

SOME EXAMPLES OF ACCOMPLISHMENTS

UNDER THE BASIC ENERGY SCIENCES

PROGRAM DURING 1985

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The Basic Energy Sciences Program supports about 1200 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.

Some Examples of Accomplishments Under the Basic Energy Sciences
Program during 1985

Table of Contents

1. Underground Imaging Using Electromagnetic Tomography
2. Laboratory Scale X-Ray Laser Demonstrated for First Time
3. Polymeric Extractants Effectively Recover Toxic or Precious Metals from Rivers or Seawater
4. New Class of High Resolution Finite Difference Methods Developed to Model Compressible Fluid Flow Problems
5. Highly Ordered Orientation of Lignin Relative to Plant Cell Walls Discovered
6. Automated Synthesis Technique Developed for Preparing Magnetostrictive Alloys
7. Cavity Nucleation and Growth During Compressive Creep Deformation of Ceramics Characterized
8. Model Molecules Designed as a Step Toward Artificial Photosynthesis
9. Carbon Monoxide Adsorbed on Nickel Catalysts Found to Modify the Chemical Properties of Nickel Itself
10. Method Developed for Separation of Coal Macerals of High Purity
11. New Type of Molecular Behavior Identified Through Laser-Excited Chemistry
12. Hexavalent Neptunium Immobilized by Chemical Bonding to Soil Constituent
13. New Fischer-Tropsch Catalysts Derived from Zeolitic Aluminoferrisilicates
14. New Static Ultra-High Pressure Record: Studies of Hydrogen and Deuterium
15. Direct Observation of Charge Density Waves with a Cryogenic Tunneling Microscope
16. Explanation of Transition-Temperature Oscillations in Thin Superconducting Films
17. High Pressure Studies Show Unique Behavior of Bonding in Actinide Metals

18. A Fast Algorithm Well Suited for Lattice Problems was Discovered
19. New Model of Ore Formation Also Looks Good for Oil Exploration
20. First High Resolution Study of Magnetic Structures Accomplished Using X-Ray Scattering
21. New Organic Metal Superconductor Successfully Designed, Synthesized and Characterized
22. New Light Thrown on Destructive Noise in Heat Exchangers
23. Experiments Lead to Better Models of Natural and Forced Convection
24. Site Studies Lead to Best Image Yet of Roots of Large Caldera
25. Elucidation of the Metabolic Pathway Leading to Methane Production from Carbon Dioxide
26. The Pigment Phytochrome was Recently Shown to Exist as Two Distinct Molecules
27. Possibility of Tritium-Breeding in Fusion Reactor Blankets Confirmed
28. Theory of Novel Semiconductor Compounds
29. Specific Transmission and Expression of Foreign Genes in Plants
30. Million-Degree Microexplosions
31. New Chemical Extractant Discovered for Treating Nuclear Wastes
32. Quantization Effects Discovered in Photoelectrochemical Systems
33. Energy-Saving Chemical Process Discovered, Patented and Moved Quickly from University to Industrial Use
34. New Mechanism Identified for Hydrogen Induced Failure
35. A Method Developed for Yielding Soluble Conducting Polymers for the First Time
36. Steel Wire with Superior Properties and Reduced Cost Achieved Through Microstructural Modification
37. Carbon Dioxide Enrichment Increases Crop Yield
38. A 200-Year Atmospheric Record from Measurements of Carbon Dioxide in Ice

1. Underground Imaging Using Electromagnetic Tomography

A new geophysical technique has been used to map the flowpaths of water in fractured rock. The method, called Alterant Geophysical Tomography (AGT), involves the use of chemical tracers such as a highly concentrated sodium chloride solution to change the electrical properties of fluids flowing through permeable fractures. Sources of electromagnetic radiation are introduced into boreholes and detectors strategically placed at various locations on the surface. The absorption of electromagnetic radiation between the sources and detectors is measured at various times (before, during, and after the introduction of the tracer). Spatial variations of the absorption can then be used to construct a three dimensional map locating the positions where the tracer affected the absorption; the methodology is related to that used in medical tomography. Changes in the absorption caused by the tracer are determined by subtracting an image representative of baseline conditions from an image obtained after the tracer is used. This method has been used successfully in a granitic rock mass to map the flow paths followed by the tracers.

Several techniques are available to the geophysicist and geologist for in situ study of water flow through a rock mass. However, until recently, none of these techniques has been able to yield high spatial resolution maps of ground water flow and differentiate between effective and total porosity. Alterant Geophysical Tomography has been shown to do both. Therefore, this technique can be used to map open fractures in rock, to distinguish between dynamic and static water pools and to delineate the principal paths taken by water injected into fractured rock systems. Geotomography should be able to provide detailed information on those types of geophysical fracture problems which can be obtained by no other means.

(Lawrence Livermore National Laboratory, R. Lytle)

2. Laboratory Scale X-Ray Laser Demonstrated for First Time

In October, 1984 Princeton University scientists announced the first demonstration of lasing action in the x-ray spectrum, using a principle that lends itself to the development of a laboratory-size x-ray laser. More recently, in March, 1985, the next big step, a successful use of multilayered mirrors for the enhancement of the stimulated x-ray radiation, was achieved.

There are many important uses for unique, high-intensity, laser produced x-rays in medicine, physics, biology and technology in general. In medicine, the finely focused x-ray laser would allow better localization in the use of CAT scanners and similar devices. Plasma physicists could make extensive use of x-ray lasers to measure temperature, impurity densities, and ion transport in fusion plasmas. In the area of solid state physics, x-ray lasers could substantially improve structural analysis of crystalline solids. X-ray microscopes would have greater resolution than can be achieved by present-day electron-beam systems.

At the heart of this approach to an x-ray laser is the utilization of a fast-recombining plasma. Initially, the plasma temperature is increased until the carbon atoms become completely ionized; that is, totally stripped of electrons. The plasma then cools rapidly by intensive radiation losses, causing ions to recombine with free electrons. Because recombination occurs primarily at the higher energy levels (outer orbits) while lower levels (inner orbits) do not capture electrons, an unstable condition known as population inversion occurs. Electrons in the higher energy levels then "avalanche" to the lower levels, creating a more stable electron configuration. In the process, each electron loses energy in the form of an x-ray photon. The lasing process occurs when the photons produced in this fashion stimulate the emission of additional photons from other ions, initiating a chain of such events. The result is an intense, coherent x-ray pulse of a single wavelength.

A carbon dioxide laser has been used to produce a dense carbon plasma column of 1-5 cm length, which is held to a 1-2 mm diameter by confinement in a strong magnetic field. A 100-fold increase of the 182 Å x-ray line has been observed in the direction along the plasma column, due to the desired stimulated-emission process. This result corresponds to an amplifier "gain" of about 6.5. By using multilayered x-ray mirrors a 100% enhancement of the stimulated radiation was achieved.

(Princeton Plasma Physics Laboratory, S. Suckewer)

3. Polymeric Extractants Effectively Recover Toxic or Precious Metals from Rivers or Seawater

Polymers containing accessible chemically active groups are being synthesized which can efficiently remove major or trace amounts of toxic or precious metals from acidic waste streams, rivers, or even sea water. The polymer itself is inactive but provides a structure to which the chemically active groups are attached, much as leaves are attached to the branches of a tree. The polymers are styrene-based with open structures similar to styrofoam. The active component in the polymeric extractant is a phosphorus-containing group which selectively extracts the metal ion of interest. The molecular composition of the group is designed for the particular metal ion to be extracted. The new extractants are synthesized by a relatively simple procedure from inexpensive chemicals. They were devised through a collaborative effort between Oak Ridge National Laboratory and the University of Tennessee. The use of these new extractants is simple, in contrast to present cleanup or recovery systems which generally require more materials or multiple separation steps to accomplish the same degree of recovery.

The extractants, contained in solid rigid structures, are immersed into the streams to be cleaned up and removed when they have become saturated. The metals collected are removed from the extractants allowing reuse of the polymeric extractant system.

Some metal ions, notably gold, silver and mercury, are actually recovered as the metals themselves, while others, e.g., uranium, are recovered but not reduced to the metal. Of particular advantage, the streams containing the metal values need not be pretreated to reduce acidity or salt content, a step necessary with previous polymeric extractants. Common metals -- iron, aluminum, chromium, etc. -- do not interfere with the process. Economic analyses of a recovery process flow-sheet using the new polymers indicate the value of the metals recovered would substantially exceed the materials and operating costs for large-scale application of the new system.

(University of Tennessee, S. Alexandratos; Oak Ridge National Laboratory, W. McDowell)

4. New Class of High Resolution Finite Difference Methods Developed to Model Compressible Fluid Flow Problems

Mathematical equations that describe physical behavior are the cornerstone for scientific and engineering advances. Calculus, for example, was developed by Isaac Newton to meet the need he had for describing gravitational forces and the motion of bodies. As science and engineering have advanced, so has applied mathematics. Of particular importance in the applications that have been made in science and engineering is that certain kinds, or classes, of equations show up time after time. The inability to fully solve these equations has limited their usefulness at times, but practical needs have led to the development of various approaches to their solutions. These approaches have relied on various techniques. Among the most important has been the use of assumptions about the importance of certain terms or parameters in the equations to simplify them, thereby facilitating solution. A second powerful tool has been the application of computers to actually carry out large numbers of numerical trial and error tests, known as numerical solutions, to arrive at answers. The availability of high speed computers has made numerical solutions extremely valuable in dealing with complex phenomena not heretofore subject to exact solutions.

This work has dealt with the development of a new class of numerical methods specifically designed for resolving, by modeling, compressible fluid flow problems. The behavior of gases over a wide range of temperatures and pressures including behavior under drastically changing conditions is of practical interest to physicists and engineers. Over the past several years substantial advances have been made in the numerical analysis of a class of equations, those known as hyperbolic partial differential equations, which include equations describing compressible gas dynamics. Among the available numerical methods are a group developed to deal with physical phenomena which are not continuous (examples of non-continuity would be the abrupt change in phase at a given temperature and pressure of a melting solid, or the change in density of material at the interface between a gas and a liquid). The methods are known as finite difference schemes. High resolution finite difference schemes which accurately resolve flows with strong discontinuities have been developed by investigators at Lawrence Berkeley Laboratory and Lawrence Livermore National Laboratory. These methods incorporate exact features of nonlinear waves, are stable near interfaces between the subject fluid and shock waves fronts or surfaces, and are highly accurate in regions where the flow is smooth. Previous computational results were not adequately resolved because of constraints of the computer technology available at the time.

These new results are fully resolved because they were obtained with an updated finite difference scheme on a modern supercomputer, (Cray-1). Thus the numerical analysis of perfect compressible flow is now on an equal footing with experimental methods. These computational tools provide an effective alternative to laboratory testing and are being incorporated into large applications programs currently in use at DOE laboratories.

(Lawrence Berkeley Laboratory, P. Colella; Lawrence Livermore National Laboratory, P. Woodard)

5. Highly Ordered Orientation of Lignin Relative to Plant Cell Walls Discovered

The world's greatest reservoir of renewable resources is comprised of trees and plants. Both woody and herbaceous plant cell walls, composed of lignocellulose, make up most of this resource. Nevertheless, the molecular structure of cell walls and the functions performed by their various constituents are far from understood. Recently a better comprehension of one component of cell walls, lignin, has been achieved. Lignin is a polymeric array of six-sided, ringed molecules, and has been studied with respect to the orientation of the polymeric arrays relative to the other cell wall constituents that make up lignocellulose. The value of this information is that our ability to break down the cell walls, to separate and recover its components, and to identify their particular functions, will be greatly enhanced by detailed knowledge of its structure. Thus this research has significance in terms of not only understanding the intrinsic structural nature of these energy resources, but also with respect to developing strategies to overcome existing problems in the use of lignocellulose for fuels and chemicals. In these studies, carried out at the Institute of Paper Chemistry in Appleton, Wisconsin, a technique employing a Raman microprobe, one which relies on light scattering and interaction to elucidate molecular structure and orientation, was used along with other approaches.

The results obtained from studies on sections of woody tissue indicate that the aromatic rings in lignin are oriented with the plane of the aromatic ring parallel to the cell wall. It used to be assumed that lignin was randomly oriented within the the cellulosic portion of the cell wall without any regular structure. The experimental results also revealed instances, possibly periodic, of perpendicular orientation of the aromatic rings relative to the cell wall plane suggesting "nodes" in molecular orientation, but the significance of this has not been explored yet.

(Institute of Paper Chemistry, R. Atalla)

6. Automated Synthesis Technique Developed for Preparing Magnetostrictive Alloys

Magnetostriction, a change in shape or volume of a material when subjected to a magnetic field, is a highly desirable property for a number of practical applications; these applications require the material to go through many cycles of being magnetized and demagnetized. Normally, materials lose their ability to go through the cycle fairly quickly. At Ames Laboratory, a new alloy was developed which does not lose this ability and a synthesis technique for the new alloy's production has been developed. The technique is automated and is highly reproducible; a number of uses for the new alloy already have been identified. The new magnetostrictive alloy is called Terfenol-D. The automated synthesis technique that has been developed provides a material that: (a) is grain oriented with circular, square, and hexagonal cross sections useful for transducer drive elements and (b) consists of single crystals with a selected axial crystallographic orientation, and (c) demonstrates the acceptability of commercial-grade starting material. Terfenol-D is a rare earth alloy of iron.

Currently the Ames Laboratory is the only source for these materials which they supply to research and prototype development programs. The projected commercial demand is approximately 2000 kg/yr (up 40 times from the present R&D demand), so a plan has been devised, in concert with industry, to develop and transfer the technology for mass production, and automation. Commercial applications for rare-earth-iron magnetostrictive materials that stand to take advantage of this new synthesis technique are underwater sonar devices for Naval defense systems, underground sonar devices for oil field exploration, micropositioners for laser mirror actuators, fuel injection systems for diesel engines, and robot components such as hands, wrists, and elbows. etc.

(Ames Laboratory, O. McMasters)

7. Cavity Nucleation and Growth During Compressive Creep Deformation of Ceramics Characterized

Ceramics have become important structural materials for a variety of applications. A phenomenon has been observed however, especially at elevated temperatures, which slowly deforms the material, weakening it and possibly leading to its failure. This phenomenon, called "compressive creep", involves the formation of cavities within the ceramic while under compression. With the goal of improving the performance of structural ceramics and also of predicting their lifetimes, the onset of cavity formation and growth has been studied using the powerful techniques of neutron diffraction. Scattering of neutrons by cavities in alumina and silicon carbide ceramic materials has provided a detailed characterization of cavity nucleation and growth processes during compressive creep.

Samples of three different ceramics, (1) an alumina containing a relatively thick and continuous, glassy grain boundary phase, (2) an alumina containing no continuous grain boundary phase, and (3) silicon carbide containing a relatively thin and continuous, glassy grain boundary phase have been characterized. The neutron scattering measurements provide a means of characterizing both the nucleation rates and the growth rates of grain boundary cavities during the early stages of creep. These studies have shown unequivocally that cavity nucleation does occur and have also identified some very significant differences in the cavity nucleation and growth phenomena of these three different ceramic systems. For example, in both aluminas cavity nucleation occurs throughout creep deformation while in the silicon carbide cavity nucleation is limited to the very early stages.

These results studies indicate that accurate predictions of the lifetimes of ceramic components at elevated temperatures can be made only when reliable models of cavity nucleation and growth are combined with proper failure criteria. Refined nucleation and growth models are currently being developed using these neutron scattering results to define the necessary modifications. In addition, the results have also suggested methods that could be employed to improve ceramic performance at elevated temperatures, e.g., by the inclusion of hard grain boundary precipitates to reduce cavity nucleation.

(Southwest Research Institute, R. Page)

8. Model Molecules Designed as a Step Toward Artificial Photosynthesis

A significant advance in the quest for an artificial photosynthetic system has been achieved: the chemical synthesis of a model "photoreaction center".

A photoreaction center -- a molecule or a group of interactive molecules -- absorbs light energy, which causes an electron to move from one end of the reaction center to another. This "charge separation" initiates the chemical reactions of photosynthesis. It is a critical step in triggering the photosynthetic process.

In nature chlorophyll is at the heart of the photoreaction center. Light is absorbed followed by rapid electrical charge separation involving other components in the photoreaction center. A key feature of nature's system is that the charge separation takes place in several successive steps. In this work, the model compounds prepared contain a chlorophyll-like molecule in the core, to which chemical groups, selected to enhance and prolong charge separation, are attached. The chlorophyll-like structure absorbs visible light, causing an electron to be transferred from it to one of the attached chemical groups. Its electron deficiency is immediately made up by an electron transferred from another neighboring chemical group.

This is the first demonstration of photoinduced charge separation by multiple electron transfer in a model system of known structure. Indeed, the present systems show a marked increase over previous model compounds in the length of time (still exceedingly brief) that the charges are maintained apart before recombination, a necessary feature where one hopes to cause useful chemical reactions this way. Future work on model systems, aimed at positioning electron donor and acceptor components in the optimum geometry for high efficiency solar conversion, will continue to draw upon current advances in research on natural photosynthesis.

(Argonne National Laboratory, M. Wasielewski)

9. Carbon Monoxide Adsorbed on Nickel Catalysts Found to Modify their Chemical Properties

Until now, studies of catalytic reactions of gases or liquids on solid surfaces could measure only the changes taking place in the molecules affected by the solid catalytic surface. Although detailed studies of surfaces of solid catalysts have been carried out, the dynamic effects that the catalytic reactions have on the catalytic surfaces itself have not been determined and nothing specific could be concluded about that aspect of catalysis.

Now it has been experimentally demonstrated, using a model system of carbon monoxide adsorbed on the surface of a nickel catalyst, that the carbon monoxide does actually modify the chemical properties of the nickel surface. By combining different state-of-the-art techniques for studying adsorbed species on single crystals, measurements were made of the reflected infrared spectra while changing the amount of carbon monoxide adsorbed on a nickel crystal surface. From the infrared frequency shifts observed at various levels of adsorbed carbon monoxide, it was concluded that they were due to modification of the chemical properties of the nickel surface itself by the carbon monoxide. Additives to solid catalysts alter surface properties and, consequently, both adsorption and chemical properties at the surface. These experiments provide an important new capability for quantitatively evaluating the effects on catalytic properties of substances added during or after the manufacture of catalysts.

(University of Pittsburgh, J. T. Yates)

10. Method Developed for Separation of Coal Macerals of High Purity

In building the knowledge base for future conversion of coal to substitute fuels or chemical feedstocks, we face some difficult facts: each coal in a coal deposit is unique in its chemical and structural makeup, and each coal is a distinct, chemically complex mixture.

Coals contain organic substances called "macerals" which may be thought of as the basic building blocks of coal. The different set of macerals in each coal have origins in different plants and plant parts, such as leaves, stems, seeds or spores. At Argonne

National Laboratory, a method has been developed for separating the macerals of a coal sample from each other. This new method for providing "pure" macerals is based on density gradient centrifugation. It is a mechanical separation taking advantage of the differences in density between the macerals and other constituents of coal to separate them from one another. Providing maceral samples or know-how for separating them is leading Argonne into many collaborative studies with university and industrial laboratories.

This development follows close on the heels of the Premium Coal Sample Program, also at Argonne National Laboratory, which has successfully processed and sealed samples of the first premium coal into 9,000 ampoules containing either five (7,500) or ten (1,500) grams of coal. These are available to scientists world wide for basic research purposes. In the past, non-uniform freshness and handling of research samples of coal from the same source seriously affected the reliability of comparisons of research results from different laboratories ostensibly using samples of the same coal. Now for the first time coal researchers will be able to compare results on identical coal samples, for years to come. The construction and successful operation of the controlled atmosphere chamber and machinery for processing a ton of coal into very small particles in an atmosphere containing less than 100 parts per million oxygen reflects ANL's rather unique ability with large inert atmosphere chambers. Eight coals are to be similarly prepared and distributed over the next two years.

(Argonne National Laboratory, G. Drykacz, K. Vorres)

11. New Type of Molecular Behavior Identified Through Laser-Excited Chemistry

Use of a unique high-resolution spectroscopic technique has led to the first observation of "chaotic" vibrational behavior of molecules.

In previous research on laser-excited chemistry, so-called "mode selection" has been attempted where the absorbed laser beam energy would excite vibrations in molecules to break bonds between specific parts of the molecules. It has been observed that the absorbed energy is usually redistributed into other well-defined vibrational modes, resulting in rupture of a different bond, or no bond at all. Also, of course, the absorption of insufficient energy fails to rupture any bond.

Heretofore, the energy range bounded between that needed for bond rupture and some level below it has been inaccessible to study because of the tendency for absorbed energy to be rapidly redistributed. Now that intermediate energy range has been observed in acetylene molecules. By using a laser to excite the acetylene molecules to upper electronic states, and then using a different laser to trigger emission of energy, the molecules' energy level falls to the intermediate vibrational region of the ground electronic state.

What was then observed was a surprise: rather than the rapid redistribution of remaining energy to well-defined vibrational states, "clumps" of 20-40 vibrational states were seen, each clump containing randomly distributed energy levels. This unusual molecular behavior provides new insight into mode-selective chemistry and the elusive capability to run chemical reactions via more energy-efficient pathways.

(Massachusetts Institute of Technology, R. Field, J. Kinsey)

12. Hexavalent Neptunium Immobilized by Chemical Bonding to Soil Constituents

Neptunium, a long-lived radioactive element produced as a by-product of nuclear power, has been considered to be more of an environmental hazard in nuclear wastes than other actinide elements (elements of atomic number 90 through 103). This is because a particular chemical form of it, the singly-charged, pentavalent oxidation state, binds less strongly to soils and thus is more mobile in ground waters than other actinide species.

The potential concentration of neptunium in ground water is extremely low; recently, advances in electrochemical measurements of actinides in extremely dilute solutions have shown that under attainable conditions in ground water, and at the extremely low dilutions that neptunium might be found in, neptunium can exist in a doubly charged, hexavalent state that is much more readily immobilized by soil. Thus there is now reason to believe that the hazard posed by neptunium may be less than previously anticipated.

(Oak Ridge National Laboratory, L. Maya)

13. New Fischer-Tropsch Catalysts Derived from Zeolitic Aluminoferrisilicates

Fischer-Tropsch catalysts have been in use for decades. Developed in the early twentieth century, these iron-based catalysts have been the workhorse for the petroleum and petrochemical industries for conversion of crude oil to more desirable, lower molecular weight hydrocarbons. Research has been focused on understanding their mechanisms with the goal of improving the selectivity of conversions promoted by this class of solid catalysts.

Zeolites are naturally occurring materials with an open structure of molecular dimensions that have been found to be selective in admitting certain sizes or shapes of molecules into their open structures. This property of selectivity can be controlled through altering the zeolite's composition and dimensions. This current research has successfully wedded the selectivity of a zeolite with the properties of a Fischer-Tropsch catalyst.

At Argonne National Laboratory, a new approach has been successfully applied to the formation of extremely small metallic iron particles (diameter $<20 \text{ \AA}$) within an aluminoferrisilicate (AFS) zeolitic structure. The iron particles are highly dispersed and have been produced in two different structures, both of which have now been shown to be active Fischer-Tropsch catalysts. A further modification procedure permits the activity and selectivity of this new Fischer-Tropsch zeolite catalyst to be modified by introduction of other elements such as nickel or cobalt. Good selectivity for producing high yields of light hydrocarbons (less than 5 carbons in the molecule) has been found in preliminary tests of these new catalysts.

