to be eliminated to maintain the high superconductivity temperature for practical applications. A controlled addition of lead oxide to the ceramic enable the formation of a low melting liquid phase and successfully overcomes the problem. The composition of the superconducting phase is made uniform throughout and zero resistivity above 100° K is attained.

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* This research was directly dependent on the availability of the Energy Research Supercomputers

13. **Point Defect Clusters Critical in Oxide Superconductor Processing**

Point defect clustering has been detected in $La_{2-x}Ba_xCuO_4$ super-conductors through measurement of their high temperature ($650^\circ$-$850^\circ$ C) electrical properties. The formation rate of clusters has been followed via relaxation of the electrical conductivity with time. The effects have been modeled by combining hopping of holes between "free" and "bound" copper sites, the latter attached to barium-barium clusters.

Point defect clusters appear to play an important role in determining the normal state electrical properties of these superconducting oxides. Understanding of normal state behavior is prerequisite to explaining the superconducting state. The sluggish rate of cluster formation, apparently determined by the slow diffusion of barium ions toward one another, may explain why the homogenization of these materials during processing from the oxides is such a time-consuming process. The small barium diffusivity may be the rate determining step. This explains why atomic scale mixing procedures prior to firing are so important if compositional homogeneity is to be attained in these important new materials.

14. **Processing Ceramic Superconductors for Maximum Current Carrying Capability**

Three major barriers to widespread commercial applications of ceramic superconductors are (1) insufficient electrical current carrying capability, (2) lack of sufficient mechanical durability, and (3) lack of adequate reproducibility for the manufacture of commercial quantities. Recent research at MIT has provided new understanding to overcome these barriers.

The electrical current carrying capability of a polycrystalline ceramic superconductor was shown to be maximized by minimizing the microcracking that ordinarily occurs in ceramics. It was demonstrated that thermal stresses inherent to different superconducting compositions and the grain size achievable through processing are the critical factors that control microcracking. It also was demonstrated that the maximum electrical current carrying capability is independent of the grain size in ceramic superconductors that have no inherent thermal stresses. In the more interesting high temperature superconductors with large inherent thermal stress, however, maximum current carrying capability was achieved in those with the finest grain sizes since microcracking in them was minimized. A further advantage is that mechanical durability and reliability are optimized at these fine grain sizes. Finally, it also was discovered that the presence of copper-rich grain boundary phases limits current carrying capability. Taken together, these original results provide critical guidelines on how to process a ceramic superconductor to achieve both the maximum electric current carrying capability and to achieve consistently reproducible superconducting behavior in a large scale manufacturing process.

# SECTION 3

## Technology Transfer, 1988 R&D 100 Award, And Small Business Innovation Research Accomplishments During FY 1988

### Technology Transfer

1. **Ion Physics Facility Construction Project Leads to Technology Transfer**
   Cryogenics Consultants, Inc. and Kansas State University (CS)

2. **License Granted for Laser Phototherapy**
   Argonne National Laboratory: D. M. Gruen, C. E. Young, and M. J. Pellin (MS)

3. **Inductively Coupled Plasma/Mass Spectrometry: An Analytical Technique Finding Increased Application**
   Ames Laboratory: R. S. Houk (CS)

4. **Metal Ion Sequestering Agents - Technology Transfer**
   University of California, Berkeley, and Lawrence Berkeley Laboratory: K. Raymond (CS)

5. **New Technique for Locating Oil and Gas Deposits to be Field Tested**
   Paramagnetic Logging, Inc. (AEP)

### 1988 R&D 100 Awards

6. **1988 R&D 100 Award - for New Process to Prepare Electrically Conducting Polymers**
   Los Alamos National Laboratory: M. Aldissi (MS)

7. **1988 R&D 100 Award - for pH Sensor for High-Temperature/High Pressure Aqueous Environments**
   Argonne National Laboratory: Z. Nagy and R. M. Yonco (MS)

8. **1988 R&D 100 Award - for Neutron Stress Monitor for Composite Constituents**
   Argonne National Laboratory: D. S. Kupperman, S. Majumdar, J. P. Singh, R. L. Hitterman, and J. Faber (MS)

9. **1988 R&D 100 Award - for 3 He/4 He Dilution Refrigerator**
   Argonne National Laboratory: K. Gray and P. Roach (MS)

10. **1988 R&D 100 Award - for Development of X-ray Microprobe/Microscope**
    Brookhaven National Laboratory: K. Jones (CS)

11. **1988 R&D 100 Award - for New Fourier Transform Electron Paramagnetic Resonance (FT-EPR) Spectrometer**
    Argonne National Laboratory: M. K. Bowman and J. R. Norris (CS)

12. **1988 R&D 100 Award - for New, Powerful Linear Prediction Spectral Analysis (LP-SPEC) Software**
    Argonne National Laboratory: Jau-Huei Tang and J.R. Norris (CS)

13. **1988 R&D 100 Award - for a Lattice Gas Algorithm**
    Los Alamos National Laboratory: G. Doolen, B. Hasslacher (EG)

# Small Business Innovation Research (SBIR) Accomplishments During FY 1988

14. **1988 R&D 100 Award - for Development of a Laser Extensometer under an SBIR Award**
    Optra, Inc., Peabody, Massachusetts

15. **SBIR-Success Story Involving Solid Wastes**
    National Recovery Technologies, Inc. (NRT) Nashville, Tennessee

# Section 3

# Technology Transfer, 1988 R&D 100 Award, And Small Business Innovation Research Accomplishments During FY 1988

## Technology Transfer

1. **Ion Physics Facility Construction Project Leads to Technology Transfer**

The successful installation of a novel cryogenic system to maintain extremely low temperatures by Cryogenics Consultants, Inc. (CCI) at Kansas State University was a principal factor in CCI being offered a contract by Air Products Corporation for a similar system. The novel cryogenic system involved was developed by CCI working along with Kansas State scientists to meet requirements of the BES sponsored construction project, the Ion Collision Physics Facility, scheduled for completion in FY 1989. The Air Products system will be used to recover helium gas that appears in tankers during the transport of liquid helium from the U.S. for Air Products' European markets.

This is the second significant spin off from this project. Earlier, Combustion Engineering, Inc.'s participation in the project contributed to that firm's capability to develop and offer high vacuum metal vessels as a new product line.

2. **License Granted for Laser Phototherapy**

An exclusive license has been granted by DOE to Summit Technology, Inc., Massachusetts, for a patent entitled "Excimer Laser Phototherapy for the Dissolution of Abnormal Growth." It has as its object the removal of abnormal tissue layers. The important difference between this procedure and others using lasers is that the excimer laser produces visible light which specifically affects the tissue to be removed without heating and damaging the surrounding tissues. The patent was issued in 1987 to BES supported scientists at the Argonne National Laboratory.

The patent is an outgrowth of research using light to desorb atomic and molecular species from surfaces. The original research aim was to understand the mechanism by which atoms and molecules desorb from solid surfaces. The patent and its potential in clinical medicine is a clear and well-defined example of technological applications resulting from basic research.

3. **Inductively Coupled Plasma/Mass Spectrometry: An Analytical Technique Finding Increased Application**

Developed at DOE's Ames Laboratory about ten years ago, the "inductively coupled plasma/mass spectrometry" (ICP/MS) technique is currently being considered as the standard means for analysis of the elemental composition of complex samples. As a quality control instrument, ICP/MS has found application in the determination of the purity of uranium and of the composition of control rods in nuclear reactors. This technique is now in the process of being approved by the EPA for environmental analyses.

The technique itself is conceptually simple: the high temperature plasma breaks a complex sample down into its constituent atoms and ionizes them. They are then analyzed in the mass spectrometer. ICP/MS is better than any other technique at simultaneous measurement of several elements at very low concentrations.

There are about 170 of these instruments, costing about $200,000 a piece, in the U.S., Canada and Europe, and two major commercial manufacturers producing them.

ICP/MS was ranked as 16th of the "30 Hottest Fields of Science" for 1987 by the Institute for Scientific Information. The listing contains the fields which appear to be developing most rapidly, based on the currency of citations in papers published during the past year.

**4. Metal Ion Sequestering Agents - Technology Transfer**

The Roberts Pharmaceutical Corp. of Eatontown, New Jersey, has applied for an exclusive license for commercial practice of a DOE-owned US Patent. The patent, entitled "Hydroxypyridonate Chelating Agents", resulted from research investigating the chemistry of the man-made heavy elements; these include plutonium, curium and californium among others. The patent describes novel organic chemical agents which will form highly stable complex chemical molecules with the ions of these metals that are in human organs, tissues or fluids. The complexes formed are relatively easily excreted from the body.

While this research originally was focused on agents that complexed with and removed plutonium, the successful results were recognized to be of much broader significance. Thus the chemistry underlying the applications developed will be redirected to produce a medicinally useful agent that is more versatile, i.e., can remove a variety of metals, and thus more attractive to public health concerns as well as commercial interests.

**5. New Technique for Locating Oil and Gas Deposits to be Field Tested**

Recently a small company, ParaMagnetic Logging, Inc. (PML), has established the feasibility, in a laboratory environment, of a new technique to be used in locating oil and gas deposits overlooked in existing reservoirs. So far, it has been impossible to systematically locate such deposits without drilling expensive holes. The oil and gas industry now uses measurements of the resistivity of geological formations to determine the presence of oil and gas in newly drilled holes. However, such measurements have been impossible to do through already existing steel pipes (borehole casings) which surround wells in existing older oil fields.

With Basic Energy Sciences' support, PML has developed a new technique which will provide resistivity measurements through cased boreholes, allowing the detection of "missed oil" and "bypassed gas." As a result of this project which demonstrated "proof-of-principle" in a laboratory experiment, PML attracted funds from a consortium of sources for a 15-month project to build and test an apparatus to demonstrate the technology in actual oil and gas fields. This technology has the potential to significantly improve the information available on proven oil reserves within the U.S.