Employing shape-selective materials, e.g., zeolites, is a potentially powerful method for improving selectivity in heterogeneous catalytic conversions. One of the most important long-range technological targets in catalysis is the efficient production of feedstock chemicals from coal or biomass sources via hydrogenation of carbon monoxide. Iron-based catalysts are preferred due to iron's availability and cost relative to other metals with similar catalytic properties. Improved performance with increasing metal dispersion has been reported for iron Fischer-Tropsch catalysts, but achieving very high dispersions has been very difficult. This new method for producing highly dispersed iron particles on zeolites is a promising new direction, and is potentially applicable to incorporation of other elements, either for Fischer-Tropsch conversion or other important energy-related catalytic processes. Currently, direct Fischer-Tropsch conversion at modest operating pressure with good selectivity to light hydrocarbons appears to be a reasonable prospect using zeolite catalysts.

(Argonne National Laboratory, L. Iton)

14. New Static Ultra-High Pressure Record: Studies of Hydrogen and Deuterium

Hydrogen and deuterium have been pressurized under static conditions to 1.47 million atmospheres and their infrared and Raman spectra measured.

An effort at the Carnegie Institution of Washington to improve techniques to subject hydrogen and deuterium to static pressures in excess of one million atmospheres (a megabar) has been supported by the Division of Materials Sciences for a number of years. This goal was established to investigate experimentally a very fundamental theoretical prediction that hydrogen will become metallic, and then superconducting, at extremely high pressures, and temperatures greater than 30°K. Until recently, it has not been possible to obtain pressures greater than 0.7 megabars. In the latest experiment, the Carnegie scientists have reached 1.47 megabars in both hydrogen and deuterium. This investigation was extremely difficult - requiring the use of very small samples and pressure calibration experiments on 'harder' materials to pressures significantly greater than two megabars. Still, metallic properties of hydrogen and deuterium were not observed, although the infrared and Raman spectra measurements made at 1.47 megabars do suggest that these materials will become metallic: this was not clear from experiments at 0.7 megabars. Theoretical predictions for the onset of metallic properties lie in the range from 0.7 to 2.1 megabars.

(Carnegie Institution of Washington, P. Bell, H. Mao and coworkers)

15. Direct Observation of Charge Density Waves with a Cryogenic Tunneling Microscope

"Charge-density waves" describe the time dependence of charge distribution at the molecular level, and are especially important in explaining the electrical behavior in semiconductors.

Recently, using a "tunneling" electron microscope able to view samples maintained at cryogenic temperatures, 78°K in this experiment, "charge-density waves" have been observed on surfaces of tantalum disulfide. This "tunneling" microscope, which uses electrons "tunneling" out of the sample itself, allows thick samples to be examined with extremely high resolution.

These observations are the first obtained for a tunneling microscope operating at 78°K and also the first direct observations of charge-density waves. The formation of charge-density waves occurs below a critical temperature, about 120-230°K for the tantalum disulfide material studied, and is accompanied by atomic displacements on the order of 0.1 to 0.25 Å. These measurements revealed distortions of less than 0.5 Å for a given atom and clearly show the systematic atomic displacements on the surface of the tantalum disulfide due to the charge-density wave.

The significance of this observation is twofold. It demonstrates the first tunneling microscope observation made at 78°K which suggests many new applications of this technique to a wide range of materials at cryogenic temperatures. The second is that it constitutes the first direct observation of charge-density waves. Charge-density waves affect the conduction properties of semiconductors and, in turn, the properties of semiconductor devices. The resolution provided by the tunneling microscope will allow a direct test of our understanding of the structure of charge-density waves which, until now, has been inferred only from indirect observations.

(University of Virginia, R. Coleman and coworkers)

16. Explanation of Transition-Temperature Oscillations in Thin Superconducting Films

The temperature at which a material becomes superconducting, the transition temperature, has been found to oscillate when the superconducting material is in the form of a thin film. A new model and experimental evidence appear to satisfactorily overcome inconsistencies previously encountered in trying to explain this phenomenon.

The current model and experiments explain these results on the basis of a film which initially becomes continuous at about 30 Å thickness, and which consists of a collection of small spheres that barely touch. This new model suggests that size quantization in a sphere is the important relationship. Utilizing this model yields a quantization condition that gives an oscillation period twice that expected for a homogeneous film, and consistent with what has been observed experimentally.

Experimental observations of the nucleation and transition temperature of thin films show that films deposited at 4°K could first become continuous as thin as 10 Å, or not until a thickness of as much as 50 Å, depending on substrate conditions. This suggests that in this thickness range agglomeration may occur with spheres that are inter-connected. Quantization conditions for a sphere are applicable since an electron spends most of its time localized within a grain and scatters as much as thirty times before it transfers to the adjacent grain. This is an adequate condition for sharp levels in a particle and transition temperature oscillations.

Thus this new model and experimental evidence favoring it lead to the conclusion that substrate conditions are vitally important in the preparation of very thin superconducting strips with optimum physical parameters.

(Brookhaven National Laboratory, M. Strongin, Queens University, N.Y., A. Paskin)

17. High Pressure Studies Show Rare Behavior of Bonding in Actinide Metals

In a collaborative effort between Oak Ridge National Laboratory and the University of Tennessee, a discovery has been made of a scientific phenomenon rare in the metallic elements. It has been seen in the actinide series of elements, and it provides insights into the understanding of electronic structure and chemical bonding of all the elements.

The electrons surrounding bound to an atom are perceived as "orbiting" its nucleus, and the "outermost" electron is typically the first one to participate in chemical bonding, i.e., the energy needed to "delocalize" it is less than for the rest of the electrons in the atom. Nomenclature for the orbits in which the electrons are found is complex; it is sufficient to note that only the actinide metals (elements 90-103) possess 5f electrons, and only in the lower few elements in the actinide series (protactinium, uranium, neptunium, plutonium) do the 5f electrons participate in metallic bonding at ordinary pressures. This has been explained by the drop in energy of those electrons in the higher actinides, making them unavailable for bonding.

The first clear evidence has been obtained that the f-electron type of metallic chemical bonding can be induced by enormous pressures in elements above atomic number 94, plutonium. The experimental evidence comes from both x-ray studies of actinide metal crystal structures and volume changes for four transplutonium elements: americium, curium, berkelium, californium and berkelium-californium alloys. Only two other examples of f-electron metallic bonding under extreme pressure are known: cerium and praseodymium in the analogous lanthanide series. It was found that when extreme pressures squeeze the atoms together, at a certain threshold pressure for each higher actinide studied, the 5f electrons enter metallic bonding, volume collapse occurs, and the crystal geometry suddenly changes. The volume collapse in some cases is striking: for curium at 440,000 atmospheres, it is 21%!

This research underscores the importance of the unique capabilities of the of the High Flux Isotope Reactor and the Transplutonium Processing Plant, without which it could not have for lack of available samples of the higher actinide metals.

(Oak Ridge National Laboratory, R. Haire; University of Tennessee, J. Peterson)

18. A Fast Algorithm Well Suited for Lattice Problems Was Discovered

Complex mathematical computations, considered hopelessly unworkable even with the aid of the most powerful supercomputers, can now be handled with the development of a fast, accurate, new procedure called the "successive linkage algorithm." Developed by a mathematician holding a joint position at Lawrence Berkeley Laboratory and the University of California at Berkeley, this algorithm is particularly well suited for lattice problems involving large summations of potentials with local interactions.

They key step in the algorithm is the identification of frequently appearing terms in a large summation together with a method for estimating the frequency with which a given term appears. A scaling and extrapolation procedure has also been discovered which enables one to accelerate convergence of lattice calculations to their limiting values -- the values obtained when the lattice becomes infinite.

"Successive linkage" can provide exact answers to certain problems, and reliable approximations to others. It has been used to evaluate thermodynamic quantities for a class of physical models including the "Ising Model" which describes ferromagnetic materials.

(Lawrence Berkeley Laboratory, A. Chorin)

19. New Model of Ore Formation Also Looks Good for Oil Exploration

Successful petroleum exploration and exploitation is becoming more and more dependent on methodical identification and evaluation of deposits that are more and more difficult to reach. This requires gathering and evaluating extensive data to assess a field's potential with a high degree of reliability. Two relatively costly methods, drilling and seismic studies, are the most common means of data gathering. New techniques for data interpretation that demand less data input or lead to more reliable assessment could significantly decrease oil prospecting and production costs.

Studies of related chemical and physical movement phenomena that occur under particular geochemical conditions have led to a novel computer program that models not only what minerals are present in a basin but also the processes over time that have led to their current spatial distribution. Exploiting recent advances in mathematical descriptions of interrelated complex phenomena, the modeling effort was initially directed toward aspects of geoenvironmental important for mining uranium ores. The approach taken was soon seen to be applicable to exploration for petroleum. From the inferred geochemical history at a given location, estimates are made regarding the previous conditions in the basin and its suitability for hydrocarbon production. This 'total' modeling approach allows for more useful information to be derived from the data and for more reliable interpretations to be made because the model is based on actual processes and faithfully adheres to fundamental physical and chemical laws. The incorporation of this practical modeling technique into petroleum companies' exploration and exploitation programs could result in a significantly enhanced success/cost ratio.

(Geo-Chemical Research Associates, P. Ortoleva)

20. First High Resolution Study of Magnetic Structures Accomplished Using X-Ray Scattering

Brookhaven National Laboratory scientists, working at the Stanford Synchrotron Radiation Laboratory with high-intensity X-rays, and using neutrons from their own High Flux Beam Reactor, have completed a comprehensive study of the structure of the magnetic field within a single crystal of holmium. Using these tools, particularly the application of high resolution X-ray scattering techniques, they found it possible to observe the very faint X-ray diffraction due to perturbations of the magnetic field's structure and symmetry in relation to the atoms and electrons in the holmium crystal.

Understanding magnetic structures and their dynamics is important to improving scientific concepts of magnetism and to the development of technologically significant magnetic materials. The usual probe of magnetic properties has been neutrons where the magnetic scattering of the neutrons is comparable with the atomic structural scattering and the two can be resolved from one another. Magnetic scattering of X-rays is only about ten one-millionths as intense as atomic structural X-ray scattering -- too weak to be studied with ordinary X-ray sources. However, with the advent of very intense beams of X-rays from synchrotron sources, X-ray scattering studies are not only possible, but can be used to obtain precise measurements of some parameters difficult to determine with neutrons.

This study has demonstrated the important role that synchrotron radiation can play in magnetic studies, and has already led to a modification of a successful theoretical model for describing the magnetic structure of holmium.

(Brookhaven National Laboratory, D. Moncton, D. Gibbs and co-workers)

21. New Organic Metal Superconductor Successfully Designed, Synthesized and Characterized

Based on principles established in earlier work, a new metal-organic compound with improved superconducting properties was designed and synthesized at Argonne National Laboratory (ANL). Tests of the superconducting properties of this new compound were favorable; they showed the highest superconducting transition temperature ($T_c=5^{\circ}\text{K}$) yet observed for a synthetic organic metal superconductor at normal pressure.

The continuing aim of this research is the development of new synthetic organic metals with a potential for use in electronic systems. Synthetic organic metals offer unparalleled promise in the search for higher superconducting transition temperatures because of the wide range of derivatives which can be synthesized at room temperature.

The compound synthesized in this work is $(\text{BEDT-TTF})_2\text{AuI}_2^-$; BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene and AuI_2^- is the linear diiodoaurate (I) anion. In all $(\text{BEDT-TTF})_2\text{X}$ systems, BEDT-TTF gives up an electron to the X^- specie, or AuI_2^- in this case. At normal pressure, the superconducting transition temperatures of $(\text{BEDT-TTF})_2\text{X}$, where X is I_3^- , IBr_2^- , or AuI_2^- , are 1.5°K , 2.8°K , and 4.98°K , respectively. The AuI_2^- derivative was the result of a rational design effort in which it was predicted that T_c would likely rise when proceeding from $\text{X} = \text{I}_3^-$ and IBr_2^- to AuI_2^- . These results clearly demonstrate the importance of a linear-symmetric anion in producing new organic superconductors and they highlight a new approach to raising T_c , i.e., metal atom insertion into such linear anions.

Commercially available BEDT-TTF (Strem Chemical Co., Inc., Newburyport, MA), used in the synthesis was prepared in a joint venture using a synthetic procedure developed by ANL.

(Argonne National Laboratory, H. Wang, M. Beno, U. Geiser, G. Crabtree, K. Carlson, J. Williams; Sandia National Laboratories, L. Azavado, J. Kwak, J. Schirber; Strem Chemical Co., M. Strem, F. Wagner, C. Sielicki)

22. New Light Thrown on Destructive Noise in Heat Exchangers

Heat Exchangers which play an important role in energy production and utilization systems are often the sources of extremely high noise levels, harmful to both man and machine. The noise is produced by a phenomenon known as "acoustic resonance" when fluids flow over the exchanger tube banks. Without a clear understanding of the underlying processes involved, it is impossible to develop a rational method for designing low noise, efficient heat exchangers. Instead, noise reduction methods are applied in an ad hoc, trial and error fashion.

In a recently completed series of experiments, the precise nature of intense noise generation in exchanger tube bundles has been determined. In a well known phenomenon, the fluid flow across a tube induces periodic, reproducible flow pattern changes at a constant location past the tube. This periodic change alone leads to a relatively low intensity single tone determined largely by the tube diameters and the flow velocity. The new results, however, show that an existing sound field in the flow interferes strongly with the usual flow pattern change and results in intense noise and vibrations. In particular, the period of the flow pattern change becomes attuned to the natural vibration frequencies of the heat exchanger enclosure (cavity modes). Such improved understanding of the mechanism of noise generation will improve the design of future energy efficient, non-noise polluting heat exchangers.

(GA Technologies, R. Blevins)

23. Experiments Lead to Better Models of Natural and Forced Convection

The transfer of heat is fundamental to the production and utilization of energy. Heat -- thermal energy -- is used to convert the energy released in burning coal or oil, in the fission process, and captured from the sun in solar-thermal devices -- to other forms of energy or is used directly. Improving the ability to both use and transfer heat more efficiently is of major practical importance.

Computers are used extensively to calculate heat transfer in energy systems, and, because of the sheer complexity of the associated numerical problems, simplifying assumptions about the nature of the flow are always necessary. Often that introduces uncertainty about the validity of the calculated results. The only way to validate such calculations is through actual experiments but suitable methods have not been available to carry out the needed rigorous and detailed tests.

Recently, techniques for simultaneous flow and temperature visualization have been developed and applied to the needed validation experiments. The flow experiments were arranged to follow as closely as possible the separate, corresponding

numerical simulations. Surprisingly, for some of the simplest possible flows a wide divergence was found between the usual simulations and the observed experimental flows. In particular, some flows which were thought to be quite smooth and uniform were not, while smoothing of temperature gradients took much longer than estimated previously. Both of these aspects of flow have large effects on heat transfer calculations. The enhanced knowledge has now been incorporated in new computer models of flow and heat transfer which are thoroughly tested for accuracy and should be widely useful for designs of important types of heat exchangers.

As these results become more widely distributed, their inclusion in the stock of engineering knowledge and practice will serve to improve the efficiency of many energy production and utilization systems.

(Stanford University, R. Street)

24. Site Studies Lead to Best Image Yet of Roots of Large Caldera

Several years ago, a nationwide search was made for sites likely to give the greatest understanding of continental thermal regimes -- areas of unusually high heat flow below the earth's surface. The sites chosen included two of the three largest collapsed volcanoes (known as calderas) in the United States.

One of these is Long Valley in California which shows clear signs of continuing volcanic activity. A deep layer of volcanic ash, known as Bishop tuff, from the initial eruption seven hundred thousand years ago, is spread hundreds of miles along the eastern side of the Sierra mountains. The most recent major eruption took place about 600 years ago. In 1982, a new vent releasing high pressure hot gases -- called a fumarole -- opened and the seismicity of the area has increased significantly in recent years.

A relatively small DOE research effort has helped stimulate a coordinated set of studies involving an unprecedented array of different techniques for the development of a three-dimensional picture of the subsurface structure and distribution of molten rock -- called magma -- in Long Valley. Current evidence points

to an active magma chamber reaching to within 5-10 km of the earth's surface. Four Federal agencies, the state of California, seven universities and several industrial firms have participated in cooperative studies as part of what has now evolved, under DOE leadership, into a national Continental Scientific Drilling Program.

Investigations have revealed the details of a complex interrelationship among the occurrences of earthquakes, the ongoing deformation of the caldera, and the shape of the magma chamber. Models of this relationship have been formulated describing the process operating within the caldera. The results are significant for improved hazard analysis, for better geothermal resource assessment, and for determination of an optimal location for a deep borehole to obtain more detailed scientific information.

(Sandia National Laboratory, J. Rundle and 21 collaborators)

25. Elucidation of the Metabolic Pathway Leading to Methane Production from Carbon Dioxide

One of the major pathways for the microbial production of methane involves the conversion of carbon dioxide to methane. This pathway, including identification of its major intermediates, enzymes and carrier molecules (cofactors), has now been elucidated.

During the biochemical reduction of carbon dioxide to methane, the carbon remains bound to carrier molecules (cofactors). The three cofactors that have been isolated are only found in bacteria which produce methane. The cofactors, in order of occurrence in the pathway are methanofuran, tetrahydromethanopterin and Coenzyme M (thioethane sulfonic acid). The presence of the enzymes responsible for these conversions has also been demonstrated. The only potentially significant factor as yet not isolated is an "activating factor" which stimulates the final step in the process, the release of methane. This work constitutes a significant contribution to man's understanding of a major biological process of the carbon cycle in nature and one that has been harnessed to produce the gaseous fuel, methane.

(University of Illinois, R. Wolfe)

26. The Pigment Phytochrome was Recently Shown to Exist as Two Distinct Molecules

The role of light in plants is not limited to photosynthesis; light also controls many aspects of plant growth and development. These effects range from the promotion of flowering to stimulation of seed germination to the spacing of leaves on a stem. Many of these nonphotosynthetic light effects have been shown to be influenced, if not controlled, by the pigment, phytochrome.

Recent studies on the structure of the protein(s) that are part of the phytochrome pigment-protein complex have led to the identification of a previously unknown phytochrome pigment complex in light-grown plants. There appears to be a different protein associated with the phytochrome pigment found in plants grown in light in comparison to the pigment complex of plants grown without light. Most of the previous investigations of phytochrome activity had utilized material from dark-grown plants. The protein from light grown plants is being isolated and chemically characterized in an effort to learn more about the chemical mechanisms that are involved in the light-induced regulation of plant growth and development, factors critical to potential increases in plant productivity and ultimately enhancement of available renewable resources. In doing this work it was the utilization of the techniques of molecular biology and use of highly specific monoclonal antibodies that enabled the workers to make distinctions between the two forms of protein.

(University of Wisconsin, P. Quail; University of Georgia, L. Pratt)

27. Possibility of Tritium Breeding in Fusion Reactor Blankets Confirmed

The fusion reaction converts hydrogen to helium releasing a considerable amount of energy. Several different reactions actually occur, depending on reaction conditions and the hydrogen isotopes involved. Tritium, a heavy, radioactive isotope of hydrogen, is a particularly valuable fuel material but is not found in nature in quantities needed on an engineering scale.

To provide tritium on the scale needed requires its production through nuclear reactions involving other elements. One particularly attractive scheme is designed to make use of those neutrons produced during the fusion process itself but which escape from the primary fusion reaction containment vessel. This vessel is surrounded by lithium containing target material to capture the escaping neutrons and react to produce tritium. The surrounding target material is called a "blanket"; the concept itself is referred to as "tritium breeding".

The possibility of producing tritium this way was confirmed experimentally at the Lawrence Livermore National Laboratory Rotating Target Neutron Source RTNS-I. Direct measurements were made of the tritium produced in small wafer-like targets of lithium hydride bombarded by high energy (14.94 MeV) neutrons. The probabilities, called "cross-sections", for tritium production as a result of neutron capture by lithium isotopes were then inferred from the measurements made. The result for the cross section for the lithium-7 isotope which is crucial to tritium breeding, agrees with the result of a recent measurement made at Argonne National Laboratory by a different, independent method. Both U.S. research results disagree with results published by U.K. researchers which had cast doubt on the feasibility of this important concept.

(Lawrence Livermore National Laboratory, R. Haight)

28. Theory of Novel Semiconductor Compounds

Predictions of structural parameters, optical characteristics and thermodynamic stability of two novel classes of ternary semiconductors have been made using theoretical electronic structure methods. The theoretical methodology first utilized mixed-basis band calculations on chalcopyrites, and pnictides and established the first microscopic description of these ternary semiconductors. It was further found that these ternary semiconductors have an anion distortion, a bond alternation and smaller band groups. The discovery of the inherent instability of bulk semiconductor alloys led to predictions of bond alternation in 64 semiconductor alloys. By conceiving of spatial arrangements of atoms that would allow bond alternation without exerting strain, total energy calculations could be made which predict that specific ternary alloys would be stable. Application of similar

theoretical models led to the prediction of 22 new ternary semiconducting compounds, mostly tellurides and antimonides, with attractive physical properties for potential energy technology applications. These successes offer insights into the creation of new complex semiconductor materials with vastly improved properties.

(Solar Energy Research Institute, A. Zunger)

29. Specific Transmission and Expression of Foreign Genes in Plants

Through new techniques in the biological sciences, it is becoming possible to selectively modify genetic materials and introduce new or modified characteristics into plants and microorganisms. Development of these techniques offers much promise for the "genetic engineering" of plants to alter yields of particularly valuable energy crop components, to more easily grow plants under marginal soil or climatic conditions, or to reduce energy requirements for cultivation. A major advance in plant genetics has been the development of a procedure for introducing "foreign" genes into plant chromosomes. This procedure is based on the ability of a particular soil microorganism Agrobacterium, to insert a piece of DNA into the chromosome of a plant using a carrier DNA entity known as a plasmid.

Introducing a "foreign" gene into the plant chromosome is only the first step in introducing a foreign gene into a plant using a carrier DNA entity known as a plasmid.

Introducing a "foreign" gene into the plant chromosome is only the first of several steps needed, however, for the new gene's coded message to be expressed. The gene's message must be translated into a protein; the protein must be synthesized at the appropriate time; made in the right tissue (i.e., roots, leaves, etc.), and localized in the correct site within the plant cell.

Dr. Anthony Cashmore of the Rockefeller University, working in collaboration with researchers in Belgium, has reported the successful transfer of a gene from Agrobacterium into a plant, and the subsequent translation into a protein in a controlled fashion. The "foreign" gene was inserted into the chromosome of a plant directly adjacent to a gene known to be encoded to produce, only under illumination, a particular protein active during

photosynthesis. The protein coded by the new gene also is synthesized only in the presence of light. Thus through controlling the specific site of the new gene, it has been possible to demonstrate effective expression of the newly introduced gene. By using other combinations of bacterial and plant genes, it was possible to manipulate not only the tissue location (i.e., those exposed to light) of the bacterial proteins but also to control the subcellular localization of these proteins. In this work, a highly significant new procedure has been demonstrated for introducing "foreign" genes into plant chromosomes and effectively influencing the manifestation of their genetic messages in the plant.

(Rockefeller University, A. Cashmore)

30. Million-Degree Microexplosions

A unique method for examining the effects on surfaces of transient, very high temperatures, pressures and densities has evolved from a research program on molecular clusters.

Research has been underway on the dynamics of formation of clusters of hundreds of atoms or molecules, each cluster having a single electric charge. Beams of such "ions" -- singly charged although very heavy on a molecular scale -- have been accelerated at energies up to 400 keV. It was found that collisions of these high energy ion beams with a surface occur in less than 0.1 trillionth of a second, generating a temperature of about 1,000,000° Celsius in the solid surface. This finding provides an important new tool for investigating properties of assemblies of atoms or molecules in very dense, hot plasmas.

It also has been found that the impact of the beam produces very small holes of 2 to 4 ten-millionths of an inch in thin carbon films. The hole size and the number of holes produced per unit area are adjustable depending on the beam intensity. This new technique, "cluster ion impact", besides providing an important new research technique, also is a promising technique for preparation of microholes for a variety of applications.

(Brookhaven National Laboratory, L. Friedman)

31. New Chemical Extractant Discovered for Treating Nuclear Wastes

A new solvent extraction process has been developed which can reduce by a factor of a hundred the volume of nuclear fuel wastes which must be subjected to long-term storage or ultimate disposal, such as burial.

The new process, called TRUEX (transuranium extraction), utilizes a chemical known as CMPO which was specifically designed and synthesized by chemists at Argonne National Laboratory to be highly selective for removing actinide elements from acid solutions. When CMPO is added to the solvent commonly used in spent nuclear fuel reprocessing, it effectively promotes full extraction of the actinides away from the nitric acid solution which results from the dissolution of the spent fuel elements. Present methods for processing irradiated fuels to recover plutonium result in much larger volumes of acidic waste solutions which, because of their actinide content, will require expensive storage in geological repositories. The volume of the new solution containing the long-lived radioactive actinide elements is far smaller than that of the original acid waste solution, which, being stripped of the actinides, can now be handled by surface storage.

The TRUEX system is highly compatible with existing fuel reprocessing technology. It is currently being evaluated by Rockwell Hanford for pilot plant testing. In full operation, ultimate savings of several hundred million dollars can be expected from reduced waste burial costs and improved recovery of plutonium from reprocessing streams. Further savings are also anticipated from other reprocessing applications of this novel chemical system.

(Argonne National Laboratory, P. Horwitz)

32. Quantization Effects Discovered in Photoelectrochemical Systems

Quantized energy levels in the photoelectrochemistry of superlattice photoelectrodes have been discovered by chemists studying solar photoconversion.

The superlattice electrodes, prepared for the chemists by state-of-the-art materials technology, are gallium arsenide wafers coated with very thin (millionth of an inch) alternating layers of gallium arsenide and gallium arsenide phosphide, grown by chemical vapor deposition on gallium arsenide wafers. These gallium semiconductor compounds are photoactive. That is, when light shines on them they release electrons, behavior which is basic to either photovoltaic cells or photoelectrochemical cells. The more energetic ("hotter") are the released electrons. In ordinary photovoltaic semiconductors, "hot" electrons quickly degrade to lower energies. But in this superlattice, electrons become trapped in the gallium arsenide layers where, from the laws of quantum mechanics, their energy is maintained at certain levels of the "quantum wells". The significance of the discovery is that electron transfer from superlattice electrodes can occur from excited states of the quantum wells, thus providing a potential means to achieve the much higher solar energy conversion efficiencies predicted for hot electrons. The superlattice electrodes should have a strong impact on photoelectrochemistry research and are likely to spawn a new generation of photoelectrochemical cells for conversion of solar energy to chemical energy or electrical power.

(Solar Energy Research Institute, A. Nozik et al)

33. Energy-Saving Chemical Process Discovered, Patented and Moved Quickly from University to Industrial Use

Study of the chemistry of coal tars has led to discovery of a clever chemical system for controlled, selective reduction of benzenoid molecules to monoenes (cyclic molecules with only one double bond). The new synthetic process uses low cost, energy-saving, safer calcium as a substitute for hazardous, costly sodium metal. Use of carefully chosen solvents or abrasives prevents surface coating of the calcium particles, which would otherwise stop the process. The synthesis has the added advantage of high yields of the products. The patented process has reached commercialization in less than 2 years from the discovery.

Monoenes are used in large volumes in the chemical industry. Most of them are relatively simple and can be produced without resort to the new type of chemistry. But some monoenes, used in production of medicines, are structurally complex molecules. Production of more these complex these types of molecules will be greatly improved and rendered more economical by this invention.

(Purdue University, R. Benkeser)

34. New Mechanism Identified for Hydrogen Induced Failure

Direct, high-resolution observations in the electron microscope of hydrogen induced fracture of solids under stress have shown that many of the commercially important metal alloys do not fail in a brittle manner as has been believed in the past. Rather than causing a brittle fracture, hydrogen enhances the local plastic behavior of the metals and causes failure by virtue of enhanced local deformation. The basis for this locally enhanced ductility is the very high mobility of hydrogen in metals and its ability to modify the stresses around defects in the metals.

Recognition of the mechanism of this type of environmentally related failure will allow improvements in both the design of alloys and systems for use in aggressive environments and in the prediction of lifetimes of engineering systems. Hydrogen induced failures are responsible for the loss of many billions of dollars of engineering systems and for the loss of many lives each year. These failures generally occur well within the "safe limits" of the operating parameters for the materials and occur unpredictably after a period of service. In the past, attempts to protect against this type of failure were based on ad hoc solutions and were mostly unsatisfactory. In many cases the "solutions" themselves caused the introduction of hydrogen into the material and thereby caused premature failure.

(University of Illinois, H. Birnbaum, I. Robertson)

35. A Method Developed for Yielding Soluble Conducting Polymers for the First Time

Recent advances have demonstrated that non-metallic, organic polymers can be produced that conduct electricity. Polyacetylene, a solid produced from acetylene gas, is the best known example, but there are others. A major challenge in developing suitable applications for polymeric conductors has been to fabricate them into selected forms without adversely affecting their conducting properties.

A new chemical system that acts as both a solvent for the monomers that will be polymerized, and as an initiator for the polymerization itself, has been developed. This system yields soluble polyacetylene and other soluble conducting polymers.

The polymerizations are carried out in arsenic trifluoride solutions using arsenic pentafluoride to initiate polymerization. Solid or liquid monomers are mixed with this solvent at room or lower temperatures, and the arsenic pentafluoride, which is a gas, introduced into the reaction vessel in measured amounts to initiate the reaction. For gaseous monomers, such as acetylene, the solvent is cooled to temperatures below the melting point of the monomer. The monomer forms a solid solution with the solvent. In every case, with the introduction of the initiating agent, polymerization occurs instantaneously to give polymers of high molecular weights. At the end of the reaction, excess arsenic pentafluoride is pumped out and the solvent is distilled from the reaction mixture to give homogeneous polymeric films. Polyacetylene films cast from solutions of acetone exhibit very poor electrical conductivity. When these films are exposed to iodine vapor, their conductivity increases a thousand-fold. Other conducting polymers, such as polyparphenylene, polynaphthalene, polyanthracene and their derivatives also have been synthesized, and all were found to be soluble in common organic solvents.

Soluble polymers permit a detailed molecular characterization of conducting polymers. This characterization is needed to guide efforts in the design and synthesis of better conducting polymers. Also the processing of conducting polymers can be studied because soluble polymers can be fabricated into a variety of shapes.

(Los Alamos National Laboratory, M. Aldissi, R. Liepins, A. Nyitray, A. Bishop, D. Campbell, S. Mzumdar)

36. Steel Wire with Superior Properties and Reduced Cost Achieved Through Microstructural Modifications

Superior properties and reduced cost have both been achieved with simple modifications in the processing procedures used to make steel wire. In steel, iron combines with carbon in different but reproducible atomic ratios forming several different, stable phases (e.g., ferrite, austenite, martensite, etc.). The properties of steel depend on the phases present, their relative proportions, their grain size and the uniformity of their dispersion throughout the steel.

Beginning with low-carbon, dual-phase steel rods, a drawing operation has been developed which produced a material with two finely dispersed iron-carbon phases in a final microstructure yielding tensile strengths in the 400,000 psi range with more than 10% residual ductility. The key to this performance is the attainment of a small-grain, recrystallized ferrite matrix within which approximately 15% of the volume is unrecrystallized austenite that is later transformed to martensite during water quenching. The process has been successfully implemented in existing commercial rod-mills. It requires no additional capital investment and because it makes the traditional heat treatments obsolete, actually results in substantial savings.

This breakthrough has significant potential for improving the international competitiveness of domestic steel speciality products. The combination of high strength, good formability, and improved low temperature ductility in these wires gives them great potential for such applications as tire cord in steel-belted radial tires. No expensive alloying additions are required and the procedures have already been successfully tried at a commercial Stelmore wire-rod production line. Patents have been awarded and licensing agreements are currently being arranged.

(University of California, Berkeley, G. Thomas and graduate students)

37. Carbon Dioxide Enrichment Increases Crop Yield

Crop yield is increased by higher levels of carbon dioxide in the atmosphere. Field data from 10 outdoor experiments involving food, forage and fiber crops provide convincing evidence that carbon dioxide enrichment enhances growth and productivity. When grown at levels twice today's atmospheric concentration, five of six crops examined yielded 31 to 82% more harvestable product. The species showing gains were black-eyed peas, soybean, sweet potato, cotton and sorghum. One crop, corn, failed to increase productivity when enriched with carbon dioxide.

Through photosynthesis, plants produce food and fiber from light and carbon assimilated as carbon dioxide. Rising atmospheric carbon dioxide is thus an important factor in the food-producing process, and effects of carbon dioxide enrichment have far reaching implications for agricultural and ecological productivity.

Much of the theory and historical data that support the idea of carbon dioxide enhancement of plant growth comes from laboratory experiments where light, nutrients, carbon dioxide levels, water and other environmental factors are controlled artificially. While short-term experiments inside such chambers are useful for studying physiological mechanisms and environmental interactions, they have produced very few reliable data on full-season growth and yield at natural light and for variable outdoor conditions.

Field studies have been emphasized in this project on the direct effects of carbon dioxide on plants; most of the research has been done with open-top or flow through chambers positioned in fields planted and maintained according to normal farming practice. Test plants are exposed to natural light, soil and other conditions while precise control is maintained of the desired carbon dioxide enrichment for an entire growth cycle.

Corn exhibited no direct yield response to carbon dioxide enrichment, although other experimental results showed a significant carbon dioxide effect on water use. Doubling carbon dioxide concentration reduced by one-third the water required to produce a normal yield of corn, and this effect is expected to enhance productivity indirectly.

(Tuskegee Institute, P.K. Biswas; USDA/ARS, L.H. Allen, B.A. Kimball; LLNL, J. Shinn; Kansas State University, E. Kanemasu)

38. A 200-Year Atmospheric Record from Measurements of Carbon Dioxide in Ice

The record of atmospheric carbon dioxide concentrations over the last two centuries has long been defined as a critical research need. A detailed knowledge of this record is important for determining the role of nonfossil carbon dioxide sources in the observed atmospheric increase, and for quantifying the sensitivity of climate to the carbon dioxide concentration.

An ice core from Siple Station, West Antarctica, available this past year, provided samples of trapped air and allowed carbon dioxide content measurement with exceptionally good time resolution (22 years). Measurements of carbon dioxide trapped in air bubbles in this ice core have finally made it possible to trace the development of the atmospheric carbon dioxide during the last two centuries.

Counting the seasonal variations of the electrical conductivity of the ice allowed the ice core to be dated with an accuracy of ± 2 years. This is important information because air bubbles become isolated from the atmosphere during a prolonged period, and thus, without an independent dating method, the entrapped air can represent a sample taking decades to centuries to isolate. The duration of the "close-off" process, the process which bounds the carbon dioxide migration in the ice core thus enabling the dating process to provide reliable results, was determined to be 22 years for the Siple core.

The mean carbon dioxide concentration plotted against the dates when the air bubbles in the ice were sealed off from the atmosphere (mean gas age) is shown in Figure 1. The Siple ice core provides an excellent record of the atmospheric carbon dioxide increase from the mid-16th century to the present, and the exceptional time resolution allows sufficient overlap with the Mauna Loa record to permit comparisons between the two sets of data. Within the limits of error, the ice core results (Figure 1) do not differ from the Mauna Loa atmospheric carbon dioxide record obtained since 1958.

(University of Bern, Switzerland; A. Neftel, E. Moor, H. Oeschger, B. Stauffer and J. Schwander. Support was provided by several U.S. and Swiss institutions and federal agencies.)

CO₂ CONCENTRATION IN THE SIPLE CORE

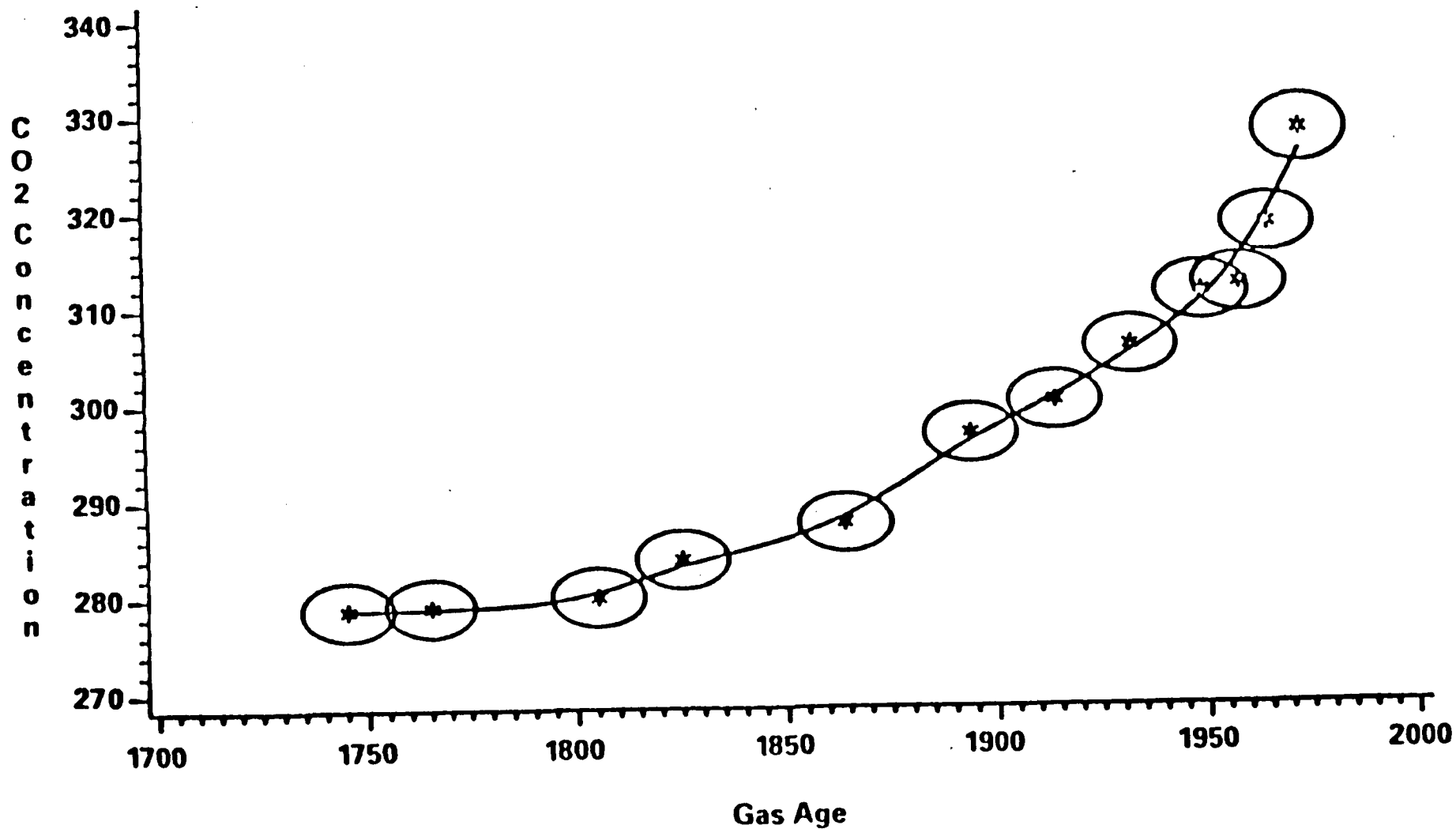


Figure 1. Measured mean CO₂ concentration plotted against the mean gas age, calibrated with the Mauna Loa record for the youngest gas age. The ellipse around each data point corresponds to the close-off time interval of 22 years and the CO₂ concentration measurement uncertainty (± 3 ppm).

September 24, 1985

Some Examples of Accomplishments Under the Basic Energy Sciences
Program during 1985

The Basic Energy Sciences Program supports about 1200 research projects. The following selection of accomplishments does not fully reflect the full 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.

Table of Contents

1. First High Resolution Study of Magnetic Structures Accomplished Using X-Ray Scattering (MS)
2. New Organic Metal Superconductor Successfully Designed, Synthesized and Characterized (MS)
3. Polymeric Extractants Effectively Recover Toxic or Precious Metals from Rivers or Seawater (CS)
4. Underground Imaging Using Electromagnetic Tomography (EG)
5. Laboratory Scale X-Ray Laser Demonstrated for First Time (AEP)
6. New Class of High Resolution Finite Difference Methods Developed to Model Compressible Fluid Flow Problems (AMS)
7. Highly Ordered Orientation of Lignin Relative to Plant Cell Walls Discovered (BER)
8. Automated Synthesis Technique Developed for Preparing Magnetostrictive Alloys (MS)
9. Cavity Nucleation and Growth During Compressive Creep Deformation of Ceramics Characterized (MS)
10. Model Molecules Designed as a Step Toward Artificial Photosynthesis (CS)
11. Carbon Monoxide Adsorbed on Nickel Catalysts Found to Modify the Chemical Properties of Nickel Itself (CS)
12. Method Developed for Separation of Coal Macerals of High Purity (CS)

13. New Type of Molecular Behavior Identified Through Laser-Excited (CS)
14. Hexavalent Neptunium Immobilized by Chemical Bonding to Soil Constituent (NS)
15. Direct Observation of Charge Density Waves with a Cryogenic Tunneling Microscope (MS)
16. New Fischer-Tropsch Catalysts Derived from Zeolitic Aluminoferrisilicates (MS)
17. New Static Ultra-High Pressure Record: Studies of Hydrogen and Deuterium (MS)
18. Explanation of Transition-Temperature Oscillations in thin Superconducting Films (MS)
19. Existence of Dimensional Crossover in Metallic Superconducting/Normal Metal Superlattices (MS)
20. Ultra High Pressure Studies Show Unique Behavior of Bonding in Actinide Metals (NS)
21. A Fast Algorithm Well Suited for Lattice Problems was Discovered (AMS)
22. New Model of Ore Formation Also Looks Good for Oil Exploration (EG)
23. New Light Thrown on Destructive Noise in Heat Exchangers (EG)
24. Experiments Lead to Yield Better Models of Natural and Forced Convection (EG)
25. Site Studies Lead to Best Image Yet of Roots of Large Caldera (EG)
26. Elucidation of the Metabolic Pathway Leading to Methane Production from Carbon Dioxide (BER)
27. The Pigment Phytochrome was Recently Shown to Exist as Two Distinct Molecules (BER)
28. Possibility of Tritium-Breeding in Fusion Reactor Blankets Confirmed (NS)
29. Theory of Novel Semiconductor Compounds (MS)
30. Center Established to Demonstrate New Design Strategy for Parallel Architecture, Algorithms and Software (AMS)
31. Specific Transmission and Expression of Foreign Genes in Plants (BER)

32. Million-Degree Microexplosions (CS)
33. New Chemical Extractant Discovered for Treating Nuclear Wastes (CS)
34. Quantization Effects Discovered in Photoelectrochemical Systems (CS)
35. Energy-Saving Chemical Process Discovered, Patented and Moved Quickly from University to Industrial Use (CS)
36. New Mechanism Identified for Hydrogen Induced Failure (MS)
37. A Method Developed for Yielding Soluble Conducting Polymers for the First Time (MS)
38. Steel Wire with Superior Properties and Reduced Cost Achieved Through Microstructural Modification (MS)
39. Successful Operation of Multiple-beam Ion Source for Heavy-Ion Fusion Accelerator Research (NS)
40. State-of-the-Art Reports on Carbon Dioxide Research (CO₂)
41. A 200-Year Atmospheric Record from Measurements of CO₂ in Ice (CO₂)
42. CO₂ Enrichment Increases Crop Yield (CO₂)

1. First High Resolution Study of Magnetic Structures Accomplished Using X-Ray Scattering

Brookhaven scientists, using X-rays from two "wigglers", one developed by the Exxon, Lawrence Berkeley Laboratory and Stanford consortium at Stanford Synchrotron Radiation Laboratory, and neutrons from the Brookhaven High Flux beam reactor have completed a comprehensive study of a holmium single crystal grown at the IBM Research Center. This study has demonstrated the use of high resolution X-ray magnetic scattering techniques to observe very faint magnetic X-ray diffraction due to magneto-elastic perturbations of the spiral magnetic ordering in holmium. This ordering has a length incommensurate with the atomic lattice spacing at temperatures above the ferromagnetic transition at 20°K thus giving rise to a temperature dependent modulation of the spiral length and hysteretic effects near the ferromagnetic transition.

Understanding magnetic structures and their dynamics is important to improving scientific concepts of magnetism and to the development of technologically significant magnetic materials. The usual probe of magnetic properties has been neutrons where the magnetic scattering of the neutrons is comparable with the atomic structural scattering and of such character that the two can be resolved from one another. Magnetic scattering of X-rays is only about ten one-millionths as intense as atomic structural X-ray scattering -- too weak to be studied with ordinary X-ray sources. However, with the advent of very intense beams of X-rays from wiggler insertion devices on synchrotron sources, x-ray scattering studies are not only possible, but can very precisely measure some parameters difficult to determine with neutrons.

The result of this study, other than proving that synchrotron radiation can play a significant role in magnetic studies, has led to a modification of the successful spin discommensuration model for the magnetic structure of holmium.

Synchrotron X-rays have other properties which have not yet been exploited. It may be possible, for example, to use very intense circularly polarized X-rays to resolve the two contributions to the magnetic moments in crystals, the orbital and the spin components.

(Brookhaven National Laboratory, D. Moncton, D. Gibbs and co-workers)

2. New Organic Metal Superconductor Successfully Designed, Synthesized and Characterized

On the basis of principles established in previous work, a new metal-organic compound, $(\text{BEDT-TTF})_2\text{AuI}_2$, aimed at improved superconducting properties, was designed and synthesized at Argonne National Laboratory (ANL). Using this new compound, the highest, ambient pressure, superconducting transition temperature ($T_C = 5^\circ\text{K}$) yet observed for a synthetic organic metal superconductor has been attained. BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene and AuI_2^- is the linear diiodoaurate (I) anion. As in all $(\text{BEDT-TTF})_2\text{X}$ systems, BEDT-TTF serves as an electron donor to the acceptor specie, X^- , or AuI_2^- in this case. Commercially available BEDT-TTF (Strem Chemical Co., Inc., Newburyport, MA), used in the synthesis was prepared in a joint venture using a synthetic procedure developed by ANL.