# 1988 R&D 100 AWARDS

6. **1988 R&D 100 Award - for New Process to Prepare Electrically Conducting Polymers**

A 1988 R&D 100 Award was presented to M. Aldissi of Los Alamos National Laboratory for his development of a process using a magnetic field to align conducting polymers. The alignment improves the conductivity of the bulk material. The polymers produced are excellent electrical conductors, equivalent to copper on a weight basis. The process developed uses a simple magnetic field to achieve orientation of long chain molecules; it is superior to the conventional alignment-by-stretching of polymers technique.

The procedure is straightforward. A magnetic field is applied during the polymerization process. The magnetic field aligns the polymers as straight fibers. In these magnetically aligned materials, electrons can hop from chain to chain with minimum energy losses. The best conducting plastics are chemically treated forms of polyacetylene, polythiophene and polypyrrole. Each one has about a quarter of the conductivity of copper along the aligned axis.

Conducting plastics have many advantages over metals. Plastics can be made into sheets, formed as thin films on other materials, or molded into specific shapes. They are lighter, stronger, often more durable, and usually cheaper to produce.

7. **1988 R&D 100 Award - for pH Sensor for High-Temperature/High Pressure Aqueous Environments**

A sensor was developed to measure the pH -- the acidity or basicity -- of aqueous systems at temperatures to 300$^{\circ}$ C and high pressures. The sensor is a combination of a very stable, reference electrode of completely new design and a novel palladium-membrane electrode that provides a thermodynamically well-defined measure of the pH. Applications of the sensor will provide continuous monitoring of the chemical composition of high-temperature, high- pressure flowing streams such as those found in the cooling systems of water-cooled nuclear reactors, in fluids that occur in "near critical" or "supercritical" extraction technology, and in geothermal energy extraction systems.

8. **1988 R&D 100 Award - for Neutron Stress Monitor for Composite Constituents**

A technique was developed to provide, for the first time, simultaneous, in situ measurements of the principal <u>internal</u> (not just surface) strains (from which stresses are calculated) of the constituents of metal and ceramic composite materials. These measurements, obtained by the application of neutron diffraction techniques involving a pulsed neutron source and a special powder diffractometer, will provide critical information for predicting mechanical properties of composites and for designing composite structures.

Industrial interest in this technique was shown by GE which, this past year, initiated a collaborative effort with Argonne National Laboratory to measure the residual stresses in the fibers of a metal matrix composite that has a potential application in aircraft gas turbine engines.

9. **1988 R&D 100 Award - for $^{3}He/^{4}He$ Dilution Refrigerator**

A "Helium-Dilution Refrigerator" for obtaining temperatures less than one degree Kelvin has been developed which eliminates many of the problems of continuously operating refrigerators. The refrigerator will have applications in cooling devices, particularly for sensitive detection instrumentation, to utilize the inherently low-noise found for low- temperature operation, and in fundamental studies of materials and physical phenomena at ultra-low temperatures. This new device will open the realm of very low-temperature research to a number of organizations, especially small universities, who cannot afford the cost of full-scale models or to those who do not have low-temperature expertise nor want to spend the time to develop it.

10. **1988 R&D 100 Award - for Development of X-ray Microprobe/Microscope**

Investigators at the National Synchrotron Light Source at Brookhaven National Laboratory received an R&D 100 Award for their development of a collimated x-ray microprobe/microscope (CXRM), a unique instrument for nondestructive determination of trace element contents in materials with very small areas. The concentrations of elements from silicon to uranium can be determined down to the level of one million atoms in 10 billionths of a gram (about 1 to 10 parts in 100 million). The ability to focus on the trace element -- the spatial resolution -- is continuously adjustable with a minimum analysis area of .001 cm by .001 cm. The instrument determines the elements present from their characteristic x-ray fluorescence; the method uses x-radiation from the light source to induce the emission of secondary, characteristic x-rays from the element being detected. The source x-rays are collimated to a small size as the basis of a microscope for elemental mapping.

11. **1988 R&D 100 Award - for New Fourier Transform Electron Paramagnetic Resonance (FT-EPR) Spectrometer**

The FT-EPR spectrometer is a Fourier Transform (FT) electron paramagnetic resonance (EPR) spectrometer that can perform all the functions of conventional, continuous-wave EPR spectrometers and electron spin echo spectrometers for most samples. Fourier Transform is a mathematical technique that is helpful in unraveling data collected by the spectrometer. The data collected is characteristic of the electrons within the molecular structures being studied and their immediate environment. New innovative, two-dimensional experiments made possible by the FT-EPR spectrometer introduce a range of new applications, including the studies of chemical mechanisms of free radical reactions, biological electron transport pathways kinetics of photochemical reactions, transport of conduction electrons in anisotropic conductors, band structure of semiconductors (including doped, amorphous silicon, and semiconducting diamonds), chemical bonding defects in insulators, and electronic structure of small metal clusters in solids.

12. **1988 R&D 100 Award - for New, Powerful Linear Prediction Spectral Analysis (LP-SPEC) Software**

LP-SPEC (linear prediction spectral analysis) is a package of computer software based on the linear prediction method. It can be used in spectral analysis, multi-exponential curve fitting, and deconvolution with better resolution and sensitivity than the more common Fourier transform (FT) algorithm. LP-SPEC is designed to: (1) perform spectral analysis similar to FT but with improved resolution and sensitivity even if signals are truncated, (2) curve-fit multi-exponential decay data and determine the total number of decaying components, the decay rate constants, and the amplitudes, and (3) determine decay functions from signals that are usually mixed with an input excitation pulse in time-resolved experiments. Unlike the conventional method using nonlinear curve fitting, no prior assumption of the exact number of components involved must be made. LP-SPEC is very useful and has potential for wide application in diverse areas such as nuclear magnetic resonance, optical spectroscopies, mass spectroscopy, image processing, voice and seismic wave analysis. It can be applied wherever conventional fast Fourier transform or Laplace transform is used in signal analysis.

13. **1988 R&D 100 Award - for a Lattice Gas Algorithm**

Dr. G. Doolen and coworkers of Los Alamos National Laboratory have received one of this year's R&D 100 Awards for a "Lattice Gas Algorithm". The significance of this algorithm is that it permits the efficient computation of two-dimensional and three-dimensional fluid flows subject to realistic boundary conditions.

Two and three-dimensional fluid flow is a practical problem which often cannot be handled by existing computer hardware. The memory and computational speed required can be well beyond the straightforward application of existing and foreseeable technology. In most instances, some simplifying assumption is made which reduces the computational effort, but often at the expense of some significant aspect of the given problem.

The computational difficulties encountered in fluid mechanics are due in large part to the need to represent the smooth, continuous behavior of fluid flow by numerical means which are intrinsically discreet with non-continuous results. To obtain smoother and smoother numerical results, it is necessary to decrease the sizes of the steps taken in time and in space, increasing the number of steps and hence the computer resources required.

A totally different approach to this problem has been proposed recently. Rather than the fluid being thought of as continuous, it can be regarded as an array, or lattice of "chunks of matter" interacting with one another according to some set of rules (hence "Lattice Gas Algorithm"). While the rules have some physical basis, the main objective in selecting them is set by the requirement that the final results of a given calculation satisfy the underlying physical laws applicable to the flow under study. When the problem is posed this way, the calculations can take advantage of the possibility of connecting many microprocessors in parallel and can be carried out in a manner more suitable for digital computers.

In practical cases, lattice gas algorithms may speed up the solution of fluid flow problems a thousand fold with currently available hardware. As the hardware continues to improve, further acceleration of the speed of calculations is to be expected. As a result, the ability to calculate more complex flows is being greatly enhanced.

## Small Business Innovation Research (SBIR) Accomplishments During FY 1988

The Office of Basic Energy Sciences manages the Small Business Innovation Research (SBIR) program, which is Department-wide except for Defense Programs (which are excluded by the enabling legislation). Since 1983, a percentage of the Department's extramural R&D budget, currently 1.25%, has been set aside for this program and used to fund about 100 Phase I proposals ($50,000 maximum) and about 50 Phase II proposals ($500,000 maximum) each year from small businesses. Two particularly important accomplishments for 1988 follow. Neither of them falls within the Basic Energy Sciences program areas; technical management of these projects was not under BES.

**14. 1988 R&D 100 Award - for Development of a Laser Extensometer under an SBIR Award**

The extensometer, developed for precise measurement of strain in materials testing by Optra, Inc., of Peabody, Massachusetts, does not contact the specimen under test, so it can operate in hostile environments including high temperatures, high radiation levels, and harsh corrosive conditions. The device has broad applications that include measurement of strain in tensile testing (including testing to fracture, where strain gauges would fail), and testing fragile materials. The applications also include measuring thermal mechanical fatigue and creep, and measuring displacements in other specialized testing of metallic, ceramic, and composite materials. The extensometer uses a dual-frequency HeNe (helium-neon) laser, that operates with a difference frequency of 250 kHz, and whose beam is split twice to provide dual beam illumination of two points on the specimen. The back-scatter from the two points is collected and heterodyned, and the Doppler shifts integrated to determine the differential lateral shift of the two illuminated points on the surface. Measurement sensitivities of 5 parts per million at frequencies up to 25 kHz make the device particularly useful in fatigue testing. The prototype was used at the Oak Ridge National Laboratory for strain measurement in a niobium-zirconium alloy incandescent at 1100°C, and an improved version is in use at NASA's Lewis Space Center. A commercial version is now being offered as a standard product, and negotiations are under way by the developer to obtain a significant investment in the product line

15. **SBIR-Success Story Involving Solid Wastes**

As a direct result of technical accomplishments under a DOE sponsored Small Business Innovation Research (SBIR) project, National Recovery Technologies, Inc. (NRT) of Nashville, Tennessee has reported by September 30, 1988, $6,400,000 in signed sales agreements. The company has developed a municipal solid waste materials recovery process that removes 80% of the glass, aluminum, and ferrous metals from a waste stream prior to its incineration. Benefits of this process include a 33% reduction in ash production, a 38% increase in total weight of wastes that can be handled, a 20% increase in boiler output, and the ability to provide municipalities with a more comprehensive solid waste disposal solution.