The continuing aim of this research is the development of new synthetic organic metals with a potential for use in electronic systems. Synthetic organic metals continue to offer unparalleled promise because of the wide range of derivatives which can be synthesized at room temperature. For example, the superconducting transition temperatures, at ambient pressure, of $(\text{BEDT-TTF})_2\text{X}$, where X is I_3^- , IBr_2^- , or AuI_2^- , are 1.5°K , 2.8°K , and 4.98°K , respectively. The AuI_2^- derivative was the result of a rational design effort in which it was predicted that T_C would likely rise when proceeding from $\text{X} = \text{I}_3^-$ and IBr_2^- to AuI_2^- . These results clearly demonstrate the importance of a linear-symmetric anion in producing new organic superconductors and they highlight a new approach to raising T_C , i.e., metal atom insertion into such linear anions.

(Argonne National Laboratory, H. Wang, M. Beno, U. Geiser, G. Crabtree, K. Carlson, J. Williams; Sandia National Laboratories, L. Azavado, J. Kwak, J. Schirber; Strem Chemical Co., M. Strem, F. Wagner, C. Sielicki)

3. Polymeric Extractants Effectively Recover Toxic or Precious Metals from Rivers or Seawater

Polymer supported extractants have been devised and are being synthesized which can efficiently remove major trace amounts of toxic or precious metals from acidic or saline waste streams, rivers, or sea water. The styrene-based polymers have active phosphorus-containing groups which selectively extract the metal ions of interest. The new extractants are synthesized by a relatively simple procedure from inexpensive chemicals. They were devised through a collaborative effort between Oak Ridge National Laboratory and the University of Tennessee. These new extractants contrast with present cleanup or recovery systems which generally require more expensive materials or multiple separation steps to accomplish the same degree of recovery.

Some metal ions, notably gold, silver and mercury, are converted by the extractant to the metals themselves, while others, e.g., uranium, are recovered but not reduced to the metal. Of particular advantage, the solutions containing the metal values need not be pretreated to reduce acidity or salt content, a step necessary with polymers previously considered. Base metals -- iron, aluminum, chromium, etc. -- do not interfere with the process. Economic analyses of the recovery process using the new polymers indicate the value of the metals recovered would substantially exceed the materials and operating costs for large-scale application of the new system.

(University of Tennessee, S. Alexandratos; Oak Ridge National Laboratory, W. McDowell)

4. Underground Imaging Using Electromagnetic Tomography

A new cross-hole geophysical technique has been used to map flowpaths in fractured rock. It is called Alterant Geophysical Tomography (AGT). The method involves the use of tracers to change the electrical properties of permeable fractures. Measurements of absorption of electromagnetic waves across a region are performed at various times (before, during, and after the introduction of the tracer). Spatial variations of the absorption are reconstructed using methods related to those used in medical tomography. Changes in the medium caused by the tracer are determined by subtracting an image representative of baseline conditions from an image obtained after the tracer is used. This method has been used in a granitic rock mass to map the flow paths followed by the tracers. Comparison of the alterant geophysical tomography images with fracture information obtained from acoustic televiewer logs have been made. These comparisons show that the AGT-image changes can be explained on the basis of fractures mapped along the edges of the region of interest.

Several techniques are available to the geophysicist and geologist for in situ study of water flow through a rock mass. However, until recently, none of these techniques have been able to yield high spatial resolution maps of ground water flow and differentiate between effective and total porosity. Alterant geotomography has been shown to do both. Therefore, this technique can be used to map open fractures and joints, delineate injection plumes, characterize grout curtains, and locate water-fill/cavities. Geotomography should be able to provide detailed information on those types of geophysical fracture problems which can be obtained by no other means.

(Lawrence Livermore National Laboratory, R. Lytle)

5. Laboratory Scale X-Ray Laser Demonstrated for First Time

In October, 1984 Princeton University scientists announced the first demonstration of lasing action in the x-ray spectrum, using a principle that lends itself to the development of a laboratory-size x-ray laser. More recently, in March, 1985, the next big step, a successful use of multilayered mirrors for the enhancement of the stimulated x-ray radiation, was achieved.

There are many important uses for unique, high-intensity, laser produced x-rays in medicine, physics, biology and technology in general. In medicine, the finely focused x-ray laser would allow better localization in the use of CAT scanners and similar devices. Plasma physicists could make extensive use of x-ray lasers to measure temperature, impurity densities, and ion transport in fusion plasmas. In the area of solid state physics, x-ray lasers could substantially improve structural analysis of crystalline solids. X-ray microscopes would have greater resolution than can be achieved by present-day electron-beam systems.

At the heart of this approach to an x-ray laser is the utilization of a fast-recombining plasma. Initially, the plasma temperature is increased until the carbon atoms become completely ionized; that is, totally stripped of electrons. The plasma then cools rapidly by intensive radiation losses, causing ions to recombine with free electrons. Because recombination occurs primarily at the higher energy levels (outer orbits) while lower levels (inner orbits) do not capture electrons, an unstable condition known as population inversion occurs. Electrons in the higher energy levels then "avalanche" to the lower levels,

creating a more stable electron configuration. In the process, each electron loses energy in the form of an x-ray photon. The lasing process occurs when the photons produced in this fashion stimulate the emission of additional photons from other ions, initiating a chain of such events. The result is an intense, coherent x-ray pulse of a single wavelength.

A CO₂ laser has been used to produce a dense carbon plasma column of 1-5 cm length, which is held to a 1-2 mm diameter by confinement in a strong magnetic field. A 100 - fold increase of the 182 - Å x-ray line has been observed in the direction along the plasma column, due to the desired stimulated-emission process. This result corresponds to an amplifier "gain" of about 6.5. By using multilayered x-ray mirrors a 100% enhancement of the stimulated radiation was achieved.

(Princeton Plasma Physics Laboratory, S. Suckewer)

6. New Class of High Resolution Finite Difference Methods Developed to Model Compressible Fluid Flow Problems

Over the past several years substantial advances have been made in the numerical analysis of hyperbolic partial differential equations, especially in the equations describing compressible gas dynamics. High resolution finite difference schemes which accurately resolve flows with strong discontinuities have been developed by investigators at Lawrence Berkeley Laboratory and Lawrence Livermore National Laboratory. These methods incorporate exact features of nonlinear waves, are stable and robust near shock waves and slip surfaces, and are highly accurate in regions where the flow is smooth. Previous computational results were under-resolved due to constraints of the computer technology available at the time. These new results are fully resolved because they were obtained with an updated low diffusion scheme on a modern supercomputer (Cray-1). Thus the numerical analysis of perfect inviscid compressible flow is now on an equal footing with experimental methods. These computational tools provide an effective alternative to laboratory testing and are being incorporated into large applications programs currently in use at DOE laboratories.

(Lawrence Berkeley Laboratory, P. Colella; Lawrence Livermore National Laboratory, P. Woodward)

7. Highly Ordered Orientation of Lignin Relative to Plant Cell Walls Discovered

Both woody and herbaceous plant cell walls, composed of lignocellulose, comprise the world's greatest reservoir of renewable resources. Nevertheless, the molecular structure of cell walls is far from understood, as is the function of their various constituents. Recently a better comprehension of one component of secondary cell walls, lignin, has been achieved. Lignin is a polymeric array of aromatic molecules and has been studied with respect to the orientation of the arrays relative to other cell wall constituents. In these studies, carried out at the Institute of Paper Chemistry in Appleton, Wisconsin, a technique employing a Raman microprobe was used along with other approaches.

The results obtained from studies on sections of woody tissue indicate that the phenyl propane units (aromatic rings) of lignin are oriented with the plane of the aromatic ring parallel to the cell wall. Heretofore lignin inclusion in the wall was assumed to be largely a matter of it being impregnated into the cellulosic portion of the cell wall in a more or less random fashion without any particular structure. The results also revealed exceptional cases of perpendicular orientation of the aromatic rings relative to the cell wall plane suggesting nodes in molecular orientation.

The work has significance in terms of not only understanding the intrinsic structural nature of these energy resources, but also with respect to gaining potential insights into improved design of cell wall degradation strategies to overcome existing key problems in the use of lignocellulose for fuels and chemicals.

(Institute of Paper Chemistry, R. Atalla)

8. Automated Synthesis Technique Developed for Preparing Magnetostrictive Alloys

An automated synthesis technique has been developed that: yields (a) grain oriented rare-earth-iron magnetostrictive alloy Terfenol-D ($Tb_{0.3}Dy_{0.7}Fe_{2.0}$) with circular, square, and hexagonal cross sections useful for transducer drive elements and (b) single crystals with a selected axial crystallographic orientation, and demonstrates the acceptability of commercial-grade starting material.

This new synthesis technique enables significant improvements to be made in the performance of transducer drive elements in jet and diesel engine fuel injection systems, submarine detection devices, and position sensing transducers in robotic systems as a consequence of the increased magnetostriction obtained in Terfenol-D. Currently the Ames Laboratory is the only source for these materials which they supply to research and prototype development programs. The projected commercial demand is approximately 2000 kg/yr (up 40 times from the present R&D demand), so a plan has been devised, in concert with industry, to develop and transfer the technology for mass production, and automation. Commercial applications for rare-earth-iron magnetostrictive materials that stand to take advantage of this new synthesis technique are underwater sonar devices for Naval defense systems, underground sonar devices for oil field exploration, micropositioners for laser mirror actuators, fuel injection systems for diesel engines, and robot components such as hands, wrists, and elbows. etc.

(Ames Laboratory, O. McMasters)

9. Cavity Nucleation and Growth During Compressive Creep Deformation of Ceramics Characterized

Powerful techniques for analyzing the diffraction of neutron beams by arrays of cavities in alumina and silicon carbide ceramic materials are providing the first statistical data that describe cavity nucleation and growth processes -- data that are needed to improve the performance and predict the lifetimes of structural ceramics. A detailed characterization of cavity evolution during compressive creep has been accomplished using small-angle neutron scattering. Samples of Coors AD-99 alumina containing a relatively thick and continuous, glassy grain boundary phase, Lucalox alumina containing no continuous grain boundary phase, and Norton NC-203 silicon carbide containing a relatively thin and continuous, glassy grain boundary phase have been characterized. The neutron scattering measurements, which provide a means of characterizing both the nucleation rates and the growth rates of grain boundary cavities during the early stages of creep, have shown unequivocally that cavity nucleation does occur and have also identified some very significant differences in the cavity nucleation and growth phenomena of these three ceramic systems. For example, in both aluminas cavity nucleation occurs throughout creep deformation while in the silicon carbide cavity nucleation is limited to the very early stages.

The results of these studies indicate that accurate predictions of the lifetimes of ceramic components at elevated temperatures can be made only when reliable models of cavity nucleation and growth are combined with proper failure criteria. Refined nucleation and growth models are currently being developed using these neutron scattering results to define the necessary modifications. In addition, the results have also suggested methods that

could be employed to improve ceramic performance at elevated temperatures, e.g., by the inclusion of hard grain boundary precipitates to reduce cavity nucleation.

(Southwest Research Institute, R. Page)

10. Model Molecules Designed as a Step Toward Artificial Photosynthesis

A significant advance in the quest for an artificial photosynthetic system has been achieved by chemical synthesis of a model photoreaction center. In nature, light is absorbed by chlorophyll, which is a porphyrin, followed by rapid electrical charge separation by other components in the photoreaction center. A key feature of nature's system is that the charge separation takes place in many successive steps. The model compounds prepared in this work contain a porphyrin core, to which are attached a quinone and dimethylaniline at opposite ends. The porphyrin part absorbs visible light which causes an electron to be transferred from the porphyrin to the quinone part. The electron deficient porphyrin then accepts an electron from the dimethylaniline part. This is the first demonstration of photoinduced charge separation by multiple electron transfer in a model system of known structure. Indeed, the present systems show a marked increase over previous model compounds in the length of time that the charges can be maintained apart before recombination, a necessary feature where one hopes to cause useful chemical reactions this way. Future work on model systems will continue to draw upon current advances in research on natural photosynthesis, for the positioning of electron donor and acceptor components in the optimum geometry for high efficiency solar conversion.

(Argonne National Laboratory, M. Wasielewski)

11. Carbon Monoxide Adsorbed on Ni Catalysts Found to Modify the Chemical Properties of Nickel Itself

Until now studies of heterogeneous catalysis (the type achieved with use of solid catalysts) could measure only the changes taking place in the molecules being affected by the catalyst -- automobile exhaust gases, for example. Nothing specific could be concluded about the effect on the catalyst itself. Now it has been experimentally demonstrated that the presence of carbon monoxide adsorbed on the surface of a nickel catalyst actually modifies the chemical properties of the nickel surface. This was achieved through superior accuracy and resolution of infrared spectral bands, by combining different state-of-the-art techniques for studying adsorbed species on single crystals, in a multipurpose ultrahigh vacuum system. It was seen that the infrared frequency shifts associated with changing the amount of carbon monoxide adsorbed on a Ni(111) crystal surface are due to modification of the chemical properties of the nickel surface itself by the adsorbed carbon monoxide. The experiments (particularly the new capability they demonstrate) make possible an important new level of understanding of the effects of substances added during or after the manufacture of catalysts.

(University of Pittsburgh, J. T. Yates)

12. Method Developed for Separation of Coal Macerals of High Purity

Two recent developments are opening a new level of detailed knowledge of coal and bringing a new dependability to collaboration on coal research. In building the knowledge base for future conversion of coal to substitute fuels and chemical feedstocks, we face some difficult facts: each coal is a chemically complex mixture, and each mine's coal differs from every other one.

One Laboratory's research on separation of the various macerals (black organic substances) which make up each coal has resulted in a method for providing very pure macerals that is now being used in several other coal research laboratories. The method is based on density gradient centrifugation. It makes available pure macerals in quantity and is yielding many productive collaborative studies between this DOE laboratory and university and industrial laboratories. In addition, the Premium Coal Sample Program has successfully processed and sealed samples of the first premium coal into 9,000 ampoules containing either five (7,500) or ten (1,500) grams of coal. These are available to scientists world wide for basic research purposes. Thus for the first time coal researchers will be able to compare results on identical coal samples, for years to come. The construction and successful operation of the controlled atmosphere chamber and machinery for processing a ton of coal into very small particles in an atmosphere containing less than 100 parts per million oxygen reflects ANL's rather unique ability with large inert atmosphere chambers. Eight coals are to be similarly prepared and distributed over the next two years.

(Argonne National Laboratory, G. Drykacz, K. Vorres)

13. New Type of Molecular Behavior Identified Through Laser-Excited Chemistry

Use of a unique high-resolution spectroscopic technique has led to the first observation of "chaotic" vibrational behavior of molecules. In previous research on laser-excited chemistry, so-called mode selection was seen when the absorbed energy excited vibrations in molecules which broke bonds between specific parts of molecules. When it happened that the absorbed energy was redistributed into other well-understood vibrational modes, a different bond or no bond at all ruptured. Also, of course, the absorption of insufficient energy failed to rupture any bond. Heretofore, the intermediate energy range, bounded between that needed for bond rupture and some level below it, has been inaccessible to study because of the tendency to redistribution. Now that intermediate range has been observed in acetylene molecules. By using a laser to excite them to high vibrational states, and then using a different laser to trigger emission of energy, the molecules get down to the intermediate region. What was then observed was a surprise: "clumps" of 20-40 vibrational states, each clump containing randomly distributed energy levels. This unusual molecular behavior provides new insight into mode-selective chemistry and the elusive capability to run chemical reactions via more energy-efficient pathways.

(Massachusetts Institute of Technology, R. Field, J. Kinsey)

14. Hexavalent Neptunium Immobilized by Chemical Bonding to Soil Constituents

Neptunium has been considered to be more of an environmental hazard in nuclear wastes than other actinide because of the chemical stability (persistence) of its singly-charged pentavalent oxidation state. This singly-charged species binds less with soils and thus is more mobile in ground waters than the other actinide species, which are multiply charged. Recent studies, however, have indicated that, under ground water conditions on the oxidizing end of the oxidation-reduction scale, neptunium can exist as a doubly-charged hexavalent species. This hexavalent state is much less mobile, and thus neptunium may not pose the degree of hazard previously thought. These findings result from advances in electrochemical measurements of actinides in extremely dilute solutions.

(Oak Ridge National Laboratory, L. Maya)

15. Direct Observation of Charge Density Waves with a Cryogenic Tunneling Microscope

Using a Tunneling Microscope, charge-density waves on cleaved surfaces of tantalum disulfide in the 1-T structure have been observed. The observations are the first obtained for a tunneling microscope operating at 78 K and also the first direct observation of charge-density waves. The formation of charge-density waves occurs below a critical temperature, about 120-230 K for this material, and is accompanied by atomic displacements on the order of 0.1 to 0.25 Å. The charge-density waves may be commensurate or incommensurate with the usual crystalline lattice of the semiconductor. These measurements revealed distortions of less than 0.5 Å for a given atom and clearly show the systematic atomic displacements on the surface of the tantalum disulfide due to the charge-density wave.

The significance of this observation is twofold. It demonstrates the first tunneling microscope observation made at 78 K which suggests many new applications of this technique to a wide range of materials at cryogenic temperatures. The second is that it constitutes the first direct observation of charge-density waves. Charge-density waves affect the conduction properties of semiconductors and these properties are very important to semiconductor devices. The resolution of this model tunneling microscope will allow a direct test of our understanding of the structure of charge-density waves which, to this time, has been inferred only from indirect observations.

(University of Virginia, R. Coleman and coworkers)

16. New Fischer-Tropsch Catalysts Derived from Zeolitic Aluminoferrisilicates

Evidence has been obtained for the formation, upon reduction, of extremely small metallic iron particles (diameter $< 20 \text{ \AA}$) in aluminoferri-silicate (AFS) materials crystallized with the ZSM-5 zeolite structure. These are the most highly dispersed Fe particles in ZSM-5 type zeolites so far reported. Small Fe particles have also been produced in AFS materials crystallized with the Offretite crystal structure. Both types of AFS materials have been shown to be active Fischer-Tropsch catalysts. A post-synthesis modification procedure permits the activity and selectivity of the AFS ZSM-5 catalyst to be modified by introduction of a second Group VIII transition element. The AFS Offretite material has the best selectivity to light hydrocarbons ($< C_5$) in the preliminary tests. Evaluation of the technological potential of these materials requires further exploration and testing under higher pressure and high conversion conditions. A surprising discovery is that the clustering of Fe^{3+} ions into small oxide particles at higher Fe concentrations in the AFS ZSM-5 greatly suppresses the Fischer-Tropsch activity of the resulting reduced catalyst. This result is contrary to experience with Fe on conventional supports, and requires further investigation.

Employing shape-selective materials, e.g., zeolites, is a potentially powerful method for improving selectivity in heterogeneous catalytic conversions. One of the most important long-range technological targets in catalysts is the efficient production of feedstock chemicals, principally light olefins, from coal or biomass sources via hydrogenation of carbon monoxide. Iron-based catalysts are to be preferred due to iron's availability and cost relative to

other Group VIII metals. Improved performance with increasing metal dispersion has been reported for iron Fischer-Tropsch catalysts, but achieving very high dispersions is very difficult. Our method of producing highly dispersed Fe on zeolites is a promising new direction, and is potentially applicable to incorporation of other transition elements either for Fischer-Tropsch conversion or other important energy-related catalytic processes. At this juncture, direct Fischer-Tropsch conversion at modest operating pressure with good selectivity to light hydrocarbons appears to be a reasonable prospect using AFS zeolite catalysts.

(Argonne National Laboratory, L. Iton)

17. New Static Ultra-High Pressure Record: Studies of Hydrogen and Deuterium

Hydrogen and deuterium have been pressurized under static conditions to 1.47 million atmospheres and the infrared and Raman spectra have been measured.

An effort at the Carnegie Institution of Washington to improve techniques to subject hydrogen and deuterium to static pressures in excess of one million atmospheres (a megabar) has been supported by the Division of Materials Sciences for a number of years. This goal is due to a very fundamental theoretical prediction that hydrogen will become metallic and then superconducting at high temperatures, greater than 30K, at extremely high pressures. Until recently, it has not been possible to obtain pressures greater than 0.7 megabars. In the latest experiment, the Carnegie scientists have reached 1.47 megabars in both hydrogen and deuterium. This investigation was extremely difficult - requiring the use of very small samples and pressure calibration experiments on 'harder' materials to pressures significantly greater than two megabars. Still, metallic properties of hydrogen and deuterium were not observed but the infrared and Raman spectral properties at 1.47 megabars do suggest that these materials will become metallic: this was not clear from experiments at 0.7 megabars. Theoretical predictions lie in the range from 0.7 to 2.1 megabars.

(Carnegie Institution of Washington, P. Bell, H. Mao and coworkers)

18. Explanation of Transition-Temperature Oscillations in Thin Superconducting Films

Controversial experiments and models have recently been presented concerning the oscillations in T_c of thin superconducting films. The behavior was formerly believed to be due to the quantum size effect (QSE) which predicts an oscillation period about half of that which was experimentally observed. The current model and experiments explains these results on the basis of a film which initially becomes continuous at about 30 Å thickness even at 15K, and which consists of a collection of small spheres that barely touch. This suggests that size quantization in a sphere is the important relationship. Utilizing this model together with Schrodingers equation yields a new quantization condition that gives an oscillation period twice that of a homogeneous film.

Experimental observations of the nucleation and T_c of thin films show that, depending on the substrate, films deposited at 4K could be first made continuous as thin as 10Å or as high as 50Å depending on substrate conditions. This suggests that in this thickness range agglomeration may occur with spheres that are inter-connected. Quantization conditions for a sphere are applicable since an electron spends most of its time localized within a grain and scatters as much as thirty times before it transfers to the adjacent grain. This is an adequate condition for sharp levels in a particle and T_c oscillations.

These results indicate that substrate conditions are vitally important in the preparation of very thin superconducting strips with optimum physical parameters. Further, these results reveal the potential importance of corollary electron microscopy studies to confirm predicted behavior and modeling.

(Brookhaven National Laboratory, M. Strongin, Queens University, N.Y., A Paskin)

19. Existence of Dimensional Crossover in Metallic Superconducting/Normal Metal Superlattices

Experiments have been performed utilizing the proximity effect in metallic superlattices (superconducting-normal metal pairs) to observe the existence of dimensional crossover in a number of physical phenomena. Earlier studies were made on NbGe superlattices where dimensional crossover was not observed because the coupling length across an insulator is very small. Proximity coupled superconductors, however, are controlled by long coupling lengths (100-200 Å) and in the case of metallic superlattices, allow many more interaction effects to be examined.

In the example of Nb-Cu metallic superlattices, a crossover was seen from 2D-strongly coupled to 2D weakly coupled to 3D behavior. Where the superlattice contains equiayers, the vortex lattice, which is proportional to the coherence length, ξ , matches the superlattice periodically, λ . The magnetic vortices are preferentially located in the normal metal, and this greatly enhances the critical field. The crossover for 2D-3D behavior occurs at $\xi = \lambda$ and the temperature dependence of the critical field varies as a function of 2D or 3D configurations. Most importantly, it has been shown that the parameter that controls both the temperature and angular dependences is the ratio of the perpendicular coherence length to the normal separator (ξ/D_{Cu}).

This is the first observation of a transition from two dimensional to three dimensional behavior in the temperature and angular dependence of the superconductivity of metallic superlattices. The sharp enhancement of the critical field is being explored for possible application in high critical field magnet technology.

(Argonne National Laboratory, I. Schuller)

20. Ultra High Pressure Studies Show Unique Behavior of Bonding in Actinide Metals

In a national laboratory-university collaboration a discovery has been made in the behavior of some of the heaviest chemical elements which will affect the understanding of electronic structure and chemical bonding of all the elements. The achievement also underscores the unique value of the HFIR and TRU, which produce these heavy elements. The first clear evidence that a type of bonding known as 5f electron metallic bonding can be made to occur in elements higher than plutonium has been shown from x-ray studies of actinide metal crystal structures and volume changes at high pressure.

Only the actinide metals (elements 89-103) possess 5f electrons, and only in some lower actinide elements (protactinium, uranium, neptunium, plutonium) do those 5f electrons participate in metallic bonding at ordinary pressures. This has been explained by the "relativistic" drop in energy of those electrons in the higher actinides, making them unavailable for bonding by taking them below the energies of other electrons, which therefore do their own different types of bonding and crystal geometry. When extreme pressures squeeze the atoms together, however, at a certain threshold pressure for each higher actinide studied, volume collapse occurs, the 5f electrons enter metallic bonding, and the crystal geometry suddenly changes. The volume collapse in some cases is striking: 21% for curium at 440,000 atmosphere.

(Oak Ridge National Laboratory, R. Haire; University of Tennessee, J. Peterson)

21. A Fast Algorithm Well Suited for Lattice Problems Was Discovered

Complex mathematical computations, considered hopelessly unworkable even with the aid of the most powerful supercomputers, can now be handled with the development of a fast, accurate, new procedure called the "successive linkage algorithm." Developed by a mathematician holding a joint position at Lawrence Berkeley Laboratory and the University of California at Berkeley, this algorithm is well suited for lattice problems involving large summations of potentials with local interactions. The key step in the algorithm is the identification of frequently appearing terms in a large summation together with a method for estimating the frequency with which a given term appears. It has features in common with both spatial renormalization and the fast Fourier Transform. A scaling and extrapolation procedure has also been discovered which enables one to accelerate convergence of lattice calculations to their limiting values which obtain when the lattice becomes infinite.

"Successive linkage" can provide exact answers to certain problems, and reliable approximations to others. It has been used to evaluate thermodynamic quantities; such as partition functions, for a class of physical models including the "Ising Model" which describes ferromagnetic materials.

(Lawrence Berkeley Laboratory, A. Chorin)

22. New Model of Ore Formation Also Looks Good for Oil Exploration

Successful petroleum exploration and exploitation is becoming more and more dependent on methodical evaluations of more difficult to reach accumulations. This requires gathering and evaluating extensive data in order to assess a field's potential. Two relatively costly methods, drilling and seismic studies, are the most common means of data gathering. New techniques for data interpretation that demand less data input or lead to more reliable assessment could significantly decrease oil prospecting and production costs.

Studies of non-equilibrium coupled chemical and transport phenomena have led to a novel computer program that models not only what minerals are present in a basin but also the processes that lead to their distribution in space and time. The modeling effort was initially directed toward aspects of geoengineering important for mining uranium ores. It exploited recent advances in the mathematical description of non-linear processes. The approach taken was soon seen to be applicable to exploration for petroleum. From the inferred history at a given location one can make estimates regarding the previous conditions in the basin and its suitability for hydrocarbon production. This 'total' modeling approach allows for more useful information to be derived from the data and for more reliable interpretations to be made because the model is based on actual processes and faithfully adheres to fundamental physical and chemical laws. The incorporation of this practical modeling technique into petroleum companies' exploration and exploitation programs could result in a significantly enhanced success/cost ratio.

(Geo-Chemical Research Associates, P. Ortoleva)

23. New Light Thrown on Destructive Noise in Heat Exchangers

Acoustic resonances occur often in many heat exchangers (integral parts of many energy utilization and production systems) when fluids flow over the exchanger tube banks. The resonances produce intense noise levels harmful to man and machine. Without a clear understanding of the underlying processes it is impossible to develop a rational method for designing low noise, efficient heat exchangers. Instead noise reduction methods are applied in an ad hoc, trial and error fashion.

In a recently completed series of experiments, the precise nature of intense noise generation in exchanger tube bundles has been determined. In a well known phenomenon, the fluid flow across a tube induces periodic shedding of vortices on the downstream side of the tube. Such periodic shedding alone leads essentially to a relatively low intensity single tone determined largely by the tube diameters and the flow velocity. However, the new measurements show that an existing sound field in the flow interferes strongly with the usual vortex shedding and results in intense noise and vibrations. In particular, through the non-linear phenomenon of entrainment the period of vortex shedding becomes attuned to the natural vibration frequencies of the heat exchanger enclosure (cavity modes). Such improved understanding of the mechanism of noise generation will improve the design of future energy efficient, non-noise polluting heat exchangers.

(GA Technologies, R. Blevins)

24. Experiments Lead to Yield Better Models of Natural and Forced Convection

Computers are used extensively to calculate heat transfer in energy systems. Because of the sheer complexity of the associated numerical problems, simplifying assumptions about the nature of the flow are always necessary. Often that introduces uncertainty about the validity of the calculated results. The only way to validate such calculations is through actual experiments but suitable methods have not been available to carry out the needed rigorous and detailed tests.

Recently techniques for simultaneous flow and temperature visualization have been developed and applied to the needed validation experiments. Those flow experiments were arranged to follow as closely as possible the separate corresponding numerical simulations and involve a rectangular enclosure with well-defined boundary conditions. Surprisingly, for some of the simplest possible flows a wide divergence was found between the usual simulations and the observed experimental flows. In particular, flows which were thought to be quite smooth and uniform were found to be very convoluted, while smoothing of temperature gradients took much longer than estimated previously. Both of these aspects of flow have large effects on heat transfer calculations. The enhanced knowledge has now been incorporated in new computer models of flow and heat transfer which are thoroughly tested for accuracy and should be widely useful for designs of important types of heat exchangers.

As these results become more widely distributed, their inclusion in the stock of engineering knowledge and practice will serve to improve the efficiency of many energy production and utilization systems.

(Stanford University, R. Street)

25. Site Studies Lead to Best Image Yet of Roots of Large Caldera

When the DOE research was started several years ago which led to the cooperative interagency effort on Continental Scientific Drilling, a nationwide search was made for sites likely to give the greatest understanding of continental thermal regimes -- areas of unusually high heat flow. The sites chosen included two of the three largest collapsed volcanoes (known as calderas) in the United States. One of these is Long Valley in California which shows clear signs of continuing volcanic activity. A deep layer of volcanic ash, known as Bishop tuff, from the initial eruption seven hundred thousand years ago, is spread hundreds of miles along the eastern side of the Sierras. The most recent major eruption took place about 600 years ago. In 1982, a new fumarole opened and the seismicity of the area has increased significantly in recent years. A relatively small DOE research effort has helped stimulate a coordinated set of studies involving an unprecedented array of different techniques for the development of a three-dimensional picture of the subsurface structure and magma distribution. Four Federal agencies, the state of California, seven universities and several industrial firms have participated in the cooperative studies. Current evidence points to an active magma chamber reaching to within 5-10 km of the earth's surface.

Investigations have revealed the details of a complex interrelationship among the occurrences of earthquakes, the ongoing deformation of the caldera, and the shape of the magma chamber. Models of this relationship have been formulated describing the process operating within the caldera. The results are

significant for improved hazard analysis, for better geothermal resource assessment, and for determination of a scientifically optimal location for a deep borehole.

(Sandia National Laboratory, J. Rundle and 21 collaborators)

26. Elucidation of the Metabolic Pathway Leading to Methane Production from Carbon Dioxide

One of the major pathways for the microbial production of methane involves the conversion of carbon dioxide to methane. This pathway, including the major intermediates, enzymes and cofactors, has now been elucidated. During the biochemical reduction of carbon dioxide to methane, the carbon remains bound to carrier molecules (cofactors). The three cofactors that have been isolated are only found in bacteria which produce methane. The cofactors, in order of occurrence in the pathway are methanofuran, tetrahydromethanopterin and Coenzyme M (thioethane sulfonic acid). The presence of the enzymes responsible for these conversions has also been demonstrated. The only potentially significant factor as yet not isolated is an "activating factor" which stimulates the final step in the process, the release of methane. This work constitutes a major contribution to man's understanding of a major biological process of the carbon cycle in nature and one that has been harnessed to produce methane gas (a fuel).

(University of Illinois, R. Wolfe)

27. The Pigment Phytochrome was Recently Shown to Exist as Two Distinct Molecules

The role of light in plants is not limited to photosynthesis, light also controls many aspects of plant growth and development. These effects range from the promotion of flowering to stimulation of seed germination to the spacing of leaves on a stem. Many of these nonphotosynthetic light effects have been shown to be mediated by the pigment, phytochrome. Recent studies on the structure of the protein(s) that are part of this pigment-protein complex have shown the existence of a new pigment (phytochrome) complex in light-grown plants. There appears to be a different protein associated with the pigment in comparison to the pigment complex of plants grown without light. Most of the previous investigations of phytochrome activity had utilized material from dark-grown plants. The protein from light grown plants is being isolated and chemically characterized in an effort to learn more about the chemical mechanisms that are involved in the light-induced regulation of plant growth and development, factors critical to potential increases in plant productivity (renewable resources). In doing this work it was the utilization of the techniques of molecular biology and use of highly specific monoclonal antibodies that enabled the workers to make distinctions between the two forms of protein.

(University of Wisconsin, P. Quail; University of Georgia, L. Pratt)

28. Possibility of Tritium-Breeding in Fusion Reactor Blankets Confirmed

Confirmation of the possibility of breeding tritium in fusion reactor blankets was obtained in measurements made at the Lawrence Livermore Rotating Target Neutron Source RTNS-I. Tritium production cross sections were inferred from direct measurements of tritium generated in wafers of ^6LiH and ^7LiH under bombardment by 14.94 MeV neutrons. The result for the ^7Li cross section, which is crucial to tritium breeding, agrees with the result of a recent measurement made at Argonne National Laboratory by a different independent method. The U.S. results disagree with results published by U.K. researchers which had cast doubt on the feasibility of the important tritium breeding concept.

(Lawrence Livermore National Laboratory, R. Haight)

29. Theory of Novel Semiconductor Compounds

Theoretical predictions of novel ternary crystalline semiconductors and of new ordered phases of alloys of binary semiconductors have been made with electronic structure methods to predict structural parameters, optical characteristics and thermodynamic stability of two novel classes comprising over twenty semiconductors.

The theoretical methodology first utilized mixed-basis band calculations on chalcopyrites, and pnictides and established the first microscopic description of ternary semiconductors. It was further found that these ternary semiconductors have an anion distortion, a bond alternation and smaller band groups. The discovery of the inherent instability of bulk semiconductor alloys led to predictions of bond alternation in 64 semiconductor alloys. By conceiving of spatial arrangements of atoms that would allow bond alternation without exerting strain total energy, calculations could be made predicting that specific ternary alloys would be stable. Application of similar theoretical models led to the prediction of 22 new ternary semiconducting compounds, such as tellurides and antimonides, with attractive physical properties for potential energy technology applications.

By new theoretical techniques, the prediction of new stable ternary semiconductors has been accomplished. The success of the technique offers insights into the creation of new complex semiconductor materials with vastly improved properties.

(Solar Energy Research Institute, A. Zunger)

30. Center Established to Demonstrate New Design Strategy for Parallel Architecture, Algorithms and Software

The University of Illinois established the new Center for Supercomputing Research and Development whose goal is to demonstrate the effectiveness of their "CEDAR" design strategy for parallel architectures and associate algorithms and software. Major support for the Center is being provided by DOE; the State of Illinois is providing faculty positions and building space. The Center for Supercomputing Research and Development will complement the new NSF Supercomputer Center also established at Illinois. The main goal of the latter facility is to provide scientists and students access to current supercomputers and to train them in how to use the current technology, while the goal of the former is to investigate new ways of building and using the next generation of supercomputers. Center faculty and staff will consist of interdisciplinary teams with expertise in problem decomposition, parallel algorithms, architectures, and networking, including close collaboration with the Mathematics and Computer Science Division at the Argonne National Laboratory. Leaders from the supercomputer industry have applauded the formation of the Illinois Center and state that such centers are the appropriate places to carry out the research required for new generations of supercomputers. (University of Illinois, D. Kuck)

31. Specific Transmission and Expression of Foreign Genes in Plants

Genetic engineering holds much promise for the development of plants that produce increased levels of usable energy resources or require less energy to cultivate. A major advance in the field of plant molecular genetics has been the development of a system that permits the introduction of "foreign" genes into plants. This system is based on the ability of a particular soil microorganism, Agrobacterium, to insert a piece of DNA into the chromosome of a plant using a carrier DNA entity known as a plasmid. The introduction of a "foreign" gene into the plant chromosome is the first step. There are then several major events which must occur for this introduction to be effective. The new gene message must be translated into a protein. The protein must be made at the appropriate time and the protein must be made in the right tissue (i.e., roots, leaves, etc.) and the protein must be localized in the correct site within the plant cell.

One BER supported investigator recently reported, along with researchers in Belgium, the transfer of a gene from Agrobacterium into a plant, and the subsequent translation into a protein in a controlled fashion. The researchers were able to insert a bacterial gene into the chromosome of a plant directly next to a specific gene that contains the information to make a protein active in photosynthesis. This photosynthesis protein is made only in the light. The protein coded by the new gene is likewise made only in the presence of light. By using other combinations of bacterial and plant genes, it was possible to manipulate not only the tissue location of the bacterial proteins but also to control the subcellular localization of these proteins.

32. Million-Degree Microexplosions

A unique way to examine the effects on surfaces of transient high temperatures, pressures and densities has been found. The program examines the mechanism of formation of clusters of hundreds of atoms or molecules, each cluster having a single electric charge. The resulting beam of these ions is accelerated at energies up to 400 keV. It was found that collisions of these high energy ion beams with a surface occur in less than 0.1 picosecond, generating a temperature of about 1,000,000° Celsius in the solid surface. The phenomenon opens the possibility of investigating properties of assemblies of atoms or molecules in very dense, hot plasmas.

The impact of the beam has, serendipitously, been shown to produce very small holes of 2 to 4 ten-millionths of an inch in thin carbon films. The hole size and density per unit area are adjustable depending on the beam intensity. Cluster ion impact is, thus, a promising technique for preparation of microholes for a variety of applications.

(Brookhaven National Laboratory, L. Friedman)

33. New Chemical Extractant Discovered for Treating Nuclear Wastes

A new solvent extraction process has been discovered which reduces the volume of nuclear fuel wastes which must be buried by a factor of a hundred. The new scheme, called TRUEX (transuranium extraction), utilizes CMPO, a highly selective actinide extractant designed and synthesized by chemists at Argonne National Laboratory. When CMPO is added to the solvent commonly used in fuel reprocessing it allows extraction of all oxidation states of the actinides away from the nitric acid medium used to dissolve fuel elements. The volume of extract is much smaller than that of the actinide-free acid solution, which can be handled by surface storage. Present methods for processing irradiated fuels to recover plutonium result in much larger volumes of acidic waste solutions which, because of their actinide content, will require expensive storage in geological repositories.

The TRUEX system is highly compatible with existing fuel reprocessing technology. It is currently being evaluated by Rockwell Hanford for pilot plant testing. In full operation, savings of several hundred million dollars can be expected from reduced waste burial costs and improved recovery of plutonium from reprocessing streams, and further savings are anticipated from other reprocessing applications of this novel chemical system.

(Argonne National Laboratory, P. Horwitz)

34. Quantization Effects Discovered in Photoelectrochemical Systems

Quantized energy levels in the photoelectrochemistry of superlattice photoelectrodes have been discovered by chemists studying solar photoconversion. The superlattice electrodes were prepared for the chemists by state-of-the-art materials technology in which very thin (millionth of an inch) alternating layers of gallium arsenide and gallium arsenide phosphide were grown by chemical vapor deposition on gallium arsenide wafers. In this superlattice, electrons become trapped in the gallium arsenide layers where, from the laws of quantum mechanics, their energy is maintained at certain levels of the "quantum wells". The significance of the discovery is that electron transfer from superlattice electrodes can occur from excited states of the quantum wells, thus providing a potential means to achieve the much higher solar energy conversion efficiencies predicted for hot electron injection pathways. The superlattice electrodes should have a strong impact on photoelectrochemistry research and are likely to spawn a new generation of photoelectrochemical cells for conversion of solar energy to chemical energy or electrical power. (Solar Energy Research Institute, A. Nozik et al)

35. Energy-Saving Chemical Process Discovered, Patented and Moved Quickly from University to Industrial Use

Study of the chemistry of coal tars has led to discovery of a clever chemical system for controlled, selective reduction of benzenoid molecules to monoenes (cyclic molecules with only one double bond). The synthetic process uses low cost, energy-saving, safer calcium as a substitute for higher cost sodium. Use of carefully chosen solvents or abrasives prevents surface coating of the calcium particles, which would otherwise stop the process. The synthesis has the added advantage of high yields of the products. The patented process has reached commercialization in less than 2 years from the discovery.

(Purdue University, R. Benkeser)

36. New Mechanism Identified for Hydrogen Induced Failure

Direct, high-resolution observations in the electron microscope of hydrogen induced fracture of solids under stress have shown that many of the commercially important metal alloys do not fail in a brittle manner as has been believed in the past. Rather than causing a brittle fracture, hydrogen enhances the local plastic behavior of the metals and causes failure by virtue of enhanced local deformation. The basis for this locally enhanced ductility is the very high mobility of hydrogen in metals and its ability to modify the stresses around defects in the metals.

Recognition of the mechanism of this type of environmentally related failure will allow improvements in both the design of alloys and systems for use in aggressive environments and in the prediction of lifetimes of engineering systems. Hydrogen induced failures are responsible for the loss of many billions of dollars of engineering systems and for the loss of many lives each year. These failures generally occur well within the "safe limits" of the operating parameters for the materials and occur unpredictably after a period of service. In the past, attempts to protect against this type of failure were based on ad hoc solutions and were mostly unsatisfactory. In many cases the "solutions" themselves caused the introduction of hydrogen into the material and thereby caused premature failure.

(University of Illinois, H. Birnbaum, I. Robertson)

37. A Method Developed for Yielding Soluble Conducting Polymers for the First Time

A new solvent/initiator system has been developed that yields for the first time soluble polyacetylene and other soluble conducting polymers. The polymerizations are done in AsF_3 solutions using AsF_5 as the polymerization initiating agent. Solid or liquid monomers are mixed with the AsF_3 solvent at room or lower temperatures, and the AsF_5 is introduced into the reaction vessel in measured amounts to initiate the reaction. For gaseous monomers, such as acetylene, the AsF_3 solvent is cooled to temperatures below the melting point of the monomer. When the monomer is introduced, a solid solution with the solvent is formed. In every case, with the introduction of the initiating agent, polymerization occurs instantaneously to give polymers of molecular weights as high as 10,000 by g.p.c. analysis. At the end of the reaction, excess AsF_5 is removed by pumping. The solvent is distilled from the reaction mixture to give homogeneous polymeric films. Polyacetylene films cast from solutions of acetone have a conductivity of about 10^{-7} . When these films are exposed to iodine vapor, the conductivity increases to about 10^{-4} . Other conducting polymers, such as polyparaphenylene, polynaphthalene, polyanthracene and their derivatives have also been synthesized, and all were found to be soluble in common organic solvents.

Soluble polymers permit for the first time a detailed molecular characterization of conducting polymers. Such characterization has been lacking and will guide efforts in the design and synthesis of better conducting polymers. Also the processing of conducting polymers can be studied because soluble polymers can be fabricated into a variety of shapes.

(Los Alamos National Laboratory, M. Aldissi, R. Liepins, A. Nyitray, A. Bishop, D. Campbell, S. Mzumdar)

38. Steel Wire with Superior Properties and Reduced Cost Achieved Through Microstructural Modification

Superior properties and reduced cost have both been achieved with simple modifications in the processing procedures used to make steel wire. Beginning with low-carbon, dual-phase steel rods, a drawing operation has been developed which produced a finely dispersed martensite/ferrite composite morphology in the final microstructure yielding tensile strengths in the 400,000 psi range with good (> 10%) residual ductility. The key to this performance is the attainment of a small-grain, recrystallized ferrite matrix within which approximately 15% of the volume is unrecrystallized austenite that is later transformed to lath martensite during water quenching. The process has been successfully implemented in existing commercial rod-mills. It requires no additional capital investment and because it makes the traditional patenting heat treatments obsolete, actually results in substantial savings.

This breakthrough has significant potential for improving the international competitiveness of domestic steel speciality products. The combination of high strength, good formability, and improved low temperature ductility in these wires gives them great potential for such applications as tire cord in steel-belted radial tires. No expensive alloying additions are required and the procedures have already been successfully tried at a commercial Stelmor wire-rod production line. Patents have been awarded and licensing agreements are currently being arranged.

(University of California, Berkeley, G. Thomas and graduate students)

39. Successful Operation of Multiple-beam Ion Source for Heavy-Ion Fusion Accelerator Research

Beginning in FY 1984, a program in accelerator research began in Basic Energy Sciences to determine the applicability of heavy ion accelerators to inertial fusion. To be successful, the highest possible beam currents must be employed, and a number of beams, ultimately 8 to 16 or more, must be used to increase the final intensity on the fusion target. During FY 1984 scientists at the Lawrence Berkeley Laboratory (LBL) demonstrated that significantly higher beam currents could be attained in a single beam than previously thought possible. Moreover, in collaboration with others they developed a theoretical model to predict the maximum current possible for a given kinetic energy, ion mass, and other parameters.

During FY 1985 emphasis in the program shifted to the technical issues involved with multiple beams. The LBL group has recently succeeded in constructing and operating a four-beam cesium ion source, including beam control and matching apparatus. This will form the basis for a so-called Multiple Beam Experiment based on four beams, independently controlled and focused but accelerated as a single group of beams. The most critical parameter, normalized beam emittance, was measured to be 0.1 microradian-meters. The combination of this very low emittance, which will enable a small beam spot when focused on a target, together with the concept of multiple beams, represents an outstanding achievement in a new direction for accelerator science in general, and for heavy ion fusion in particular.

40. State-of-the-Art Reports on Carbon Dioxide Research

The Carbon Dioxide Research Division, DOE, prepared four State-of-the-Art (SOA) Reports in 1985. These Reports cover the Carbon Cycle, Climate Modeling, First Detection, and Vegetative Response. The Reports document what is known, unknown and uncertain about CO₂ data and research results and outline the research required to reduce the remaining unknowns and uncertainties.

The publication of the SOA Reports is an important milestone in the federal government's CO₂ research program. They provide an accounting of the program's progress during the seven years since a workshop of 75 leading scientists assembled in Miami Beach, Florida, to discuss the then current understanding of the carbon cycle and the possible consequences of increases in atmospheric CO₂. During this time, the DOE and other Federal agencies, including NSF, NOAA, NASA, EPA, USGS and USDA, have sought to implement the recommendations of the Miami conference. More than \$110 million has been spent conducting CO₂ research.

More than eighty scientists from five nations participated in the preparation of the five reports which also were extensively peer reviewed.

One purpose of these reports is to motivate scientists to examine the research needs and devise approaches for meeting these needs.

The SOA Reports were prepared also as background material for a Statement of Findings (SOF) Report to be published in 1986. It will synthesize the SOA

Reports and other studies and present the rationale for the further studies needed to provide a firm scientific basis for convincing, societal assessments regarding the potential impacts of energy-related activities.