By September 30, 1988, NRT already had received sales orders for their equipment from organizations in Florida, Illinois, New Jersey, Pennsylvania, Texas, Wisconsin, Ontario (Canada), and West Germany. This SBIR project by then had produced revenues well over 10 times the Government funding. It also has led to an SBIR project with EPA to develop a method for separation of chlorinated plastics from solid waste.

# SECTION 4

## Other Accomplishments During FY 1988

## Materials Sciences

1. **Structure and Vibrational Properties of Glassy Germanium Diselenide**
   Argonne National Laboratory: S. Susman, D. Price, K. Volin, P. Vashista, and I. Ebbsjo

2. **Superplastic Forming of Structural Ceramics**
   University of Michigan: I-Wei Chen and R. Kolia

3. **Whisker Toughening Ceramics**
   Oak Ridge National Laboratory: P. F. Becher, P. Angelini, C. H. Hsueh, and T. N. Tiegs

4. **New NMR Technique Developed**
   Lawrence Berkeley Laboratory: A. Pines

5. **Nondestructive Ceramic Testing**
   Los Alamos National Laboratory: H. Frost, et al.

6. **Mechanical Properties Microprobe Provides Advanced Ceramic-Ceramic Composite Characterization**
   Oak Ridge National Laboratory: W. C. Oliver; and Rockwell Science Center: D. B. Marshall

7. **Positron Beams Detect defects at Interfaces**
   Brookhaven National Laboratory: B. Nielsen, K. G. Lynn and D. O. Welch; and IBM Corporation: G. W. Rubloff

8. **Calculation of the Energy-Band Structure for a New Permanent Magnet Material**
   University of Missouri at Kansas City: W. Y. Chiang, Z.-Q. Gu, and Xue-Fu Zhong

9. ***Droplets of Helium Simulated by Quantum Statistical Mechanics**
   Georgia Institute of Technology: U. Landman (with AMS)

10. ***Advanced Understanding of Grain Boundary Structure via Combined X-ray Diffraction and Computer Modeling**
    Massachusetts Institute of Technology: I. Majid, P. D. Bristowe and R. W. Balluffi (with AMS)

11. **Acoustic Emission from Intergranular Subcritical Crack Growth**
    Pacific Northwest Laboratory: R. H. Jones and M. A. Friesel

12. **Aluminum-Based Intermetallics: Potential Super-Aluminum Alloys**
    Oak Ridge National Laboratory: W. D. Porter, W. C. Oliver and E. P. George

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* This research was directly dependent on the availability of the Energy Research Supercomputers

## Chemical Sciences

13. **Antarctic Ozone Hole Theory Confirmed**
University of California, Irvine: F. S. Rowland

14. **Major Advance in Laser Science**
Sandia National Laboratory/Albuquerque: A. Smith

15. **Association Model for Coal Solubility Developed**
Pennsylvania State University: P. Painter

16. **Laser Behavior Supports Ice Age Periodicity Model**
Georgia Institute of Technology: R. Roy

17. **First Polymeric Precursor to Boron Carbide Ceramic Produced**
University of Pennsylvania: L. Sneddon

18. ***Stable Negative Calcium Ion Produced and Energy Level Calculated**
Vanderbilt University: C. F. Fischer; the University of Toronto: J. B. Lagowski and S. H. Vosko; and the University of Tennessee (with AMS)

19. **New Electric Field System More Efficient than Mechanical Stirring for Extractive Separations**
Oak Ridge National Laboratory: C. Byers, and T. Scott

20. **Heat of Vaporization Measured for the Heaviest Element Yet - Fermium**
Oak Ridge National Laboratory: R. Haire and C. Gibson

21. **Cooling of Ions with an Electron Beam Verified**
Oak Ridge National Laboratory: S. Datz; and CERN (European Center for Nuclear Research)

22. **First Negative-Ion ESDIAD Experiments Demonstrated**
National Institute of Standards and Technology (formerly the National Bureau of Standards): T. Madey

## Engineering and Geosciences

23. **Molybdenum Ore Formation in an Active Hot Springs System**
Los Alamos National Laboratory: F. Goff; and University of Utah Research Institute: J. Hulen

24. **New Evidence for Mobility of Elements in Sedimentary Basins**
Oak Ridge National Laboratory: S. E. Drummond, et al.

25. **Scientific Drilling, Laboratory Studies Yield New Approach to Search for Hydrocarbon Resources**
Los Alamos National Laboratory: T. Shankland; and Lawrence Livermore National Laboratory: A. Duba

26. **Efficient Removal of Large Amounts of Heat**
University of California at Los Angeles: V. Dhir

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27. **Instrumentation for Thermophysical Property Measurements in Complex Fluid Mixtures Applied to Replacements for Chlorofluorocarbons**
National Institute of Standards and Technology (formerly the National Bureau of Standards): N. A. Olien, and J. Sengers

28. **Advanced Methods Devised for Modeling Hydrocarbon Reservoirs**
State University of New York at Stony Brook: G. Hanson, and W. Meyers

29. **Modeling of Colored Noise in Nuclear Systems**
University of California at San Diego: K. Lindenberg, and B. West

## Applied Mathematical Sciences

30. **IEEE Gordon Bell Prize for Parallel Computer Speedup Won by Sandia**
Sandia National Laboratories/Albuquerque: R. Benner, J. Gustafson, and G. Montry

31. **New Adaptive Method for the Computation of Combustion Problems**
Northwestern University: A. Bayliss and B. Matkowsky, and Argonne National Laboratory: M. Minkoff

32. **Programming Environment Devised for Constructing Parallel Programs**
Argonne National Laboratory: J. Dongarra, D. Sorensen, K. Connolly, and J. Patterson

33. **High-Degree Low-Diameter Interconnection Networks**
Los Alamos National Laboratory: V. Faber and J. Moore

34. **The Interaction of a Benzene Ring with a Noble Gas Atom**
Supercomputing Computations Research Institute, Florida State University: M. Moncreiff

## Energy Biosciences

35. **Development of *Arabidopsis* as an Experimental System for Plant Research**
Michigan State University, MSU/DOE Plant Research Laboratory: C. Somerville

36. **Molecular Analyses of Hydrogenases in Anaerobic Bacteria**
University of Georgia: H. Peck; Ohio State University: J. Reeve; and University of California at Riverside: D. Arp

37. **Chromosome Studies Lead to Potential New Crop for Diversifying Southern U.S. Agriculture**
University of Georgia: W. Hanna

## Advanced Energy Projects

38. **Short Wave Length High Intensity Light Source**
University of Illinois at Chicago: C. K. Rhodes

## Carbon Dioxide Research

39. **Seasonal $CO_2$ Fluxes: 50% Uptake Rate of Industrial $CO_2$ Emissions by Oceans Confirmed**
Lamont-Doherty Geological Observatory, Columbia University: T. Takahashi and D. Chipman

40. **Global Circulation Models: Regional Climate Representation Compared**
Lawrence Livermore National Laboratory: S. Grotch and M. MacCracken

41. ***Dynamical Model of the Chemical Processes in the Troposphere and the Stratosphere**
Lawrence Livermore National Laboratory: D. J. Wuebbles and K. E. Grant (with AMS)

42. **Carbon Dioxide Boosts Crop Yields**
Brookhaven National Laboratory: U.S. Department of Agriculture, Agriculture Research Service, Yazoo City, Mississippi

43. **$CO_2$ Increases Biomass, Improves Water-Use, and Delays Senescence of a Salt-Marsh Ecosystem**
Environmental Research Center, Smithsonian Institution: B. Drake

# Section 4

# OTHER ACCOMPLISHMENTS DURING FY 1988

## Materials Sciences

1. **Structure and Vibrational Properties of Glassy Germanium Diselenide**

Scientists at the Argonne National Laboratory have successfully combined theoretical calculations and neutron diffraction and scattering experiments to elucidate the structure of glassy germanium diselenide (g-$GeSe_2$) and its vibrational properties. Glasses such as $GeSe_2$ made up of two elements are important technologically; they have potential applications to electronic switches and photocopiers, as optical components for infrared systems, and in batteries or fuel cells. An understanding of electrical charge and mass transport processes in these glasses is necessary to effectively use them. Two key problems are involved: (1) microscopic atomic structure within the glasses; and (2) vibrational properties of the bonds between the atoms in the structure. In this research, the glass structure has been examined by computer simulation techniques and experimentally using neutron and X-ray diffraction. The vibrational properties have been investigated using Raman spectroscopy and inelastic neutron scattering techniques.

The computer simulations suggested a structure for g-$GeSe_2$ in which the atoms form geometric units, each of which has a germanium atom at the center surrounded by 4 selenium atoms at the corners of the tetrahedron. A majority of the tetrahedra are connected at the corners. These corner- shared tetrahedra form rings consisting of 5, 6 or 7 Ge-Se bonds. The comparison of this calculated structure with the results of the diffraction experiments gave very good agreement.

The Raman spectroscopy results also are consistent with the computer simulations having features that are best correlated with vibrations of tetrahedra belonging to 5- and 7-fold rings and not clusters with intermediate-range order as earlier believed.

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* This research was directly dependent on the availability of the Energy Research Supercomputers

## 2. Superplastic Forming of Structural Ceramics

Mullite-zirconia ceramic matrix composites have been produced which for the first time have mechanical properties suitable for large deformation, superplastic forging. Mullite is an unusually stable ceramic that is used for its ability to withstand temperatures up to 1600° C. Zirconia is an unusually tough ceramic which is stronger than most steels at room temperature. Mullite-zirconia composites were made containing micrograins as small as 1500 atom diameters. At such small sizes, micrograins can flow, much like sand particles in a water-saturated slip. It was found that such a fine grained mullite-zirconia composite could be readily deformed, was highly resistant to fracture and did not exhibit microcracking. Mullite- zirconia composites were forged to a 50 percent reduction in original height within 2 minutes under the application of a small forging force at 1350° C. In addition, it was found possible to modify the engineering properties of the composites by controlling the size, shape, and amount of mullite phase or by varying the processing method.