41. A 200-Year Atmospheric Record from Measurements of CO₂ in Ice

An ice core from Siple Station, West Antarctica, available this past year, provided samples of trapped air and allowed CO₂ content measurement with exceptionally good time resolution (22 years). Measurements of CO₂ trapped in air bubbles in this ice core have finally made it possible to trace the development of the atmospheric CO₂ during the last two centuries.

The record of atmospheric CO₂ concentrations over the last two centuries has long been defined as a critical research need. A detailed knowledge of this record is important for determining the role of nonfossil CO₂ sources in the observed atmospheric increase, and for quantifying the sensitivity of climate to the CO₂ concentration.

Counting the seasonal variations of the electrical conductivity of the ice allowed the ice core to be dated over the last 200 years with an accuracy of +2 years. This is important information because air bubbles become isolated from the atmosphere during a prolonged period, and thus, without an independent dating method, the entrapped air can represent a sample taking decades to centuries to isolate. The duration of the close-off process was determined to be 22 years for the Siple core.

The mean CO₂ concentration plotted against the dates when the air bubbles in the ice were sealed off from the atmosphere (mean gas age) is shown in Figure 1. The Siple ice core provides an excellent record of the atmospheric CO₂ increase from the mid-16th century to the present, and the exceptional time resolution allows sufficient overlap with the Mauna Loa record to permit comparisons

between the two sets of data. Within the limits of error, the ice core results (Figure 1) do not differ from the Mauna Loa atmospheric CO₂ record obtained since 1958.

(University of Bern, Switzerland; A. Neftel, E. Moor, H. Oeschger, B. Stauffer and J. Schwander. Support was provided by several U.S. and Swiss institutions and federal agencies.)

CO₂ CONCENTRATION IN THE SIPLE CORE

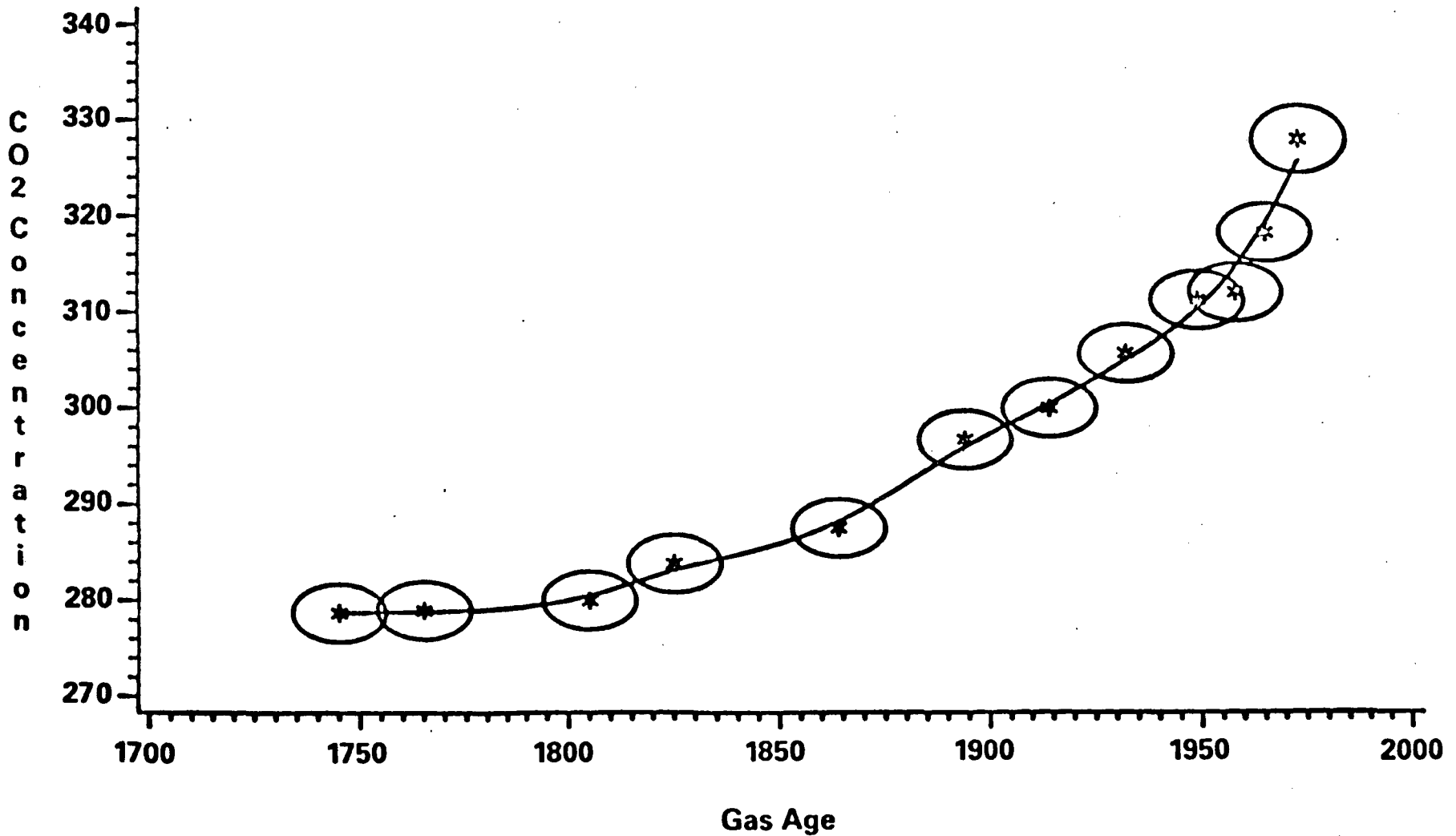


Figure 1. Measured mean CO₂ concentration plotted against the mean gas age, calibrated with the Mauna Loa record for the youngest gas age. The ellipse around each data point corresponds to the close-off time interval of 22 years and the CO₂ concentration measurement uncertainty (± 3 ppm).

42. CO₂ Enrichment Increases Crop Yield

Crop yield is increased by higher levels of CO₂. Field data from 10 new outdoor experiments involving food, forage and fiber crops provide convincing evidence that CO₂ enrichment causes greater growth and productivity. When grown at CO₂ levels twice today's atmospheric concentration, five of six crops examined yielded 31 to 82% more harvestable product. The species showing gains were black-eyed peas, soybean, sweet potato, cotton and sorghum. One crop, corn, failed to increase productivity when enriched with CO₂.

Carbon dioxide enhancement of plant growth is an important direct effect of rising atmospheric CO₂. Through photosynthesis, plants produce food and fiber from light and carbon assimilated as CO₂. Rising atmospheric CO₂ is thus an important factor in the food-producing process, and effects of CO₂ enrichment have far-reaching implications for agricultural and ecological productivity.

Much of the theory and historical data that support the idea of CO₂ - enhancement of plant growth come from laboratory experiments where light, nutrients, CO₂ levels, water and other environmental factors are controlled artificially. While short-term experiments inside such chambers are useful for studying physiological mechanisms and environmental interactions, they have produced very few reliable data on full-season growth and yield at natural light and for variable outdoor conditions.

Field studies have been emphasized in this project on the direct effects of CO₂ on plants; most of the research has been done with open-top or flow through chambers positioned in fields planted and maintained according to regular farming practice. Test plants are exposed to natural light, soil

and other conditions while the chambers maintain precise control of the desired CO₂ enrichment for an entire growth cycle.

Although corn exhibited no direct yield response to CO₂ enrichment; although other experimental results show a significant CO₂ effect on water use.

Doubled CO₂ reduced by one-third the water required to produce normal yield of corn, and this effect is expected to enhance productivity indirectly.

(Tuskegee Institute, Biswas; USDA/ARS, Rogers, Allen, Kimball; LLNL, Shinn; Kansas State University, Kanemasu)

ACCOMPLISHMENTS 1985

CHEMICAL SCIENCES

Million-Degree Microexplosions

A unique way to examine the effects on surfaces of transient high temperatures, pressures and densities has been found. The program examines the mechanism of formation of clusters of hundreds of atoms or molecules, each cluster having a single electric charge. The resulting beam of these ions is accelerated at energies up to 400 keV. It was found that collisions of these high energy ion beams with a surface occurs in less than 0.1 picosecond and generates a temperature of about 1,000,000° Celsius in the solid surface. The phenomenon opens the possibility of investigating properties of assemblies of atoms or molecules in very dense, hot plasmas.

The impact of the beam has, serendipitously, been shown to produce very small holes of 2 to 4 ten-millionths of an inch in thin carbon films. The hole size and density per unit area are adjustable depending on the beam intensity. Cluster ion impact is, thus, a promising technique for preparation of microholes for a variety of applications.

(Brookhaven National Laboratory, L. Friedman)

Enhanced Separation of Trans-Uranium Elements Greatly Reduces Volume of Nuclear Wastes

Present methods for processing irradiated nuclear fuel to recover plutonium result in considerable volumes of highly radioactive waste solutions of transuranium elements in nitric acid. The burial of large volumes of these solutions in geological repositories constitutes a major and very expensive problem. Chemists have now discovered a new solvent extraction process, called TRUEX (transuranium extraction), which reduces the quantities of wastes which must be buried by a factor of a hundred or more. The new scheme utilizes CMPO, a highly selective actinide extractant designed and then synthesized by the same chemists. When CMPO is added to the solvent commonly used in fuel reprocessing it allows extraction of all oxidation states of the actinides away from the nitric acid medium. The volume of extract is much smaller than that of the actinide-free acid solution, which can then be handled by surface storage.

The TRUEX system is very compatible with existing fuel reprocessing technology. It is currently being evaluated by Rockwell Hanford for pilot plant testing. In full operation, savings of several hundred million dollars can be expected from reduced waste burial costs and improved recovery of plutonium from reprocessing streams.

(ANL, P. Horwitz)

Quantization Effects Discovered in Photoelectrochemical Systems

Quantized energy levels in the photoelectrochemistry of superlattice photoelectrodes have been discovered by chemists studying solar photoconversion. The superlattice electrodes were prepared for the chemists by state-of-the-art materials technology in which very thin (millionth of an inch) alternating layers of gallium arsenide and gallium arsenide phosphide were grown by chemical vapor deposition on gallium arsenide wafers. In this superlattice, electrons become trapped in the gallium arsenide layers where, from the laws of quantum mechanics, their energy is maintained at certain levels of the "quantum wells". The significance of the discovery is that electron transfer from superlattice electrodes can occur from excited states of the quantum wells, thus providing a potential means to achieve the much higher solar energy conversion efficiencies predicted for hot electron injection pathways. The superlattice electrodes should have a strong impact on photoelectrochemistry research and are likely to spawn a new generation of photoelectrochemical cells for conversion of solar energy to chemical energy or electrical power.

(Solar Energy Research Institute, A. Nozik, et al)

New Light in an Important Field: How a Catalyst Is Affected by Catalysis

Until now studies of heterogeneous catalysis (the type achieved with use of solid catalysts) could measure only the changes taking place in the molecules being affected by the catalyst -- automobile exhaust gases, for example. Nothing specific could be said about the catalyst's own experience. Now it has been experimentally demonstrated that the presence of carbon monoxide adsorbed on the surface of a nickel catalyst actually modifies the chemical properties of the nickel surface. This was achieved through superior accuracy and resolution of infrared spectral bands, by combining different state-of-the-art techniques for studying adsorbed species on single crystals, in a multipurpose ultrahigh vacuum system. It was seen that the infrared frequency shifts associated with changing the amount of carbon monoxide adsorbed on a Ni(111) crystal surface are due to modification of the chemical properties of the nickel surface itself by the adsorbed carbon monoxide. The experiments (particularly the new capability they demonstrate) make possible an important new level of understanding of the effects of substances added during or after the manufacture of catalysts.

(University of Pittsburgh, J. T. Yates)

Coal Science Enhanced by a New Technique and a New Service

Two recent developments are opening a new level of detailed knowledge of coal and bringing a new dependability to collaboration on coal research. In building the knowledge base for future conversion of coal to substitute fuels and chemical feedstocks, we face some difficult facts: each coal is a chemically complex mixture, and every mine's coal differs from every other.

One Laboratory's research on separation of the various macerals (black organic substances) which make up each coal has resulted in a method for providing very pure macerals that is now being used in several other coal research laboratories. The method is based on density gradient centrifugation. It makes available pure macerals in quantity and is yielding many productive collaborative studies between this DOE laboratory and university and industrial laboratories. In addition, the Premium Coal Sample Program has successfully processed and sealed samples of the first premium coal into 9,000 ampoules containing either five (7,500) or ten (1,500) grams of coal. These are available to scientists world wide for basic research purposes. Thus for the first time coal researchers will be able to compare results on identical coal samples, for years to come. The construction and successful operation of the controlled atmosphere chamber and machinery for processing a ton of coal into very small particles in an atmosphere containing less than 100 parts per million oxygen reflects ANL's rather unique ability with large inert atmosphere chambers. Eight coals are to be similarly prepared and distributed over the next two years.

(ANL, G. R. Dyrkacz and K. S. Vorres)

Model Molecules Designed as a Step Toward Artificial Photosynthesis

A significant advance in the quest for an artificial photosynthetic system has been achieved by chemical synthesis of a model photoreaction center. In nature, light is absorbed by chlorophyll, which is a porphyrin, followed by rapid electrical charge separation by other components in the photoreaction center. A key feature of nature's system is that the charge separation takes place in many successive steps. The model compounds prepared in this work contain a porphyrin core, to which are attached a quinone and dimethylaniline at opposite ends. The porphyrin part absorbs visible light which causes an electron to be transferred from the porphyrin to the quinone part. The electron deficient porphyrin then accepts an electron from the dimethylaniline part. This is the first demonstration of photoinduced charge separation by multiple electron transfer in a model system of known structure. Indeed, the present systems show a marked increase, over previous model compounds, in the length of time that the charges can be maintained apart before recombination, a necessary feature where one hopes to cause useful chemical reactions this way. Future work on model systems will continue to draw upon current advances in research on natural photosynthesis, for the positioning of electron donor and acceptor components in the optimum geometry for high efficiency solar conversion.

(Argonne National Laboratory, M. Wasielewski)

New Extractant Polymers Discovered Which Recover or Decontaminate from Mercury, Gold, etc.

Styrene-based polymers with active phosphorus-containing groups have been discovered which efficiently and economically recover major or trace amounts of certain toxic or precious metals from waste streams, ground waters, rivers or sea water. They were devised through a collaborative university-national laboratory effort. The new extractants are synthesized by a simple procedure from inexpensive chemicals. They contrast with present cleanup or recovery systems, which generally require more expensive extractant materials or multiple separation steps to accomplish the same degree of recovery. Some metal ions, notably gold, silver and mercury, are converted by the extractant to the metals themselves, while others, e.g., uranium, are recovered but not reduced to the metal. The waters need not be pretreated to reduce acidity or salt content as was the case with previous extractant polymers. Base metals do not interfere with the process. The value of the metals recovered substantially exceeds the anticipated materials and operating costs for large-scale application of the new system.

(Univ. of Tennessee, S. Alexandratos and ORNL, J. McDowell)

New Type of Molecular Behavior and New Insights into Laser-Excited Chemistry

Use of a unique high-resolution spectroscopic technique has led to the first observation of "chaotic" vibrational behavior of molecules. In previous research on laser-excited chemistry, so-called mode selection was seen when the absorbed energy excited vibrations in molecules which broke bonds between specific parts of molecules. When it happened that the absorbed energy was redistributed into other well-understood vibrational modes, a different bond or no bond at all ruptured. Also, of course, the absorption of insufficient energy failed to rupture any bond. Heretofore, the intermediate energy range, between enough for bond rupture and too little for that, has been inaccessible to study because of the tendency to redistribution. Now that intermediate range has been observed in acetylene molecules. By using a laser to excite them to high vibrational states, and then using a different laser to trigger emission of energy, the molecules get down to the intermediate region. What was then observed was a surprise: "clumps" of 20-40 vibrational states, each clump containing randomly distributed energy levels. This unusual molecular behavior provides new insight into mode-selective chemistry.

(M.I.T., R. W. Field and J. L. Kinsey)

Energy-Saving Chemical Process Discovered, Patented and Moved Quickly from University to Industrial Use

Study of the chemistry of coal tars has led to discovery of a clever chemical system for controlled, selective reduction of benzenoid molecules to monoenes (cyclic molecules with only one double bond). The synthetic process uses low cost, energy-saving, safer calcium as a substitute for higher cost sodium. Use of carefully chosen solvents or abrasives prevents surface coating of the calcium particles, which would otherwise stop the process. The synthesis has the added advantage of high yields of the products. The patented process has reached commercialization in less than 2 years from the discovery.

(Purdue Univ., R. A. Benkeser)

Multiphoton Absorption: Guiding Theory Established

Quantitative measurements have been made for the first time of the role of random fluctuations in wavelength on the simultaneous absorption of two photons by a single atom. The results confirm a theory developed in 1968 that predicts that an atom will more readily absorb photons simultaneously, the more nearly identical the photons are to each other.

The experiment compared the wavelength distribution of laser light directed into a cell containing sodium atoms with the distribution of the light absorbed and re-emitted by the sodium. The two-photon absorption phenomenon was found to be fundamentally different from the single-photon absorption. The latter depended only on the light intensity and the wavelength, while the former depended on both the light intensity and the relationship between the two wavelengths. The absorption was found to be maximized as the difference between the wavelengths diminished. These results are important to the understanding of multiphoton absorption, an area of growing technological importance.

(University of Colorado, S. Smith)

A Chemically Useful Tunable Vacuum Ultraviolet Laser Source Developed

Chemists (and physicists) requiring vacuum ultraviolet sources sometimes find synchrotron radiation unsuited to their needs, due to either inadequate intensity per pulse or use of apparatus too unwieldy to transport and move into a synchrotron radiation facility. Such scientists have hoped for the advent of suitable laser sources.

An intense vacuum ultraviolet laser with output in the chemically important region of the hydrogen Lyman-alpha absorption, 122nm, has been developed. The laser output is tunable over a range of wavelengths from 115 to 130 nm. The technique used to produce the vacuum ultraviolet light involves conversion of three low energy photons into a single higher energy vacuum ultraviolet photon. The medium in which the energy conversion occurs is atomic mercury vapor, utilizing a fundamental property of the atom. By substituting other atomic media instead of mercury, it is possible to produce laser emission over virtually the entire wavelength region from 120 to 200 nm. As with other lasers, the vacuum ultraviolet pulse is a few nanoseconds long with a very narrow energy distribution. It has an output intensity many orders of magnitude greater, per pulse, than available from synchrotron sources.

(ANL, F.H. Tompkins)

Indirect Polarimetric Detector for Liquid Chromatography

A new general purpose detector for liquid chromatography has been devised which promises to have wide impact in analytical chemistry. The detector monitors the optical rotation induced in a polarized laser beam by an optically active flowing solvent. Eluted solutes which are not optically active or which have a different optical activity from the solvent are detected indirectly by the change in optical rotation as they pass through the detector. This general purpose detector can measure as little as 10 billionths of a gram of solute, which is one to two orders of magnitude smaller than can be measured using conventional index of refraction detectors most commonly used today. The new detector will permit determination of many substances such as saturated hydrocarbons, fatty acids and aliphatic alcohols at concentrations at which they frequently are found in energy-related raw materials and products.

(Ames Laboratory, E. Yeung)

ACCOMPLISHMENTS 1985

NUCLEAR SCIENCES (CS-ADMIN.)

Unique Behavior of Bonding in Actinide Metals

In a national laboratory-university collaboration a discovery has been made in the behavior of some of the heaviest chemical elements which will affect the understanding of electronic structure and chemical bonding of all the elements. The achievement also underscores the unique value of the HFIR and TRU, which produce these heavy elements. The first clear evidence that a type of bonding known as 5f electron metallic bonding can be made to occur in elements higher than plutonium has been shown from x-ray studies of actinide metal crystal structures and volume changes at high pressure.

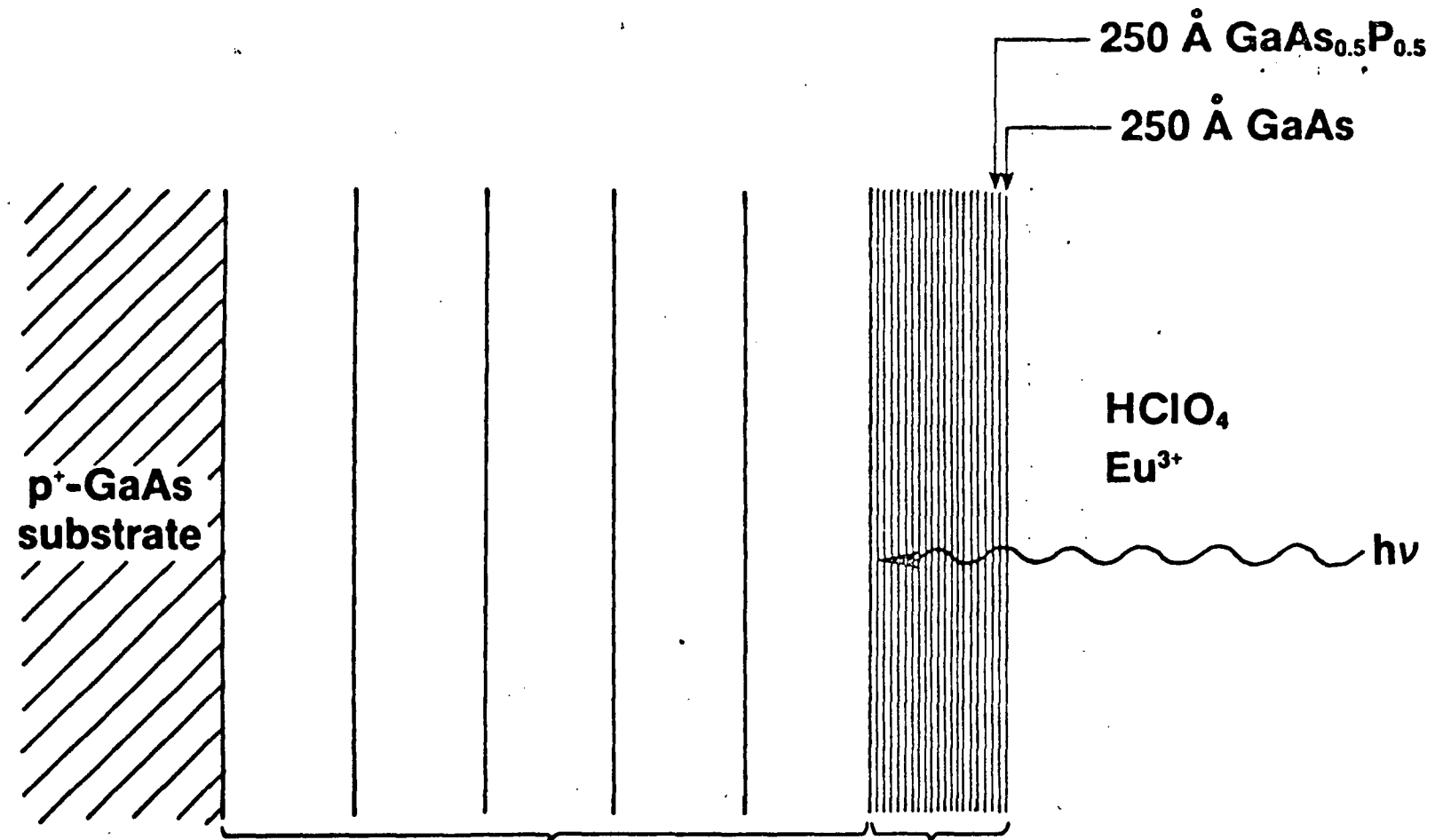
Only the actinide metals (elements 89-103) possess 5f electrons, and only in some lower actinide elements (protactinium, uranium, neptunium, plutonium) do those 5f electrons participate in metallic bonding at ordinary pressures. This has been explained by the "relativistic" drop in energy of those electrons in the higher actinides, taking them out of availability for bonding by taking them below the energies of other electrons, which therefore do their own different types of bonding and crystal geometry. But when extreme pressures squeeze the atoms together, at a certain threshold pressure for each higher actinide studied, volume collapse occurs, the 5f electrons enter metallic bonding, and the crystal geometry suddenly changes. The volume collapse in some cases is striking: 21% for curium at 440,000 atmospheres.