These results create the possibility of similarly deforming ceramic components or parts into desired and specified complex shapes. It would permit the achievement of some shapes that cannot be made otherwise, and would replace the conventional and costly two-step process of sintering and machining. It is especially desirable to eliminate the machining process in ceramics because it generally introduces surface defects which inevitably lead to brittleness and a degradation in engineering properties and behavior. Ceramic machining is also very expensive. Such superplastic forming technology has been developed and practiced in the aerospace industry with metal alloys, resulting in considerable benefits in energy consumption, productivity, and system performance due to design advantages. Similar developments in ceramic manufacturing now seem promising, and if fully realized, could be truly revolutionary.

## 3. Whisker Toughening Ceramics

Ceramics can be made tougher, i.e., much more resistant to fracture, by reinforcement with very strong microscopic "whiskers" of materials such as silicon carbide. Such toughening by "whisker" reinforcement techniques has been shown theoretically and experimentally. Electron microscopy has revealed that toughening results when the whiskers can pin cracks together. Theoretical analyses of this and other toughening mechanisms have provided detailed descriptions of the observed toughening effects and defined the critical properties of the ceramic and whisker materials.

While there is considerable interest in ceramics (e.g., for superconductors and heat engine components), their brittleness must be overcome. The current results provide a framework for identifying and addressing the factors controlling the mechanical response of ceramic composites. This has established a fundamental basis for the design of toughened ceramic systems which is now being explored by numerous groups.

## 4. New NMR Technique Developed

Nuclear Magnetic Resonance (NMR) is an extremely powerful tool for understanding the structure and dynamical motions of atoms in condensed phase materials. A new NMR technique, called stationary orbit spinning (SOS), has been devised which extends the application of high resolution NMR to solid state materials containing quadrupolar nuclei such as oxygen-18, sodium-23, and aluminum-27. Materials which include these elements are catalysts, minerals, polymers, and ceramic superconductors.

The SOS technique spins the sample rapidly on two axes; this removes both first and second order broadening effects which have hampered the application of NMR to many materials.

Alexander Pines of Lawrence Berkeley Laboratory who conducted this work was the recipient of DOE's E. O. Lawrence Memorial Award in 1988 for outstanding innovations in nuclear magnetic resonance spectroscopy.

5. **Nondestructive Ceramic Testing**

Ultrasonic nondestructive testing has been extended through a new water- immersion technique that promises some major applications in the area of ceramic science and technology. This extended technique is able to find deleterious defects (such as millimeter-sized voids) in "green bodies" prior to sintering. This water immersion technique eliminates the problems associated with transducer-specimen contacts under dry conditions. A better understanding of the sintering process can be anticipated with this new capability to track the evolution of unwanted voids, inclusions, cracks delaminations, etc., from pre-firing through post-firing states. The technique will be particularly useful for quality control in preparing the new ceramic superconductors.

6. **Mechanical Properties Microprobe Provides Advanced Ceramic-Ceramic Composite Characterization**

The mechanical properties microprobe (MPM) has been successfully used to measure the mechanical properties of the interface between fiber and matrix in ceramic fiber-ceramic matrix composites. These composites achieve their strain-tolerant behavior from the energy needed to pull the fibers out of the matrix. The mechanical properties of these composites change as a function of the forces between the matrix and the fiber. The MPM technique now allows these forces to be measured directly on individual fibers by pushing on the end of the fibers and measuring the forces needed to push a fiber into the matrix.

These techniques greatly reduce the development costs associated with an exciting new class of structural materials. The techniques that have been developed can be used to characterize a sample consisting of only a few fibers, thus a single piece of the material (consisting of hundreds or thousands of fibers) can be used repeatedly after various exposures. These techniques should reduce the costs of developing these composites by a factor of between ten and one hundred.

7. **Positron Beams Detect Defects at Interfaces**

A variable-energy positron beam was able to reveal the presence of defects at buried interfaces formed by several state-of-the-art microelectronics processes. A nondestructive method, the positron beam is able to detect defects in overlayers, substrates and near buried interfaces with a sensitivity and flexibility not obtainable by other methods.

The quality of solid-solid interfaces is important in many technologies, ranging from protective coatings to electronic integrated circuits. Furthermore this is a period of great activity in scientific studies of the nature and properties of solid-solid interfaces such as grain boundaries and interphase interfaces. Consequently, a nondestructive method, suitable for in situ studies, for detecting the formation of defects, and characterizing their nature, concentration, and distribution at and near buried interfaces will be an important tool for scientific studies as well as for process development and quality control.

8. **Calculation of the Energy-Band Structure for a New Permanent Magnet Material**

The energy-band structure for the recently discovered magnet material neodymium-iron-boride has been determined for the first time by a first- principles quantum mechanical calculation. The calculated results yielded an electron spin density distribution that showed an unusual and extraordinary orientation of the spin density in a particular direction in the crystal structure of the material. The calculated spin magnetic moments were in good agreement with neutron scattering data. They predict and explain the unique and useful intrinsic magnetic properties of this material.

This is the only detailed theoretical explanation of the new and attractive neodymium-iron-boride permanent magnet system which has provided a basic microscopic understanding of the observed magnetic properties. This theoretical accomplishment is significant because of the extremely complicated tetragonal crystal lattice of this material which contains 68 atoms per unit cell. This calculation points the way to the discovery of other permanent magnet materials with superior properties and provides guidance to experimentalists and technologists as to candidate systems for their future efforts.

### 9. *Droplets of Helium Simulated by Quantum Statistical Mechanics

Bound systems of helium-4 atoms have been studied at 3 Kelvin. Three systems, 75, 150 and 294 atoms, have been studied and compared with calculations for the absolute zero temperature case. As in nature, the atoms do condense to a liquid droplet of 57, 120 and 270 atoms, respectively; the remaining atoms form the saturated vapor over the liquid. Extensive studies have been undertaken on the largest drop - it is found that the quantum mechanical nature of the atoms is evident for all but the zero point motion is largest on the surface of the droplet. The density of the large droplet near its center is in good agreement with bulk helium-4 in nature. Calculations are now underway to study self-trapped positrons in the droplet.

This is the first simulation of a large scale system of quantum mechanical particles in an inhomogeneous environment - it will likely become an interesting prototype for studies of this nature and it has the nearly unique capability of comparison with the real world. The memory size and speed of the ETA-10 at Florida State University was crucial to the success of this project.

### 10. *Advanced Understanding of Grain Boundary Structure via Combined X-ray Diffraction and Computer modeling

Grain boundaries play a critical role in the determination of mechanical and physical properties of crystalline metals and ceramics. For the first time, a technique to determine absolute grain boundary structure factors by X-ray diffraction has been developed. This new information is of decisive importance since it provides direct information about the absolute strength of the displacement field of the atoms in the grain boundary core.

The displaced atoms in the grain boundary produce characteristic scattering which can be measured and compared with the scattering predicted by atomistic models of the boundary structure. Molecular dynamical computer simulation techniques (using the "embedded atom" model) have also been developed for calculating dynamical grain boundary structures and corresponding structure factors for direct comparisons with the experimental results. These techniques have been implemented on the supercomputers atFlorida State University. Absolute structure factors for a series of [001] twist boundaries in gold have been measured; good agreement between measured and calculated values has been obtained.

These results prove that the displacements of the core atoms in the boundaries with large twist angles are relatively small. This result is in marked contrast to previous predictions of much larger atomic displacements based on measurements of relative structure factors by other investigators. The present results remove a long-standing anomaly in the determination of boundary structure by combined diffraction and computer modeling and increase our confidence in present methods, such as the embedded atom method, for calculating realistic grain boundary structures. The advances made on this program are a major step in increasing our understanding of the nature of this important structural defect.

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* This research was directly dependent on the availability of the Energy Research Supercomputers

11. **Acoustic Emission from Intergranular Subcritical Crack Growth**

Corrosion cracking is a major cause of component failure in the electric power, petrochemical, and oil exploration industries. Currently, industries are only able to monitor crack growth intermittently and, frequently, components fail before the next inspection because of accelerated crack growth. An on-line system to monitor crack growth would help alleviate this problem.

Acoustic signals are emitted during intergranular stress corrosion cracking. Though acoustic emissions had been previously correlated with transgranular stress corrosion of brass, evidence of emission during intergranular stress corrosion had not been documented. The relationship found in this research between acoustic emissions and crack propagation offers some promise for development of a non-destructive on-line process; the next step is to establish a correlation between the source of acoustic signals and the crack extension process. This is needed before acoustic emission detection can be developed as a reliable on-line monitor.

12. **Aluminum-Based Intermetallics: Potential Super-Aluminum Alloys**

Aluminum-based intermetallic alloys have been shown to possess many of the outstanding properties required of a super-aluminum alloy for high temperature structural applications. Hot hardness tests show that these intermetallic alloys ( > 50 wt % aluminum) with the ordered cubic crystal structure retain their strength much better than a widely used titanium- based alloy even at temperatures up to $1000^{\circ}$ C (commercial aluminum alloys melt between $500^{\circ}$ and $600^{\circ}$ C). A minimum in hardness, which should lead to a maximum in fracture toughness, has been found at the composition 25 atomic % aluminum, 8 atomic % titanium and 67% atomic % iron.

The study of aluminum-based intermetallics could result in a new class of structural alloys having low densities ( < 1/2 that of nickel-based superalloys), good oxidation resistance and high-temperature strength. Weight reductions in aerospace structural alloys are essential for significant energy savings and lower operating costs. The low density and high strengths of these aluminum-based ternary intermetallics are stimulating a great deal of interest.

## Chemical Sciences

13. **Antarctic Ozone Hole Theory Confirmed**

In September, 1986, Professor F. S. Rowland of the University of California, Irvine, advanced a theory, backed by modeling studies with collaborators at the National Center for Atmospheric Research (NCAR), that ozone depletion in the Antarctic atmosphere was caused mainly by reactions of chlorine nitrate ($ClNO_3$ - a gas) with hydrogen chloride (HCl -- also a gas) on polar water ice clouds. Rowland's chlorine nitrate explanation was one of the first of many (including reactions with chlorine-oxygen and bromine-oxygen molecules, volcanic aerosols, and a hyperactive sun) which followed in a flurry of activity by scientists from many disciplines to explain the source of the ozone hole. Recent laboratory results at simulated Antarctic conditions from two separate research groups, at the NASA Jet Propulsion Laboratory and Stanford Research Institute (performed with NASA support) have validated the chlorine nitrate hypothesis.