(ORNL, R. G. Haire and Univ. of Tennessee, J. R. Peterson)

Neptunium May Be Better Pinned Down in the Environment than Previously Thought

Neptunium has been considered to be more of an environmental hazard in nuclear wastes than other actinides because of the chemical stability (persistence) of its singly-charged pentavalent oxidation state. This singly-charged species binds less with soils and thus is more mobile in ground waters than the other actinide species, which are multiply charged. Recent studies, however, have indicated that, under ground water conditions on the oxidizing end of the oxidation-reduction scale, neptunium can exist as a doubly-charged hexavalent species. This hexavalent state is much less mobile, and thus neptunium may not pose the degree of hazard previously thought. These findings result from advances in electrochemical measurements of actinides in extremely dilute solutions.

(ORNL, L. Maya)



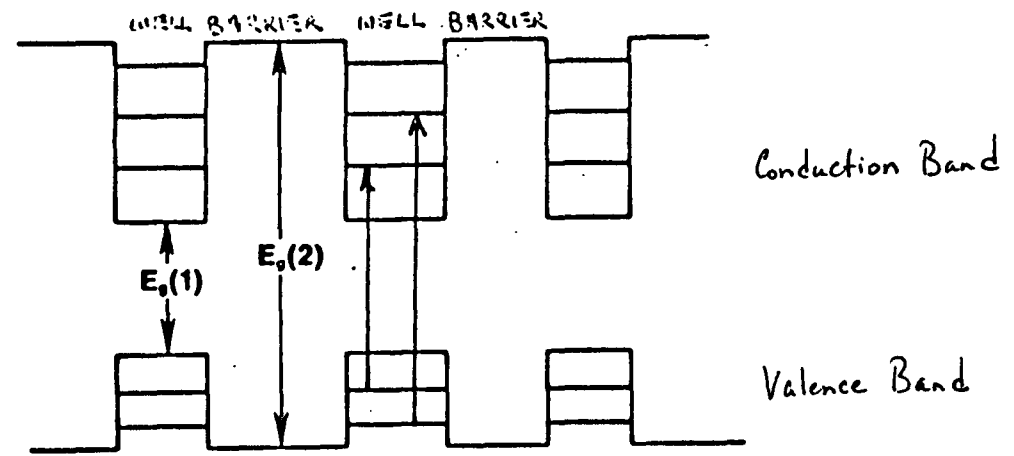
Buffer layers
five 2 μ layers of
GaAs_{1-x}P_x,
x = 0 → 0.25

Superlattice
20 periods
1 μ total thickness

Strained-Layer Superlattice Photoelectrode

Logic

Quantum Wells/Superlattices



1102.k

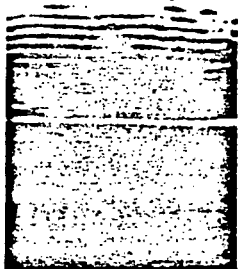


Fig. 1 SEM photograph of SLS cross-section; outer surface is at top. Wavy layers reflect strain from lattice mismatch.

MATERIALS SCIENCES

Typical Technical Accomplishments FY 1985

1. Identification of Important Phenomenon Causing High-Temperature Alloy Instability
2. Protective Alumina Scale Adherence Greatly Improved by Small H₂S Additions
3. First Observations of Grain Boundary Structural Transformations Induced by Solute Segregation
4. Research on Interface Science Results in Improved Composite Dental Filling Materials
5. Steel Wire with Superior Properties and Reduced Cost Achieved through Microstructural Modification
6. Better Understanding of Hydrogen Behavior in Metals Using Ion Beams for Characterization
7. New Mechanism Identified for Hydrogen Induced Failure
8. Automated Synthesis Technique Developed for Preparing Low-Cost High-Performance Magnetostrictive Alloy
9. Cavity Nucleation and Growth in Alumina and Silicon Carbide Ceramics Better Understood Using the New Small Angle Neutron Scattering Technique
10. Radiation Induced Amorphization Found in Actinide Doped Crystalline Phases
11. Improved Analysis and Testing Method Developed for High Temperature Creep Deformation of Ceramics
12. New Metastable Semiconductor Alloys Grown by Organometallic Vapor Phase Epitaxy
13. New Technique for Determining Organic Sulfur Content in Coal
14. New Fischer-Tropsch Catalysts Derived from Zeolitic Aluminoferrisilicates
15. New Technique for Surface Modification of Materials in Strongly Segregating Alloy Systems
16. Design, Synthesis, and Characterization of a New Organic Superconductor, with the Highest Reported Ambient Pressure Transition Temperature
17. A New Technique for Determining Ground State Phase Diagrams of Organic Superconductors

18. A Method Developed for Yielding Soluble Conducting Polymers for the First Time
19. Electron Hybridization Effects Help Explain the Crystal Structure of Plutonium
20. Mixed Oxide Electrodes Developed Which Have Greater Electrocatalytic Activity
21. Voltammetric Characterization of Conducting Materials at Electrode Potential Values Beyond the Limits Set by Solvent Breakdown
22. New Static Ultra-High Pressure Record: Studies of Hydrogen and Deuterium
23. Development of a Unique Source of Low-Energy Positrons and Its Application to the Study of Surfaces
24. First High Resolution Study of Magnetic Structures by Scattering of X-rays
25. Metallic Superlattices Using the Inexpensive Technique of Sputtering
26. Explanation of Transition-Temperature Oscillations in Thin Superconducting Films
27. New Sensitivity Level Achieved with Infrared Spectroscopy
28. High Resolution Neutron Time-of-Flight Technique used to Determine Complex Structures from Powder Diffraction
29. Existence of Dimensional Crossover in Metallic Superconducting/Normal Metal Superlattices
30. Theory of Novel Semiconductor Compounds
31. First Results of Bond Strengths and Vibrational State Determinations in Amorphous Metals Using Raman Scattering

Don, ✓

7/29/85

Here is our complete
list of '85 accomplishments.
I gave a copy to Dave.
There are some good
ones here.

/Lou

IDENTIFICATION OF IMPORTANT PHENOMENON CAUSING
HIGH-TEMPERATURE ALLOY INSTABILITY

TECHNICAL RESULT:

The diffusion of interstitial carbon atoms in platinum-carbon alloys has been shown to induce a counter flow of substitutional platinum atoms and, concomitantly, removal of platinum from down-stream surfaces (re carbon) and deposition on up-stream surfaces. This phenomenon is noteworthy since interstitial solute flows normally do not couple strongly to fluxes of substitutional atoms; in this case it is thought to arise as a result of strong binding between the carbon atoms and vacancies so that flow of carbon causes a parallel flow of vacancies which produces an exactly antiparallel flow of platinum. Evidence is accruing that large interstitial impurity--vacancy binding energies are common in metals and research is continuing on the generality of the reported phenomenon.

SIGNIFICANCE:

This phenomenon has significant implications for the dimensional and compositional stability of metallic alloys in high-temperature service under conditions where flows of interstitial solutes occur. For example, it is possible that gradients of helium or tritium in a fusion first wall would result in loss of effective wall thickness or in significant partitioning or segregation of alloying and impurity elements. However, the continuing research underway, which aims to identify and understand the nature of this phenomenon, will lead to methods of inhibiting these effects and of designing alloys with reduced susceptibility to diffusion induced instabilities. (Research conducted by K. H. Westmacott, Lawrence Berkeley Laboratory.)

PROTECTIVE ALUMINA SCALE ADHERENCE GREATLY IMPROVED
BY SMALL H₂S ADDITIONS

TECHNICAL RESULT:

A remarkable improvement in the adherence of protective Al₂O₃ scales formed on stainless-like steels has been found when the oxidizing environment is slightly contaminated with sulfur-containing gases. The improved adherence is obvious visually, and much reduced scale cracking has been confirmed by in situ acoustic emission measurements. Studies reveal that the mode of scale growth is altered by the sulfur: In the sulfur-free environment oxygen ions migrate inward across the scale to form new oxide at the metal/scale interface; this growth mode produces high stresses in the scale and leads to cracking and spalling. With sulfur present aluminum ions migrate outward to produce new scale at the free surface - a growth mode that leads to little or no stressing of the interface.

SIGNIFICANCE:

This investigation demonstrates that significant improvements in oxidation/sulfidation resistance can be achieved by deliberately inducing scale growth mechanisms that lead to lower stresses. Both isothermal and thermocyclic applications are benefitted. These results suggest the practical application of the deliberate use of additives, such as H₂S or others if such are discovered, for the purpose of improving the mechanical integrity of Al₂O₃ scales. (Research conducted by D. Shores, University of Minnesota.)

FIRST OBSERVATIONS OF GRAIN BOUNDARY STRUCTURAL TRANSFORMATIONS
INDUCED BY SOLUTE SEGREGATION

TECHNICAL RESULT:

The first definitive observations have been obtained that show solute segregation to grain boundaries causes a change of the structure of the boundaries from that seen in pure materials. It has been known for some time that solute present at boundaries can have a significant effect on the mechanical properties of materials, and render them brittle and susceptible to fracture at low stresses, but it has not been known why the properties of the boundary are so dramatically affected. In the present work, advanced transmission electron microscopy has revealed that gold segregation to grain boundaries in iron-gold alloys causes the dislocation structure of the interface to change from that in pure iron. Each boundary dislocation network is considered a two-dimensional periodic phase and the structural transformation from one network to another has been studied as solute segregation and boundary misorientation are varied; the results are presented in the form of a grain boundary phase diagram. A similar study is in progress on grain boundaries in metallic oxides (ceramics); a structural transformation is observed, but of a different kind than in iron.

SIGNIFICANCE:

This study has shown, for the first time, that solute segregation causes a change in the structure of grain boundaries in both metals and ceramics. If grain boundary structural changes can be linked to changes in properties (which is to be studied but has not yet been done), then it becomes feasible to consider designing special boundary structures that give rise to desirable bulk materials properties. The long range goal of this

research is to build up a large enough base of scientific understanding that special processing treatments can be developed to obtain interfaces that produce desirable bulk properties for both mechanical and electronic applications. (Research conducted by K. Sickafus and S. L. Sass, Cornell University.)

RESEARCH ON INTERFACE SCIENCE RESULTS IN IMPROVED
COMPOSITE DENTAL FILLING MATERIALS

TECHNICAL RESULT:

Technology transfer from a fundamental ceramic corrosion investigation to quality control on an industrial production line has been achieved as a result of specific research result--that the effective surface charge (or electrochemical potential) is very high for glass and zero for polymers. This finding turns out to be critical to a company encountering problems in manufacturing dental-filling composites of extremely small glass particles coated uniformly with a thin polymer coating. The company sought advice from the scientists involved in the corrosion work, installed equipment for measuring the change in surface charge during the coating process in manufacturing, and at last report was enjoying its success.

SIGNIFICANCE:

The application of this research has long-range implications for significant property improvements of many types of composite materials where coupling agents are utilized. This research has lead to a technique for assuring the routine application of one monolayer of coupling agent and thereby making it possible to optimize the strength of composites by assuring maximum bonding between constituents of the material. (Research conducted by G. L. McVay and B. P. McGrail, PNL.)

STEEL WIRE WITH SUPERIOR PROPERTIES AND REDUCED COST
ACHIEVED THROUGH MICROSTRUCTURAL MODIFICATION

TECHNICAL RESULT:

Superior properties and reduced cost have both been achieved with simple modifications in the processing procedures used to make steel wire. Beginning with low-carbon, dual-phase steel rods, a drawing operation has been developed which produces a finely dispersed martensite/ferrite composite morphology in the final microstructure yielding tensile strengths in the 400,000 psi range with good (> 10%) residual ductility. The key to this performance is the attainment of a small-grain, recrystallized ferrite matrix within which approximately 15% of the volume is unrecrystallized austenite that is later transformed to lath martensite during water quenching. The process has been successfully implemented in existing commercial rod-mills. It requires no additional capital investment and because it makes the traditional patenting heat treatments obsolete, actually results in substantial savings.

SIGNIFICANCE:

This breakthrough has significant potential for improving the international competitiveness of domestic steel specialty products. The combination of high strength, good formability, and improved low temperature ductility in these wires gives them great potential for such applications as tire cord in steel-belted radial tires. No expensive alloying additions are required and the procedures have already been successfully tried at a commercial Stelmor wire-rod production line. Patents have been awarded and licensing agreements are currently being arranged. (Research conducted by G. Thomas and graduate students, University of California, Berkeley/LBL.)

BETTER UNDERSTANDING OF HYDROGEN BEHAVIOR IN METALS
USING ION BEAMS FOR CHARACTERIZATION

TECHNICAL RESULT:

New experimental methods employing high-energy ion accelerators have been used in conjunction with theory to investigate the behavior of hydrogen in metals, and important fundamental advances have been achieved in two areas. The first concerns the strong trapping of hydrogen which occurs at lattice vacancies and helium bubbles introduced in a radiation environment. For the first time, using the new experimental techniques, the strength of hydrogen trapping by vacancies and helium bubbles has been accurately measured in eight metals and alloys, and theoretical models have been developed that are capable of predicting the measured trap strengths with no free parameters. The second area of advancement relates to the release of hydrogen from metals at their surfaces. The development of suitable ion-beam procedures have allowed surface-controlled release rates to be reliably measured for the first time, and these rates have been determined as a function of the state of surface oxidation. For a bare-metal iron surface the observed rate is closely approximated by a new theoretical approach.

SIGNIFICANCE:

The trapping mechanisms and surface-barrier effects characterized in the present investigation are important to a variety of hydrogen-related technologies. For example, trapping and surface permeability must both be understood to predict the retention, recycling, and permeation of implanted tritium in fusion reactor components. Hydrogen embrittlement of structural alloys in fission reactors can be affected substantially by trapping at vacancies and helium clusters. Hydrogen storage in metal hydrides depends

critically upon the permeability of the surface for hydrogen uptake and release. (Research conducted by S. M. Myers and W. R. Wampler, SNL, in collaboration with F. Besenbacher and J. K. Norskov, Denmark. Follow-on, FY 1983.)

NEW MECHANISM IDENTIFIED FOR HYDROGEN INDUCED FAILURE

TECHNICAL RESULT:

Direct, high-resolution observations in the electron microscope of hydrogen induced fracture of solids under stress have shown that many of the commercially important metal alloys do not fail in a brittle manner as has been believed in the past. Rather than causing a brittle fracture, hydrogen enhances the local plastic behavior of the metals and causes failure by virtue of enhanced local deformation. The basis for this locally enhanced ductility is the very high mobility of hydrogen in metals and its ability to modify the stresses around defects in the metals.

SIGNIFICANCE:

Recognition of the mechanism of this type of environmentally related failure will allow improvements in both the design of alloys and systems for use in aggressive environments and in the prediction of lifetimes of engineering systems. Hydrogen induced failures are responsible for the loss of many billions of dollars of engineering systems and for the loss of many lives each year. These failures generally occur well within the "safe limits" of the operating parameters for the materials and occur unpredictably after a period of service. In the past, attempts to protect against this type of failure were based on ad hoc solutions and were mostly unsatisfactory. In many cases the "solutions" themselves caused the introduction of hydrogen into the material and thereby caused premature failure.

(Research conducted by H. K. Birnbaum and I. M. Robertson.)

AUTOMATED SYNTHESIS TECHNIQUE DEVELOPED FOR PREPARING LOW-COST
HIGH-PERFORMANCE MAGNETOSTRICTIVE ALLOY

TECHNICAL RESULT:

An automated synthesis technique has been developed that: yields (a) grain oriented rare-earth-iron magnetostrictive alloy Terfenol-D ($Tb_{0.3}Dy_{0.7}Fe_{2.0}$) with circular, square, and hexagonal cross sections useful for transducer drive elements and (b) single crystals with a selected axial crystallographic orientation, and demonstrates the acceptability of commercial-grade starting material.

SIGNIFICANCE:

This new synthesis technique enables significant improvements to be made in the performance of transducer drive elements in jet and diesel engine fuel injection systems, submarine detection devices, and position sensing transducers in robotic systems as a consequence of the increased magnetostriction obtained in Terfenol-D. Currently the Ames Laboratory is the only source for these materials which they supply to research and prototype development programs. The projected commercial demand is approximately 2000 kg/yr (up 40 times from the present R&D demand), so a plan has been devised, in concert with industry, to develop and transfer the technology for mass production, and automation. Commercial applications for rare-earth-iron magnetostrictive materials that stand to take advantage of this new synthesis technique are underwater sonar devices for Naval defense systems, underground sonar devices for oil field exploration, micro-positioners for laser mirror actuators, fuel injection systems for diesel engines, and robot components such as hands, wrists, and elbows, etc.

(Research conducted by O. D. McMasters, Ames Laboratory.)

CAVITY NUCLEATION AND GROWTH IN ALUMINA AND SILICON CARBIDE CERAMICS
BETTER UNDERSTOOD USING THE NEW SMALL ANGLE NEUTRON SCATTERING TECHNIQUE

TECHNICAL RESULT:

Powerful techniques for analyzing the diffraction of neutron beams by arrays of cavities in these ceramic materials are providing the first statistical data that describe cavity nucleation and growth processes--data that are needed in order to improve the performance and predict the lifetimes of structural ceramics. A detailed characterization of cavity evolution during compressive creep has been accomplished using small-angle neutron scattering. Samples of Coors AD-99 alumina containing a relatively thick and continuous, glassy grain boundary phase, Lucalox alumina containing no continuous grain boundary phase, and Norton NC-203 silicon carbide containing a relatively thin and continuous, glassy grain boundary phase have been characterized. The neutron scattering measurements, which provide a means of characterizing both the nucleation rates and the growth rates of grain boundary cavities during the early stages of creep, have shown unequivocally that cavity nucleation does occur and have also identified some very significant differences in the cavity nucleation and growth phenomena of these three ceramic systems. For example, in both aluminas cavity nucleation occurs throughout creep deformation while in the silicon carbide cavity nucleation is limited to the very early stages.

SIGNIFICANCE:

The results of these studies indicate that accurate predictions of the lifetimes of ceramic components at elevated temperatures can obtain only when reliable models of cavity nucleation and growth are combined with proper failure criteria. Refined nucleation and growth models are currently

being developed using these neutron scattering results to define the necessary modifications. In addition, the results have also suggested methods that could be employed to improve ceramic performance at elevated temperatures, e.g., by the inclusion of hard grain boundary precipitates to reduce cavity nucleation. (Research conducted by R. A. Page, Southwest Research Institute.)

RADIATION INDUCED AMORPHIZATION FOUND IN ACTINIDE DOPED CRYSTALLINE PHASES

TECHNICAL RESULT:

Damage ingrowth models have been developed for radiation-induced macroscopic swelling which fit the observed dose dependence of several crystalline ceramic materials, relevant to nuclear waste forms, which have been doped with a short-lived actinide to investigate the effects of alpha decay on the microstructures and physical properties. The swelling behavior of ^{235}Pu doped zircon is in excellent agreement with the behavior of the natural mineral which has been undergoing damage for 600 million years. These data are critically important because design-limiting parameters such as fracture toughness and leach rate increase with cumulative dose in proportion to the macroscopic swelling. Transmission electron microscopy analyses reveal that damage to the zircon results from daughter recoil nuclei emitted in the alpha decay process.

SIGNIFICANCE:

Relevant fundamental understanding obtained from radiation damage studies have had considerable impact in nuclear waste management and the techniques developed have led to two accepted standard procedures for radiation effects testing. This work establishes actinide-doping as the only accelerated laboratory test that can accurately simulate both microscopic and macroscopic behavior over geologic times. From another perspective, this study demonstrates that the so-called metamict minerals reach that condition by predictable displacement damage; environmental changes which occur during this time produce only secondary effects. (Research conducted by G. J. Exarhos and W. J. Weber, Battelle Pacific Northwest Laboratories.)

IMPROVED ANALYSIS AND TESTING METHOD DEVELOPED FOR HIGH
TEMPERATURE CREEP DEFORMATION OF CERAMICS

TECHNICAL RESULT:

A damage theory has been developed that accounts for the fact that high temperature creep deformation data obtained by simple bend tests on ceramic materials, which has been the common method of creep testing in ceramics, presents problems in data reduction due to complex stress profiles. The overall difficulty is that the tensile behavior is different than the compressive behavior in the same test sample due to the preferential formation of voids and cracks at locations that are in tension. This theory has been: (a) used to extract room-temperature tensile stress-strain data from room temperature bending data, and (b) used to analyse elevated-temperature creep phenomena. The results successfully account for several phenomena which have been observed in the creep behavior of ceramics. Thus a simple theory for creep deformation in ceramics has been developed which successfully and quantitatively predicts the difference in behavior of ceramics at high temperatures when they are in a state of tension, compression, and bending.

SIGNIFICANCE:

The analysis developed in this research is significant because it will permit energy systems designers to make more reliable predictions of creep deformation and gives research and quality control laboratories an improved and more reliable creep testing procedure. Effectual use of ceramic components in advanced, high-temperature, energy-related heat engines will require extensive understanding of the behavior of and design criteria for brittle materials (ceramics). Component designers are excessively cautious and conservative in their choice and application of structural ceramics.

A primary reason for the designers' cautiousness is related to the uncertainty that exists between standard laboratory bend tests and the actual mechanical behavior of complex engineering components exacerbated by the fact that real engineering components are subjected to multiaxial rather than uniaxial loads. (Research conducted by Drs. A. R. Rosenfield, D. K. Shetty, and W. H. Duckworth, Battelle Columbus Laboratories.)

NEW METASTABLE SEMICONDUCTOR ALLOYS GROWN BY
ORGANOMETALLIC VAPOR PHASE EPITAXY

TECHNICAL RESULT:

The prospects for synthesizing systems of advanced III/V compound semiconductor alloys that are immiscible, i.e., those with miscibility gaps, have been dramatically improved by the recent development of a new technique which allows the growth of all alloys, even those which should phase-separate. This technique, called organometallic vapor phase epitaxy or OMVPE, has recently been demonstrated to be capable of growing several III/V semiconductor alloys for the first time. The resultant new materials were found to be mirror smooth, and have high structural perfection and long minority carrier lifetimes. Excellent quality alloys of all compositions, even those directly in the center of a miscibility gap, could be grown. Further developments have allowed the growth of four component (quaternary) alloys containing Ga, In, As, and Sb. The properties, including energy band gap and lattice constant, of the GaAsSb and GaInAsSb alloys in the range of solid immiscibility have been studied for the first time.