### 14. Major Advance in Laser Science

Scientists at Sandia National Laboratory/Albuquerque have made a major advance by developing the most spectrally intense source of tunable laser- like coherent radiation to-date operating in a technologically important region of the electromagnetic spectrum, in the vacuum ultraviolet. Three different laser wavelengths in mercury vapor were successfully combined to yield a fourth and shorter output wavelength. When optimized, the four-wave mixing resulted in an extraordinarily bright source of photons between 120 and 140 nanometers (1 nanometer is $10^{-7}$ cm). Over this narrow region, the source is orders of magnitude greater in intensity than is available from a synchrotron. Synchrotrons, on the other hand, have output over a wide range of the electromagnetic spectrum not accessible to lasers. It is not the first time this sum-frequency mixing technique has been used in this spectral region, but it is the first time that it was used to produce a sufficiently intense light source to make it of interest outside the research laboratory.

### 15. Association Model for Coal Solubility Developed

Understanding, interpreting, and predicting the solubility behavior of coal have been advanced by modifying contemporary theories of polymer physical chemistry to devise a new model of the coal "molecule". This advance was made possible through an improved ability to account for strong hydrogen bond interactions in coal solubilization.

The model developed links fundamental organic units together in chains which are in turn chemically interconnected to form very large molecular networks. This model successfully predicts phase behavior of coal solutions. The theory on which it is based is expressed using parameters that can be determined experimentally.

Many key structural characteristics (e.g. molecular weight) are being determined for the first time, and extension of the model to the characterization of coal liquefaction products, and the intermediate products leading to the formation of coke and other carbon types which are formed in the use of coal is a further possibility.

The significance of these findings is that coal can be viewed as a polymeric material. Since coal is a very complicated and varying material, the traditional tools or organic and physical chemistry cannot be applied, and this much-needed model may be expected to be of major use in resolving problems associated with our understanding and utilization of coal in the future.

### 16. Laser Behavior Supports Ice Age Periodicity Model

Scientists at the Georgia Institute of Technology studying the properties of laser radiation have observed a wholly unanticipated relationship between measurements involving the laser radiation and modeling of the climate cycle. The results on the properties of laser radiation support the physical basis for the "stochastic resonance model" used to describe the climate cycle. This model accounts for the regular variations with periodicities near 100,000 years observed in the Earth's climate. A direct relationship of this cyclic feature in this model has been identified with the onset of ice ages.

The "stochastic resonance model" calls for some kind of cooperative interaction between periodic and random fluctuations of the Earth's motion. The interaction produces a result that is amplified from either the periodic behavior or the small random fluctuation imposed upon it. A surprising analogy exists in the ring laser. In experiments with a ring laser, the amplification either in a clockwise or counter-clockwise direction was varied in a periodic fashion. Such a bistable system is a necessary, but not sufficient, condition for observation of stochastic resonance. The artificial introduction of noise into the laser was the random fluctuation that increased the signal to noise ratio, a result in total contradiction to intuition. The increase in the ratio is a valid signature for stochastic resonance.

To explain the climate variation, the Earth's wobble is the periodic motion that interacts with some undefined random fluctuation to produce the 100,000 year periodicity.

### 17. First Polymeric Precursor to Boron Carbide Ceramic Produced

Boron carbide and boron nitride are important ceramic materials owing to their extreme hardness, thermal stability, and radiation-proof characteristics, and new, high-yield preparations of these materials are challenging the creativity of organometallic chemists. A new route to pure ceramic boron carbide ($B_4C$) has been discovered which uses a transition metal catalyst (based on iridium) to react gaseous pentaborane with acetylene. The resulting product, vinylpentaborane, is then polymerized by heating at low temperature, while further heating above 140° C forms a hard, crosslinked polymer which may then be pyrolyzed at 1000° C to give a high yield of boron carbide.

In related chemistry, indicative of this approach, acetylenes have been reacted with borazine, $B_3N_3H_6$, an analog of benzene, in the presence of tiny, catalytic amounts of a rhodium complex. The intermediates produced also undergo thermally induced polymerization resulting in polymeric precursors that upon pyrolyzing under ammonia at 1000° C produce near white boron nitride ceramic materials. These are the first reported transition metal catalyzed reactions of borazine.

These synthetic examples indicate the new approaches being investigated to provide suitable ceramic precursors which may be reacted to form hard, thermally resistant, and radiation-proof materials suitable in many new applications of a ceramic nature, an area that has only recently gained the directed attention of organometallic and inorganic chemists.

### 18. *Stable Negative Calcium Ion Produced and Energy Level Calculated

It was recently discovered that the combination of a calcium atom and an electron produces a stable negative ion. The report of this discovery is based on research results obtained on two separate BES supported university projects. An experimental group at the University of Tennessee that uses facilities at Oak Ridge National Laboratory and a theoretical group at Vanderbilt University were involved. The significance of the accomplishment is the establishment of a new computational technique to determine atomic structure of heavy atoms with much higher accuracy than possible before, a result that will improve spectroscopic diagnostics and assist laser development.

Recently stable and metastable negative ions have been of interest: the correlation-energy contributions, which are purely quantum mechanical in nature, are as large as the electron affinities. Immediately following the experimental determination that the negative calcium ion could exist in a stable state, quantum mechanical calculations were undertaken to explore the extent of the stability of such negative ions. Two calculations of the energy states and electron affinity were undertaken to elucidate the stable ground states of calcium and also scandium. The first used the highly accurate multiconfigurational Hartree-Fock method including relativistic corrections and the second was the much less accurate but more easily interpretable density-functional (DF) method. The Hartree-Fock calculation was performed on the Energy Research CRAY X/MP at Livermore and the results were in very good agreement with the experimental observations.

This result illustrates the power of modern multibody quantum mechanical theory. These calculations provide excellent agreement with an experimental measurement of the electron affinity - a quantity dominated by quantum mechanical effects.

* This research was directly dependent on the availability of the Energy Research Supercomputers

19. **New Electric Field System More Efficient than Mechanical Stirring for Extractive Separations**

A new liquid-liquid extraction technique has been discovered which increases the extraction efficiency at markedly reduced energy consumption. The technique uses an electric field to break up the extracting liquid phase into micron-sized droplets, greatly increasing the mass transfer surface area. This is accomplished by introducing the extracting liquid phase into a second, less dense liquid containing the sample to be purified. The extracting liquid phase is introduced through a nozzle located between two electrodes. The resulting microdroplets sink through the sample phase, extracting selected components from it, and coalesce into larger drops and eventually into a continuous phase as they leave the region of the electric field.

The electric field is imposed only at the interface between the two phases, and not throughout the entire system. The resulting energy consumption of the new system is less than 1% of that of currently used mechanical systems. This offers the potential for considerable energy savings for such applications as purification of metals, pharmaceuticals, chemical reagents, and processing of nuclear wastes. Several patent applications have been filed.

20. **Heat of Vaporization Measured for the Heaviest Element Yet - Fermium**

Heat of vaporization is a very fundamental property used in describing metals and other materials. The higher it is, the stronger the bonding between atoms or molecules of the substance. The heat of vaporization of metallic fermium, element number 100, has been measured. This is the highest atomic number element for which this basic thermodynamic quantity has been determined. A value of 33 Kcal/mole was found. Compared with the value for einsteinium, element number 99 in the actinide series of elements, 32 Kcal/mole, and with the values for europium and ytterbium in the lanthanide series, 42 and 36 Kcal/mole respectively, it has been confirmed that fermium is divalent in its elemental metallic phase. This trend toward an increased stability of the divalent oxidation state with increasing atomic number, which starts with californium, number 98, is unique to the actinide series and is further confirmed with this measurement on fermium. The measurement was made with about one nanogram (1 billionth of a gram) of fermium-255, which has an alpha decay half-life of about 20 hours. It was thought that einsteinium would be the last element for which this measurement would be possible (the measurement was made in 1983), because of availability and handling problems. These high atomic number actinides are products of the DOE's unique heavy element production program at Oak Ridge National Laboratory. An understanding of the fundamental chemical and physical properties of the actinides is necessary to guide intelligent decisions with regard to their handling and waste disposal.

21. **Cooling of Ions with an Electron Beam Verified**

In a collaborative effort involving Oak Ridge National Laboratory and the European Center for Nuclear Research (CERN), scientists supported by BES have demonstrated that a beam of ions can be cooled when exposed to a beam of electrons. In the experiment, a beam of protons traveling with an energy of 50 Mev was merged co-linearly with a 28 Kev beam of electrons. The diameter of the ion beam was decreased from centimeters to millimeters within one second of merging; this decrease is due to a substantial reduction in the random motion of the ions brought about when energy of the ions in the beam is transferred, by collision, to the electrons. The results are important to the improved design of a cooled heavy ion storage ring, a device that will underpin the next generation of atomic physics experiments, and the design of new synchrotron radiation sources.

### 22. First Negative-Ion ESDIAD Experiments Demonstrated

Electron-stimulated desorption ion-angular-distributions (ESDIAD) is an experimental method which provides direct information about the structure of molecules adsorbed on surfaces. It is particularly useful for determining bonding structures of atoms or molecules on single-crystal surfaces because the ions ejected upon electron bombardment leave the surface on a path determined by the orientation of the bond which is ruptured. Neutral and negative as well as positive species are formed.

For the first time, measurements of fluoride ion electron stimulated desorption angular distributions were made for several molecules adsorbed on ruthenium surfaces. The ions were derived from parent molecular adsorbates, and new structural information, unique and complementary to that from positive ion ESDIAD experiments, was obtained. A major technical challenge of separating the large secondary electron signal from the considerably weaker negative ion signal was overcome using time-of-flight techniques.

These important results add to our understanding, by direct structural determination, of how molecules adsorb, interact with, and desorb from catalytic surfaces. They also provide information which may be the surface analog of gas-phase dissociative ionization

## Engineering and Geosciences

### 23. Molybdenum Ore Formation in an Active Hot Springs System

Fundamental geoscience research includes studies of underground transport processes which bear on both waste isolation and formation and recovery of energy resources. These processes often are driven by heat associated with the intrusion of molten rock from deep in the earth's interior into the shallower parts of the earth's crust. The manifestation of these intrusions, such as ore bodies, most often reflect processes which took place many millions of years ago. To study natural transport processes as they occur, geoscientists look for areas with hot springs and other signs of high heat flow, such as Long Valley in California and Valles Grande in New Mexico. DOE has been drilling a series of holes at these locations as part of the interagency Continental Scientific Drilling Program. Whenever possible, a continuous core of rock is obtained from these holes as well as samples of the groundwaters seeping through the rock at various levels.

Recent drilling at Sulfur Springs in the Valles Caldera has unexpectedly encountered the world's first known occurrence of the economically important ore called molybdenite actually being deposited in an active hot spring system. The ore is deposited from very dilute solutions at temperatures typically twice or more as high as the normal boiling point of water. The deposition process is closely related to the one which was speculated to have formed the molybdenite ore body extensively mined at Climax, Colorado. The new observations throw additional light on the processes by which comparatively rare substances are leached from a large body of rock and deposited in high concentration at a particular location.

Molybdenite is a bluish-gray mineral similar in appearance and texture to graphite, is widely used as a lubricant, but is also the principal source of molybdenum, a critical component of high-performance, impact-resistant steels. The mineral typically occurs in deposits formed at great depths and high temperatures. By contrast, the unusual molybdenite intersected in this corehole in New Mexico has apparently been deposited at shallow levels and at less than half the typical temperature of formation.

## 24. New Evidence for Mobility of Elements in Sedimentary Basins

Over the past few years, a combination of field and laboratory studies have revealed that common organic acids or anions, e.g., acetic acid or acetate ions, occur and can persist for millions of years at substantial concentrations in the hot pore waters that permeate most sedimentary basins to depths of several kilometers.

High temperature mineral solubility and electrochemical experiments have demonstrated that acetate ions, an important organic species found in basinal waters, forms bonds with metal ions in solution increasing the mobility of metals and the solubility of minerals in sedimentary basins. Formation constants for the complexes of acetate with $Fe^{2+}$ have been determined from 50 to 300° C. Experiments to measure the formation constants with other metal, i.e., $Zn^{2+}$ and $Al^{3+}$, and organic species are in progress.

Although more work is needed to assess the full implications of this research, several significant conclusions and some provocative suggestions have emerged. Simple organic species such as acetate have an extraordinary and largely unexpected potential to bond with metals in hydrothermal solutions. Acetate complexes of ferrous iron are considerably weaker than those for zinc and aluminum and yet are ten times stronger than the analogous ferrous chloride complexes. This evidence clearly indicates for the first time that organic complexes must be considered in any mass transport calculations designed to model the metal content of sedimentary brines. In fact, it is quite likely that previously ignored organic complexes are a dominant factor in the metal behavior in many of these fluids. This would explain the geochemist's long-standing inability to explain both the high levels of metals in basinal fluids and the overwhelming evidence of kilometer-scale transport of "insoluble" mineral phases in ancient sedimentary basins.

These findings will be important in predicting the location and extent of the permeable channels in sedimentary material which result from the movement of these organic-laden waters and which provide a migration path for hydrocarbons. Even in the absence of experimental evidence on organic complexes of actinides at high temperatures, the present results indicate the need for care in siting radioactive waste repositories in strata with access to organic material. In summary, this research has opened up a new field in organic hydrothermal geochemistry which will influence the interpretation of a wide range of processes in sedimentary systems.

## 25. Scientific Drilling, Laboratory Studies Yield New Approach to Search for Hydrocarbon Resources

U.S. researchers working with colleagues from West Germany have, as a result of models developed by U.S. researchers, measured the electrical resistance of shales from two West German continental drilling boreholes in Konzen and in Musterland. The results of these studies may be used in developing exploration strategies for undiscovered hydrocarbons.

The two shales were quite different in their electrical resistivities. The resistivity of one shale was very dependent on water content, similar to behavior seen in other rocks; the resistivity of the other, a black shale, was virtually independent of water saturation and was 1000 times lower than the resistivity of ordinary rocks.

The unusual electrical behavior of the black shale is attributed to the presence of carbon at grain boundaries. This carbon was produced by natural heating of the shale precursors as they were first deposited in sediments and then covered over. The heating resulted in loss of light hydrocarbons from the sediments accompanied by the production of a grain boundary carbon residue. The light hydrocarbons often migrate toward the surface and are lost to the atmosphere unless they encounter an impermeable barrier where they could concentrate to become a hydrocarbon resource such as natural gas or oil. Layers of rock with low electrical resistance, such as these black shales, can be detected from the surface with electromagnetic methods (i.e., methods using radio waves). This scenario for resource formation implies that electrical resistance anomalies in the 5 to 20 km depth region could be associated with a hydrocarbon resource at shallower depths and that electromagnetic exploration techniques could be used to find deeply buried oil and gas source rocks. More detailed electrical and seismic imaging techniques could then be employed to search for potential oil and gas reservoirs in overlying strata.

26. **Efficient Removal of Large Amounts of Heat**

A major problem in engineering design is to provide for heat removal from a system as rapidly as it is being produced; otherwise the system will get hotter and hotter until it fails. Typically, in current energy systems, damage can arise in the presence of heat fluxes larger than about ten kilowatts per square centimeter. In familiar terms that is comparable with trying to crowd the maximum heat generated by about 15 four-ring electric kitchen ranges into an area of about a square inch. The engineering design problem is to find a means for more rapid removal of heat.

Recent work on turbulent flows in pipes carried out at the University of California at Los Angeles has demonstrated a practical approach to coping with this problem. It was found that rapid injection of cooling liquid along the circumferences of a pipe can disrupt the so-called thermal boundary layer which resists efficient heat transfer from the wall of the pipe to the bulk of the flowing liquid. On removal of that boundary layer, there is essentially no significant obstruction to heat transfer, and heat fluxes of tens of kilowatts per square centimeter can be handled with relative ease.

This discovery has an immediate impact on the design studies for future fusion reactors, where large thermal stresses are expected. One can easily imagine other nearer term applications, such as the operation of internal combustion engines and turbines at much higher temperatures where the thermal efficiency of those energy conversion systems would be greatly enhanced.

27. **Instrumentation for Thermophysical Property Measurements in Complex Fluid Mixtures Applied to Replacements for Chlorofluorocarbons**

The design of equipment and development of associated methodology for measurement of the thermophysical properties in complex fluid mixtures has been underway for the past five years. The objective of this work has been to determine the properties of hydrocarbons over a range of physical conditions expected in the production of synthetic fuels. Such data are needed for engineering design purposes and also for evaluating the chemical properties and reactivities of trace chemicals produced along with the synthetic fuels. The results of this research, however, are creating an impact in a different area of more immediate interest to DOE.

It is now well established that commonly used commercial refrigerants cause depletion of the earth's ozone layer. To avoid a potential world-wide environmental catastrophe, while preserving the usefulness and energy efficiency of refrigerating and air-conditioning equipment, it is crucial that new, environmentally benign refrigerants be found. The new refrigerants must adhere to certain standards to make them useful. To meet those standards the refrigerants must have some very precisely prescribed thermophysical properties. The properties of interest include heat capacity, boiling point, latent heat of condensation, densities of the liquid and gaseous states, and so on.

The apparatus developed to obtain high precision thermophysical data on synthetic fuel organic chemicals is now being used to obtain data on other chemicals that can be used as replacement refrigerants for those currently in use commercially. A number of different groups including both industry and other elements of the Department of Energy are now supporting research dependent on the equipment and methodology developed with BES support in the search for new materials.

28. **Advanced Methods Devised for Modeling Hydrocarbon Reservoirs**

Many of the world's most prolific oil fields produce from carbonate reservoirs. Carbonates (limestones and dolomites) typically go through several complex stages of recrystallization during their evolution from unconsolidated sediments, through burial, to hardening into rocks. These rocks commonly have permeable and porous zones capable of holding significant quantities of fluids, including hydrocarbons (i.e.,oil or natural gas). Tracking these changes in the reservoir rock in order to understand when voids formed, when hydrocarbons were entrapped, and when and how voids became plugged is very difficult but important both for prospecting for petroleum and for its production.

Researchers at the State University of New York at Stony Brook have been studying rocks from a 300 million-year old geological formation in the Illinois Basin as examples of carbonate reservoir rocks. They have been expanding the use of geochemistry in deciphering the recrystallization history using trace elements (substances present in very small amounts) and isotopes (whose ratios determine the atomic weight of elements in a given sample). They have not only combined the power of many existing geochemical methods, often only used separately, but have also developed new approaches using the full set of rare-earth elements and isotopes of the particular rare-earth element called neodymium. This has allowed pinpointing what part of the present rock reflects the primary chemistry of the original seawater and what part reflects later large fluid-rock interactions as the basin evolved through geologic time. Further, it can now be determined whether the fluids circulated through the basement (older rock) or represent a direct contribution from rainwater. The results of this research are providing improved models for sedimentary basins for helping guide both the search for hydrocarbon resources and their production from known fields.

29. **Modeling of Colored Noise in Nuclear Systems**

The jumble of frequencies we hear as noise has many analogs in the physical world. Audible noise results from fluctuations in air pressure. The analogs result from similar fluctuations in some other quantity of interest such as wave length of light, mechanical force, or concentration of some particular substance. Since "white light" features the full range of visible wave lengths, noise is called "white noise" when it also features a very broad range of frequencies. Likewise, "Colored noise" features one or more narrow ranges in the frequency region of interest.

In a major power plant, audible noise is produced by various mechanical activities, each producing some frequency or range of frequencies of sound, but all heard jumbled up together. Over the years, mathematical theories have been developed to analyze the audible noise associated with large facilities such as nuclear reactors, including how it is built up from the various sources that contribute to it. The "noise" observed is the sum of these outputs. The same mathematics can be used to analyze various analogs of audible noise observed in nuclear systems, such as fluctuations in the magnitudes of pump-induced forces or even in the changing concentrations of the atoms undergoing reactions. "Noise" of various origins is important, however, because of the help it provides in diagnosis of different aspects of reactor behavior and safety.

Theories currently used in treating "noise" and its components assume that the noise contains a broad band of frequencies, i.e., "white noise", is unchanging with time, and is additive as if it came from an external source. Experimental and theoretical work has shown that these assumptions are often wrong. For instance, noise associated with non-destructive analysis of the remaining amount of reactor fuel (with the fluctuations here coming from unavoidable differences among samples) shows non-white and nonstationary characteristics as determined from the detailed measurements called noise statistics. In this instance, the time-varying character of the "noise sources" must be taken into proper account. As another example, random structural vibrations enter into the equations for noise statistics in a closely coupled rather than an additive way. The accurate determination of the statistics of reactor behavior is a crucial element of safety analysis and design of control systems.

Recent research carried out at the University of California at San Diego has addressed the effects of "non-standard" noise features such as might have an effect on reactor behavior. The research has identified the mathematical equations needed to take proper account of multiplicative (as opposed to additive) noise, and of colored (as opposed to white) noise. Account also is taken of the important differences between "internal" noise and "external" noise. Appropriate measures for the characterization of the noise have been identified. Furthermore, the differences between truly random contributions usually labeled as "noise" (such as those produced by structural vibrations) and those that arise from "chaos" (such as those produced by complicated, deterministic processes) have been analyzed.

The formulation of this approach to studying the effects of noise in complex systems is generic, and should find many applications in addition to the analysis of the behavior of nuclear reactors

## Applied Mathematical Sciences

### 30. IEEE Gordon Bell Prize for Parallel Computer Speedup Won by Sandia

Sandia National Laboratories scientists have discovered new methods for solving complex scientific problems at unprecedented speedups. Innovative methods and algorithms for parallel computing are providing speedups by more than a thousand-fold on problems important in modeling energy production systems. These prize-winning speedups have broken through a psychological barrier about the general purpose effectiveness of large numbers of parallel processors working on the same problem.

Speedups are a measure of the increased speed at which a problem can be solved on a multiprocessor parallel computer in comparison with a single processor from the same systems. If the speedups scale proportionally to the number of processors employed, then computing systems can be enhanced simply by adding more processors.

This achievement required developing mathematical and computational methods for solving problems on a parallel processing machine. The algorithms developed were programmed to run on a "hypercube" parallel computer consisting of 1,024 processors, each of which has the computing power of a modern personal computer. The computer is the NCUBE/Ten, a massively parallel hypercube computer system put into operation at Sandia National Laboratory/Albuquerque in 1987 - currently the only NCUBE/Ten in operation anywhere.

The processors are linked together so that they work simultaneously on different parts of a single problem. On three practical, full scale scientific applications in wave propagation, solid mechanics, and fluid flow, the Sandia scientists achieved speedups of 1,020, 1,019, and 1,011 respectively - almost the maximum of 1,024.

This research was awarded the first Gordon Bell Award of the IEEE for producing the largest speedup on real application problems on a general purpose multiprocessor computer. These techniques will lead to rapid increases in the computational power available to apply to the complex problems of energy production and supply and to fundamental research in physical processes.

### 31. New Adaptive Method for the Computation of Combustion Problems

A new, highly efficient, and accurate adaptive pseudo-spectral method has been developed and applied to characterize the behavior of advancing fronts in both solid and gaseous fuel combustion. This marks the first use of adaptiveness for pseudo-spectral methods (in which the solution is expanded in a sum of Chebyshev polynomials).

Most recently, the method was implemented on a problem on solid fuel combustion governed by a highly nonlinear system of partial differential equations. This type of combustion is being investigated as an innovative method for synthesizing advanced metallic and ceramic materials for use in high temperature engine components.

In initial studies, Argonne and Northwestern researchers determined that the temperature and velocity of the advancing combustion front underwent a sequence of bifurcations (in which a single solution to the equations splits into two different solutions, depending on the value of a critical parameter). At first these quantities remained constant; then, as a parameter proportional to the activation energy of the reaction was increased, they became sinusoidally oscillatory. As the parameter was increased further, the sinusoidal oscillations evolved into relaxation oscillations with narrow, sharply peaked spikes in time. They subsequently became doubly periodic via a secondary bifurcation.

Prior computations in the literature suggested that the period might continue to double via a cascade of period doubling bifurcations, thus providing a route for the development of chaotic behavior. However, these results were not conclusive because the computations had to be stopped due to the limited accuracy of the computational method. Using the new procedure, it was established that rather than such a cascade to chaos, the doubly periodic behavior ceases to exist above a critical value of the controlling parameter, and the quantities recover their single periodic character. This is the first such demonstration of its kind and is providing new insight into a problem that involves sensitive, large scale scientific computations on supercomputers.

This work was carried out on the Cray 2 computers at the NMFECC.

32. **Programming Environment Devised for Constructing Parallel Programs**

Researchers at Argonne National Laboratory's Advanced Computer Research Facility have now designed new software tools that provide an efficient and effective method for writing scientific software that can be transported from one manufacturer's machine architecture to any other. The main tool is a package called SCHEDULE, which serves as an interface between the user's Fortran program and the intrinsic architectural design details of a computer system. SCHEDULE is designed for developing and analyzing parallel programs for scientific computations in which an algorithm is defined in terms of processes and dependencies among the processes. An important advantage of SCHEDULE is that it allows complete portability of user programs - a critical issue, given the diversity of advanced architectures now commercially available. The graphics post-processor in the package enables programmers to trace a program during execution and to expose serial bottlenecks that inhibit parallelization.

33. **High-Degree Low-Diameter Interconnection Networks**

Los Alamos researchers have invented a new class of networks with greatly reduced diameter -- i. e., the maximum number of steps required to go from one node in the network to any other. Using a graph theoretical technique called "Cayley coset graphs," vertex symmetric graphs can be proven to describe optimal global communication algorithms for networks of computers. Because each node of the network looks essentially like any other node, large networks can be built out of simple components to provide scalable computer power for large scale computational problems as well as wide area network connections for a distributed scientific community.

For example, a hypercube of diameter 7 (i.e., each node is connected to its 7 nearest neighbors) only 128 nodes can be connected. A Faber-Moore graph of diameter 7 can connect up to 60, 480 processors.

### 34. The Interaction of a Benzene Ring with a Noble Gas Atom

Perhaps the largest ab initio electronic structure calculation ever attempted has been done on the four processor Serial No. 1 CDC/ETA Systems supercomputer, the ETA-10E at Florida State University. The calculation is a geometric optimization of a benzene ring in the presence of a noble gas atom. Two well-known major ab initio electronic structure packages were moved with a minimum of modification to the ETA-10 in 1988, GAMESS and ATMOL. The gain of performance over these packages running on the CDC 205 was between 1.4 and 2.0, but further substantial gains are expected when the Multitasking Library becomes available and is installed and when more than one processor is utilized. The large main memory made it possible to attack the record setting project, the first application of GAMESS on the ETA-10.

A thorough understanding of large molecules is vitally important to the Department in a number of ways. As an example, molecules with benzene rings are common in petroleum products: the Department would like to discover more efficient methods of extracting the energy from petroleum sources and ways to use petroleum more effectively as lubricants.

## Energy Biosciences

### 35. Development of *Arabidopsis* as an Experimental System for Plant Research

Arabidopsis is a very small higher plant that was primarily studied as a biological oddity until Dr. Somerville of the Michigan State University/DOE Plant Research Laboratory in the early and mid 1980's showed how easily mutations in this plant could be induced, recognized and employed for studying many different plant processes. The ease with which this plant can be grown (requiring a few square yards as opposed to acres) and studied (containing the least known amount of DNA of any higher plant, making molecular biological studies much easier) now makes it the most commonly used plant system for basic biological research.

### 36. Molecular Analyses of Hydrogenases in Anaerobic Bacteria

Molecular hydrogen is believed to be the primary "currency" involved in the transfer of energy within consortia of anaerobic bacteria. The enzymes responsible for forming and consuming hydrogen in anaerobic bacteria, hydrogenases, have been the subject of detailed study at the Universities of California (Riverside) and Georgia and Ohio State University from the mid 1980's to the present. Three forms of hydrogenase may be categorized based on the metal cofactors present in the enzyme. These are the iron-containing form (Fe form), a nickel-iron-containing form (NiFe form), and the selenium- nickel-iron form (SeNiFe form). Analysis of the DNA that encodes these proteins shows that there is little overall similarity between the forms, with only a few small identical regions. Relating these differences to potential different biological functions is presently under study in several systems; the methanogenic, the sulfate-reducing (the subject of the DNA sequencing studies described above) and the nitrogen-fixing bacteria. The potential role of hydrogenase in recycling hydrogen produced as a byproduct during the biological fixation of nitrogen by the enzyme nitrogenase also is currently under study. It is hoped that this energy intensive and potentially wasteful process can be made more effective by recycling the the energy lost in the formation of hydrogen back to the nitrogen-fixing bacteria. Recent results on methane forming bacteria have shown that in comparison to other anaerobic bacteria there is an unusual association of the hydrogenase molecule with a large number of electron-carrying protein molecules called ferridoxin. The significance of this interaction is under study.

### 37. Chromosome Studies Lead to Potential New Crop for Diversifying Southern U.S. Agriculture

As an outgrowth of DOE supported basic plant genetic studies on the behavior of chromosomes (the structures of cells that carry genetic information) during the hybridization of distantly related plants, a new crop for the southern U.S. may be emerging. The work which was done at Tifton, Georgia collaboratively with the University of Georgia and the USDA involves two species of the semi-tropical grass genus of Pennisetum. By combining highly desirable genetic and agronomic features of both species, new hybrids have been produced. The hybrids have extremely attractive characteristics in terms of high grain yield, tolerance of drought, fertilizer use, short growing season, and low stature and stiff stalks for easy harvesting. Preliminary tests on the use of the grain for animal feeding have been highly encouraging. The grain protein level is high and the amino acid profile of the protein is nutritionally well balanced.

If this crop is accepted commercially, it will represent a diversification of cropping that offers opportunities in double cropping (two crops annually), a new crop rotation member as well as a crop that is plastic enough to be grown under changing conditions of climate. Without the initial studies on chromosome behavior, the conditions and information base may not have been adequate to pursue this idea.

## Advanced Energy Projects

### 38. Short Wave Length High Intensity Light Source

A light source of record intensity has been made operational at the University of Chicago. Based on a KrF* laser/amplifier system, the source produces extremely short pulses of coherent ultraviolet light with an energy and focusability yielding an intensity of 40 million terawatts per square centimeter. (One terawatt is a million megawatts; one megawatt is a million watts; the total power radiated by a typical light bulb is on the order of 100 watts.) At such intensities, the electric field associated with the light beam is more than 10-fold stronger than the field holding electrons in an atom. Exposing atoms to such an intense light can lead to the discovery of novel atomic and nuclear phenomena, some of which may be of profound scientific and, possibly, practical consequence. The work leading to the operation of this innovative source of intense light was funded by Basic Energy Sciences; appropriate experiments, currently underway, are being funded from other sources.

## Carbon Dioxide Research

### 39. Seasonal $CO_2$ Fluxes: 50% Uptake Rate of Industrial $CO_2$ Emissions by Oceans Confirmed

An extensive field sampling program has shown that the largest source of $CO_2$ entering the atmosphere is from the Pacific equatorial belt (approximately $0.8 \times 10^{15}$ g C annually) while the southern ocean represents the largest sink for the transfer of $CO_2$ from the atmosphere to the ocean (approximately $2.8 \times 10^{15}$ g C). These findings support the hypothesis that approximately 50% ($2 - 2.5 \times 10^{15}$ g C) of the annual industrial emission of $CO_2$ is taken up by the oceans.

Seasonal ocean $CO_2$ fluxes must be understood to construct accurate models of the carbon cycle. These models must agree with contemporary concentrations. Specifically, the models must account for the potential uptake and change in uptake of $CO_2$ by the oceans.

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* This research was directly dependent on the availability of the Energy Research Supercomputers.

The world's oceans are dynamic $CO_2$ reservoirs containing about 50 times as much $CO_2$ as the atmosphere. Because of their large capacity, they play an important role in regulating atmospheric $CO_2$ content and, hence, the global climate. The reservoir capacity is controlled by complex dynamic interactions among ocean circulation, biological activities, and chemical reactions. Although it is considered that about 50% of industrial $CO_2$ has been taken up by the oceans, it is not known how the climatic changes induced by an increase in atmospheric $CO_2$ might effect oceanic $CO_2$ uptake. Since the seasons represent short-term climate changes, systematic observations of seasonal variability of oceanic $CO_2$ chemistry in various climate zones are needed to gain insight into the governing processes and the nature of the oceanic $CO_2$-climate feedback processes. During the past several years, measurements have been made of the oceans' geographical and seasonal variability in the air-sea $pCO_2$ difference (i.e. the driving potential for air-sea $CO_2$ transfer); concentrations of total $CO_2$, oxygen, and nutrient salts dissolved in sea water; and other oceanographic variables. These measurements have been conducted aboard academic research ships, U.S. Coast Guard vessels, and commercial containerships that cross the oceans at regular intervals.

**40. Global Circulation Models: Regional Climate Representation Compared**

An extensive intercomparison of four general circulation models (GCMs) concluded that although model simulations of the present climate often agree well with observations and with each other when comparing global scale, seasonal or annual averages, significant disagreements become apparent as the spatial extent is reduced, particularly when detailed, regional distributions are examined.

These results call into question the ability of these models to project the amplitude of future climatic changes on anything approaching the smaller, regional scale of a state or even a few states. Such detail is essential if accurate regional impact or resource assessment studies are to be conducted.

To estimate potential climatic changes induced by increasing concentrations of carbon dioxide and other energy-related trace gases, scientists rely on theoretically-based numerical models or GCMs. The difficult questions is the predictions of the extent, pattern and timing of the changes that will occur. Generally, verification studies have focused on the adequacy of model representations of global scale features of the climate rather than on model behavior on sub-continent and finer scales. In addition, the focus has usually been on the accuracy of predictions at tropospheric and stratospheric level, rather that at the surface where local variations can be large but where the predictions are most needed. Nor have there generally been detailed, regional intercomparisons among the results of different models.

As an initial step to determine the extent of agreement among models and between models and observations, a detailed intercomparison of the ability of four GCMs to simulate surface air temperature and precipitation for the recent $CO_2$ concentration ($1xCO_2$) and for a doubled $CO_2$ concentration ($2xCO_2$). This study examined model performance over a range of domains from global to regional.

On the global scale, the predicted median temperatures of the models are within 2°C of the observed median temperature. However, as the domain becomes smaller, the disagreements generally increase, particularly over land during the Northern Hemisphere summer. Differences in the median temperatures between individual models and observations span a range of nearly 12°C from -4.8 to + 6.8°C in such cases. The ability of the models to simulate present precipitation patterns is also limited. Again, over small scales the ranges in model estimates and differences from observations tend to increase

To study the $CO_2$ effect on climate, each of the models has performed essentially the same "experiment" to determine the climatic sensitivity to a doubling of the $CO_2$ concentration. Although in this case models can only be compared with each other because there is no observational data set for a $2xCO_2$ condition. All models indicate global warming comparing model results at $2xCO_2$ to $1xCO_2$. However, again, the previously stated conclusions are the same, GCMs are not capable of providing reliable regional results.

### 41. *Dynamical Model of the Chemical Processes in the Troposphere and the Stratosphere

A Chemical-Radiative-Dynamical model of the troposphere and stratosphere has been developed. In FY 1988 the variation of the solar flux with altitude, latitude, and season was modeled with improved accuracy. The improvement accounts for multiple scattering by clouds and aerosols and can be used to determine solar heating rates and photodissociation rates. Also, the calculation of the absorption of infrared radiation in the upper stratosphere was substantially improved. The resultant net heating rates are extremely important to correctly model the transport processes and the derived atmospheric temperature changes under the dynamic chemical conditions. These improvements affect the most significant factors of the model; they are both determining factors in the feedback to other atmospheric processes.

This model has been applied to a number of research studies focused toward improving the understanding of the role of atmospheric chemistry plays in global climate changes. For example, measurements of carbon-14 created by previous atmospheric nuclear tests were utilized to trace atmospheric transport processes.

Understanding of chemical and biological effects of anthropogenic perturbations to atmospheric trace gases is a nontrivial problem which is now well recognized to have global implications. The results of this study have been presented in numerous national and international forums in the last year. These studies have contributed significantly to several important reports on Global Change. Without the CRAYs at Livermore, the Department's studies would not have kept pace with other international efforts, much less have been one of the pace setters.

### 42. Carbon Dioxide Boosts Crop Yields

Jointly conducted research by DOE and U.S. Department of Agriculture demonstrates increased crop yield when crops are grown at higher levels of $CO_2$. Most data have been obtained with open-top chambers (OTC) which maintain $CO_2$ concentration at about 600 ppm. USDA is reporting crop yield increases of 30% (soybeans) to 80% (cotton) when grown in OTCs at these high $CO_2$ levels. Planned tests with a new method called Free-Air-$CO_2$-experiment (FACE) are being publicized. This new approach employs a circular array of standpipes to maintain desired levels of $CO_2$ over approximately $100m^2$ of experimental area, and it avoids disturbance to plants from the plastic OTC barriers. Tests of the FACE concept by DOE/USDA involve scientists from BNL and DOA Agriculture Research Service conducting experiments at Yazoo City, Mississippi.

### 43. $CO_2$ Increases Biomass, Improves Water-Use, and Delays Senescence of a Salt-Marsh Ecosystem

A field experiment with salt-marsh plants found that elevated $CO_2$ (690 ppm) levels caused increased photosynthesis and fixation of carbon for an important wetlands ecosystem on the Chesapeake Bay. Increased numbers of shoots and more biomass were measured for a $C_3$ ($C_3$ and $C_4$ are shorthand terms for two different major classes of plants) community. These responses were not observed,

* This research was directly dependent on the availability of the Energy Research Supercomputers.

however, in an adjacent $C_4$ community. These observations of differential response based on carbon fixation pathways are a first-time confirmation of biochemical theory for plants growing at elevated $CO_2$ in the field.

Elevated $CO_2$ also decreased water loss by plants growing in both $C_3$ and $C_4$ communities. The decrease of water use, about 25% for $C_3$ plants and about 35% for $C_4$ plants, and the increase of photosynthesis, generates more growth per unit of water consumed, which is commonly expressed as improved water- use efficiency. This effect of $CO_2$ on water use offers profound implications because all terrestrial plants experience periods of water stress. Relaxation of the stress by increased $CO_2$ not only would improve plant growth, but reduced transpiration could also alter the hydrology of ecosystems and crops, thus making water available for other uses.

Senescence or end-of-season mortality of plants was delayed by $CO_2$ in both communities. The longer growing season permitted plants of both $C_3$ and $C_4$ communities to fix carbon for a longer period; the combined effects of increased photosynthesis, improved water-use efficiency and delayed senescence enabled the ecosystem to sequester more carbon relative to the net amount fixed by the ecosystem at today's concentrations of $CO_2$ (350 ppm). This one-year field experiment illustrates dramatic initial response to $CO_2$; observations are continuing in order to determine if such responses are sustained for the long-term, and to provide explanations of the complex interactions involving $CO_2$ enrichment, water stress, temperature, the role of salinity and interactions involving other nutrients.