SIGNIFICANCE:

The results of this research are particularly significant because they establish the basic ability to grow metastable III/V alloys by OMVPE. It is expected that OMVPE will now be used to grow alloys in many other semiconductor materials which until now has not been possible because of their miscibility gaps. The excellent properties exhibited by these new metastable semiconductor alloys suggest that they may be useful for the fabrication of electronic devices such as high efficiency tandem solar cells

and infrared detectors for fiber optic communication systems. The OMVPE method is suitable for scale-up to for large-scale production operations. (Research conducted by Professor G. B. Stringfellow, University of Utah.)

NEW TECHNIQUE FOR DETERMINING ORGANIC SULFUR CONTENT IN COAL

TECHNICAL RESULT:

A measurement technique for determining the organic sulfur content in coal has been developed that uses thin coal foils or powdered coal in a transmission electron microscope. The chief advantages of the technique are that the measurements are simple, accurate, and direct and use the conventional X-ray detection apparatus found on nearly every electron microscope. Furthermore, the method measures the sulfur content in extremely small volumes of material, less than one cubic micrometer. Thus, the sulfur concentrations in the various hydrocarbon "phases" which exist in coal--phases which variously come from wood cells, bark, roots, leaves, spores, pollens, and semi-burnt wood can be accurately determined.

SIGNIFICANCE:

The ability of this technique to analyze sulfur in the subfractions of coal is an important advance in coal science and it offers the possibility of seeing what phases of the coal lose sulfur more rapidly when the coal is heated, chemically cleaned, or microbially cleaned. Sulfur is found in coal in two principal forms: mineral sulfur such as pyrite and as individual sulfur atoms distributed through the carbonaceous matter. Elimination of the first of these from coal can be made by grinding the coal into fine powder and separating the heavier pyrite from the lighter carbonaceous matter by gravity means; mineralogists use this kind of gravity separation for handling ores all the time. Separation of the remaining sulfur from coal--the distributed sulfur (termed organic by coal chemists) is most difficult. It can be done by heating, by chemical reactions or by microbial means. (Research conducted by C. A. Wert, University of Illinois.)

NEW FISCHER-TROPSCH CATALYSTS DERIVED FROM ZEOLITIC ALUMINOFERRISILICATES

TECHNICAL RESULT: Evidence has been obtained for the formation, upon reduction, of extremely small metallic iron particles (diameter $< 20 \text{ \AA}$) in aluminoferri-silicate (AFS) materials crystallized with the ZSM-5 zeolite structure. These are the most highly dispersed Fe particles in ZSM-5 type zeolites so far reported. Small Fe particles have also been produced in AFS materials crystallized with the Offretite crystal structure. Both types of AFS materials have been shown to be active Fischer-Tropsch catalysts. A post-synthesis modification procedure permits the activity and selectivity of the AFS ZSM-5 catalyst to be modified by introduction of a second Group VIII transition element. The AFS Offretite material has the best selectivity to light hydrocarbons ($< C_5$) in the preliminary tests. Evaluation of the technological potential of these materials requires further exploration and testing under higher pressure and high conversion conditions. A surprising discovery is that the clustering of Fe^{3+} ions into small oxide particles at higher Fe concentrations in the AFS ZSM-5 greatly suppresses the Fischer-Tropsch activity of the resulting reduced catalyst. This result is contrary to experience with Fe on conventional supports, and requires further investigation.

SIGNIFICANCE: Employing shape-selective materials, e.g., zeolites, is a potentially powerful method for improving selectivity in heterogeneous catalytic conversions. One of the most important long-range technological targets in catalysis is the efficient production of feedstock chemicals, principally light olefins, from coal or biomass sources via hydrogenation of carbon monoxide. Iron-based catalysts are to be preferred due to iron's

availability and cost relative to other Group VIII metals. Improved performance with increasing metal dispersion has been reported for iron Fischer-Tropsch catalysts, but achieving very high dispersions is very difficult. Our method of producing highly dispersed Fe on zeolites is a promising new direction, and is potentially applicable to incorporation of other transition elements either for Fischer-Tropsch conversion or other important energy-related catalytic processes. At this juncture, direct Fischer-Tropsch conversion at modest operating pressure with good selectivity to light hydrocarbons appears to be a reasonable prospect using AFS zeolite catalysts. (Research conducted by L. E. Iton, Materials Science and Technology Division, Argonne National Laboratory.)

NEW TECHNIQUE FOR SURFACE MODIFICATION OF MATERIALS IN STRONGLY SEGREGATING ALLOY SYSTEMS

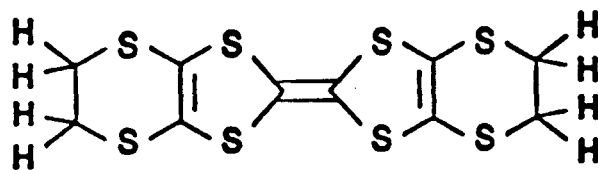
TECHNICAL RESULT: A number of alloy systems have been identified in which the dilute component strongly segregates to the surface. For example, at a bulk concentration of 5 at.% Li in a Cu-Li alloy, it is found that the surface layer to consist almost entirely of Li. Furthermore, when such a materials is bombarded with Ar^+ ions, having energies of a few kiloelectron volts, sputtered atoms originating for the most part (85%) in the very first layer are ejected virtually 100% as Li^+ ions. Application of a small negative potential of 40 volts to the target returns most of the sputtered Li^+ ions to the surface, thus resulting in a dramatic decrease in effective sputtering yield. Surprisingly, the Li-overlayer can be maintained even under quite high fluences of bombarding ions, aided by radiation-enhanced diffusion of Li from the bulk. Theoretical modeling calculations of these complicated and interrelated processes have been made and are in accord with the experimental findings. Experiments currently under way at the plasma device PISCES at UCLA, which simulates the edge plasma conditions expected in a full scale power-producing fusion reactor, show that Cu-Li has potential as an effective impurity control systems.

SIGNIFICANCE: There is a technological need for materials with surface properties characteristic of one materials and bulk properties characteristic of another. This need is usually addressed by the use of a variety of coating, plating, or cladding techniques, although there are many problems associated with the fabrication, integrity, durability and maintenance of such coatings, especially in hostile environments. This study has identified a new class of materials in which many of these problems could be circumvented: dilute strongly segregating alloys which

provide self-sustaining coatings with potential applications to corrosion and oxidation resistance, hydrogen permeation and embrittlement problems, improved vacuum materials, and materials which reduce plasma contamination and erosion of structural components in fusion devices. The materials identified to date as candidates for further study include dilute alloys of lithium, gold, aluminum and beryllium. Although these elements are present in the alloy at concentrations ranging from a few parts per million up to about 10 at.%, they dominate the surface composition and properties as a result of thermodynamic and/or radiation-related segregation processes. (Research conducted by Alan R. Krauss and Dieter M. Gruen, Materials Science and Technology Division, Argonne National Laboratory.)

DESIGN, SYNTHESIS, AND CHARACTERIZATION OF A NEW ORGANIC SUPERCONDUCTOR,
WITH THE HIGHEST REPORTED AMBIENT PRESSURE TRANSITION TEMPERATURE

TECHNICAL RESULT: The highest ambient pressure superconducting transition temperature ($T_c = 5$ K) yet observed for a synthetic metal organic superconductor has been achieved in a new synthesis at Argonne. The compound, $(\text{BEDT-TTF})_2\text{AuI}_2$, was designed and synthesized on the basis of principles established in previous work. BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene, (see Figure 1), and AuI_2^- is the linear diiodoaurate (I) anion. As in all $(\text{BEDT-TTF})_2\text{X}$, $\text{X} = \text{anion}$, systems, BEDT-TTF serves as an electron donor while the anion is the acceptor specie.



BEDT-TTF

Figure 1

Commercially available BEDT-TTF (Strem Chemical Co., Inc., Newburyport, MA), which has been prepared in a joint venture using an Argonne synthetic procedure, was used in the synthesis of $(\text{BEDT-TTF})_2\text{AuI}_2$.

Significance: The continuing aim of this research is the development of new organic synthetic metals with a potential for use in electronic systems. Organic synthetic metals continue to offer unparalleled promise because of the wide range of derivatives which can be synthesized at room temperature. For example, the superconducting transition temperatures, at ambient pressure, of $(\text{BEDT-TTF})_2\text{X}$, $\text{X} = \text{I}_3^-$, IBr_2^- , and AuI_2^- , are $T_c = 1.5$ K, 2.8 K, and 4.98 K, respectively. The AuI_2^- derivative was the result of a rational

design effort in which it was predicted that T_c would likely rise when proceeding from $X = I_3^-$ and IBr_2^- to AuI_2^- . These results clearly demonstrate the importance of a linear-symmetric anion in producing new organic superconductors and they highlight a new approach to raising T_c , i.e., metal atom insertion into such linear anions. (Research conducted by Hau J. Wang, Mark A. Beno, Urs Geiser, G. W. Crabtree, K. Douglas Carlson and Jack M. Williams of Argonne National Laboratory; Larry J. Azevedo, James F. Kwak, and James E. Schirber of Sandia National Laboratories; and Michael E. Strem, Frank S. Wagner and Charles F. Sielicki, Strem Chemical Company.)

A NEW TECHNIQUE FOR DETERMINING GROUND STATE PHASE DIAGRAMS OF ORGANIC
SUPERCONDUCTORS

TECHNICAL RESULT: Since the discovery of superconductivity in organic metals much research has been concentrated on the details of the pressure stabilized metallic state. Pressure suppresses the spin density wave (SDW) transition. Previous attempts at understanding the competition between the SDW and superconductivity were hampered by imprecise pressure measurements in solid media and because electrical contacts on crystals usually did not survive several temperature or pressure cycles. A contactless technique was developed which avoids these problems. The technique uses the relatively narrow electron spin (ESR) resonance signal of the metallic state of organic metals. The low-field ESR resonance is measured with a radio frequency coil wound directly on a single-crystal sample mounted inside a pressure vessel. Helium gas pressure techniques allow studies at kilobar pressures and temperatures as low as 1 K. This technique allows indefinite cycling of pressure and temperature without harming the sample.

SIGNIFICANCE: This technique is useful because the ESR signal and the measured absorption in the rf coil are strongly dependent upon the magnetic state of the sample. In the high-temperature, high-pressure regime, the ESR signal is narrow and the susceptibility is independent of temperature, indicative of Pauli paramagnetism. The SDW transition is very sharp as one decreases the temperature at constant pressure, typically having a width in temperature of 0.1 K. The superconducting state at high pressure and the Meissner currents induced in the sample lead to a change in the inductance of the rf coil. Both the lower and upper critical fields are observed. The metallic, spin density wave, and superconducting phases have been successively observed. The technique has provided the first microscopic

demonstration that the superconducting phase extends, in temperature, below the spin density wave phase along an isobar. (Research conducted by L. J. Azevedo and J. E. Schirber, Sandia National Laboratories, Albuquerque; J. M. Williams, Argonne National Laboratory.)

A METHOD DEVELOPED FOR YIELDING SOLUBLE CONDUCTING POLYMERS FOR THE FIRST TIME

TECHNICAL RESULT: A new solvent/initiator system has been developed that yields for the first time soluble polyacetylene and other soluble conducting polymers. The polymerizations are done in AsF_3 solutions using AsF_5 as the polymerization initiating agent. Solid or liquid monomers are mixed with the AsF_3 solvent at room or lower temperatures, and the AsF_5 is introduced into the reaction vessel in measured amounts to initiate the reaction. For gaseous monomers, such as acetylene, the AsF_3 solvent is cooled to temperatures below the melting point of the monomer. When the monomer is introduced, a solid solution with the solvent is formed. In every case, with the introduction of the initiating agent, polymerization occurs instantaneously to give polymers of molecular weights as high as 10,000 by g.p.c. analysis. At the end of the reaction, excess AsF_5 is removed by pumping. The solvent is distilled from the reaction mixture to give homogeneous polymeric films. Polyacetylene films cast from solutions of acetone have a conductivity of about 10^{-7} . When these films are exposed to iodine vapor, the conductivity increases to about 10^{-4} . Other conducting polymers, such as polyparaphenylene, polynaphthalene, polyanthracene and their derivatives have also been synthesized, and all were found to be soluble in common organic solvents.

SIGNIFICANCE: Soluble polymers permit for the first time a detailed molecular characterization of conducting polymers. Such characterization has been lacking and will guide efforts in the design and synthesis of better conducting polymers. Also the processing of conducting polymers can be studied because soluble polymers can be fabricated into a variety of shapes. (Research conducted by M. Aldissi, R. Liepins, A. Nyitray, A. Bishop, D. Campbell, and S. Mzumdar, Los Alamos National Laboratory.)

ELECTRON HYBRIDIZATION EFFECTS HELP EXPLAIN THE CRYSTAL STRUCTURE OF PLUTONIUM

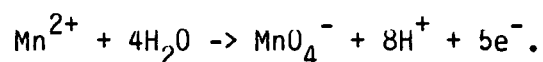
TECHNICAL RESULT: The magnetic properties of cerium and light actinide compounds have been shown to arise from a highly-anisotropic, interionic interaction between the resonant hybridization of moderately delocalized f-electrons with band electrons. This hybridization was first treated by Coqblin and Schrieffer for the case of a single f electron to explain the behavior of dilute Ce^{+3} compounds. For the work described here, the hybridization was extended for the general case of (n) f-electrons. The calculations thus include the limiting cases of spin-orbit coupling, L-S and j-j, and the case of intermediate coupling (IC), and also include the possibility of long-period antiferromagnetic structures. As an example of IC, Pu^{+3} in PuSb was studied. The theoretical results reproduce closely the experimentally observed magnetization vs. temperature curve of PuSb. The predicted phase transition from a low-temperature, ferromagnetic phase to a long-period, antiferromagnetic phase at about 75 K also agrees with experiment.

SIGNIFICANCE: It has become clear in the last few years that the f-electron behavior in elemental plutonium falls in the transitional regime between localized and band behavior. The unusual crystallographic behavior (many allotropes) of plutonium apparently arises from this source. This work shows that the key to understanding the behavior of f-electron systems in the IC regime is that the f-electrons belonging to one atom interact with those belonging to another atom primarily through hybridization with non-f band electrons. When treated with appropriate mathematical formalism, this information allows the possibility of fundamental understanding of the unusual crystallographic behavior of elemental plutonium. (Research

conducted by Bernard R. Cooper, Pradeep Thayamballi, and Amiotava Banerjea,
West Virginia University; J. C. Sperlet and W. Muller, European Institute
for Transuranium Element; U. Vogt, Swiss Federal Institute of Technology.)

MIXED OXIDE ELECTRODES DEVELOPED WHICH HAVE GREATER ELECTROCATALYTIC
ACTIVITY

TECHNICAL RESULT: Oxygen-rich electrodes (e.g., $\text{PbO}_2/\text{BiO}_{2.5}$ and $\text{PbO}_2/\text{AsO}_{2.5}$) were found to have much greater electrocatalytic activity for supporting electrochemical oxidations which require simultaneous transfer of oxygen from water to the reaction products. The electrode materials were prepared by electrodeposition from Pb(II) solutions. An example of the kind of reactions that are catalyzed is



The heterogeneous rate constant for this reaction at Pb/BiO_2 electrodes is more than 100 times that for pure PbO_2 . Oxygen poor electrodes (e.g., $\text{PbO}_2/\text{TlO}_{1.5}$) exhibit decreased electrocatalytic activity compared to PbO_2 .

SIGNIFICANCE: Anodic, oxygen-transfer coupled reactions have very large activation energies at conventional electrodes. Very high applied voltages are needed to drive these reactions and considerable energy is wasted decomposing water. Many of these reactions are observed to proceed slightly faster if oxide is present at the electrode surface; however, the role of the oxide is not well understood. The result described above allows a large series of mixed-oxide electrodes to be prepared for a fundamental study that will correlate bulk and surface properties to electrocatalytic activity and will also give insight into corrosion reactions at oxide protected metals.

Oxidative oxygenation reactions are used in the chemical industry for many products. Low yields at traditional electrodes have resulted in many oxygenation reactions being done indirectly by awkward use of chemical intermediates. This research has applications in electroanalytical

chemistry, electrosynthesis, oxidative desulfurization, degradation of toxic wastes, and electrochemical energy conversion and storage. With respect to the latter, note that the manganese in the reaction shown above has an equivalent weight of about 11 grams while that of lead in the lead-acid battery is about 100 grams. (Research conducted by Dennis C. Johnson, Ames Laboratory, Iowa State University.)

VOLTAMMETRIC CHARACTERIZATION OF CONDUCTING MATERIALS AT ELECTRODE POTENTIAL VALUES BEYOND THE LIMITS SET BY SOLVENT BREAKDOWN

TECHNICAL RESULT: The technique of square-wave modulated hydrodynamic voltametry (QMHV) has been demonstrated to be applicable for study of anodic reactions at conducting materials at potential values well beyond the limits set by breakdown of aqueous solvent systems to produce O_2 . QMHV generates plots of the transport-coupled component of total current vs. applied potential for a rotated disc electrode. While applying QMHV at a Pt electrode, the O_2 evolution reaction was found to catalyze other anodic oxygen-transfer reactions. The catalytically active species are monolayers of PtOH. The catalytic effect of the O_2 evolution is important because, in electrosyntheses with various oxide covered electrodes, the evolution of O_2 is avoided as being detrimental to the yield.

SIGNIFICANCE: QMHV can be used to characterize materials with highly effective rates of anodic oxygen-transfer catalysis which are applicable to electrosynthesis, oxydesulfurization, electroanalysis, and electrochemical degradation of certain organic wastes. QMHV shortens from days or weeks to minutes the time needed to determine the yield for transport-coupled faradaic reaction which occur simultaneously with transformations of the material surface or breakdown of the solvent. QMHV also is applicable to the study of cathodic processes (e.g., hydrogenation catalysis) and the corrosion properties of conducting materials.

The results of this research have been commercialized. The transient but effective activity of monolayers of PtOH and AuOH is used by Dionex Corp., Sunnyvale, CA, for sensitive, electrocatalytic detection in liquid chromatography. The detection technique, known as "Pulsed Amperometric

Detection", uses a three-step potential waveform with the faradaic detection and electrode reactivation processes based on anodic oxygen-transfer reactions. Electroanalytical detection to the sub-ppm level is now easily achieved for all alcohols, polyalcohols, carbohydrates, amines, aminoacids, aminoglycosides, small proteins, and virtually all organic sulfur-containing compounds. Electroanalysis in any one of these categories was never imagined possible 5 years ago. (Research conducted by Dennis C. Johnson, Ames Laboratory, Iowa State University.)

NEW STATIC ULTRA-HIGH PRESSURE RECORD: STUDIES OF HYDROGEN AND DEUTERIUM

TECHNICAL RESULT: Hydrogen and deuterium have been pressurized under static conditions to 1.47 million atmospheres and the infrared and Raman spectra have been measured.

SIGNIFICANCE: An effort at the Carnegie Institution of Washington to improve techniques to subject hydrogen and deuterium to static pressures in excess of one million atmospheres (a megabar) has been supported by the Division of Materials Sciences for a number of years. This goal is due to a very fundamental theoretical prediction that hydrogen will become metallic and then superconducting at high temperatures, greater than 30K, at extremely high pressures. Until recently, it has not been possible to obtain pressures greater than 0.7 megabars. In the latest experiment, the Carnegie scientists have reached 1.47 megabars in both hydrogen and deuterium. This investigation was extremely difficult - requiring the use of very small samples and pressure calibration experiments on 'harder' materials to pressures significantly greater than two megabars. Still, metallic properties of hydrogen and deuterium were not observed but the infrared and Raman spectral properties at 1.47 megabars do suggest that these materials will become metallic: this was not clear from experiments at 0.7 megabars. Theoretical predictions lie in the range from 0.7 to 2.1 megabars. (Research conducted by Drs. P. Bell, H. Mao and their co-workers at the Carnegie Institution of Washington. See their recent publication, Physical Review Letters 55, 99 (1985).)

DEVELOPMENT OF A UNIQUE SOURCE OF LOW-ENERGY POSITRONS AND ITS APPLICATION
TO THE STUDY OF SURFACES

TECHNICAL RESULT: Scientists at Brookhaven and their collaborators have developed a unique high intensity source of variable low momentum positrons, much greater than that achieved by the ordinary radioactive sources. This is accomplished by heavily irradiating a small pellet of ordinary copper in Brookhaven's High Flux Beam Reactor, removing the pellet and placing it in a ultra-high vacuum system by remote control, and evaporating the pellet and condensing it into a very intense thin film source of positrons. This facility has been used to perform the first positron annihilation study of the motion of electrons on the surface of aluminum. The result, clearly reveals that the electrons on the (100) crystalline face of aluminum move more slowly than the electrons in the bulk material and the distribution is different for electron motion in the plane of the surface from motion perpendicular to the surface plane.

SIGNIFICANCE: When a positron, which is an antielectron, has a close encounter with an electron in a material, they annihilate, giving rise to two energetic gamma rays which can be detected to give information on the number of electrons in the materials with a certain momentum if the positron momentum is known. The electron momentum distribution so determined has been used to improve our understanding of the electronic properties and the defect structures in materials. In the past, the beams of positrons have been produced by the radioactivity of certain nuclei with half-lives near an hour. The positron beam intensities practical with this technique has been a severe limitation, especially if a low positron momentum is needed. Low

positron momenta are required to probe electronic and defect properties near surfaces.

The new Brookhaven high intensity source should remove the major experimental limitations of positron annihilation characterization of surfaces. The key to obtaining higher intensity positron beams is to produce thin films -- so low momentum positrons are not absorbed -- of highly radioactive samples which produce low momentum positrons. Normal copper is about 70% Cu⁶³. This type of copper emits a significant portion of its positrons in a low lying narrow band of momenta. The momentum of the positrons can be varied by using magnetic and electrostatic fields.

The results of the experiment on the aluminium surface are inconsistent with the two extant theoretical concepts of positron annihilation on a surface. These experiments provide a challenge to develop a more adequate theory.

Prior to annihilation with an electron, a positron can form an atom -- a positronium, is much like a hydrogen atom chemically but is ultra-light, weighing only about one two-thousandth as much as hydrogen. It also should be a powerful probe of surfaces, especially of those properties where hydrogen adsorption is important such as in various catalytic processes.

These neutral beams will be developed by a consortium of scientists from AT&T Bell Laboratories, Brandeis University, City College of New York and Brookhaven partially supported by the National Science Foundation. Due to the neutrality of these beams it may be possible to demonstrate surface diffraction of positronium. (Research conducted by Dr. K. Lynn of Brookhaven National Laboratory and his co-workers and collaborators. See their recent publication, Physical Review Letters 54, 1702 (1985).)

FIRST HIGH RESOLUTION STUDY OF MAGNETIC STRUCTURES BY SCATTERING OF X-RAYS

TECHNICAL RESULT: Brookhaven scientists, using X-rays from two wigglers, one developed by the Exxon, Lawrence Berkeley Laboratory and Stanford consortium at Stanford Synchrotron Radiation Laboratory, and neutrons from the Brookhaven High Flux Beam Reactor, have completed a comprehensive study of a holmium single crystal grown by Dr. Gambino at IBM Research. This study has illustrated the ability of high resolution X-ray magnetic scattering studies to observe very faint magnetic X-ray diffraction due to magneto-elastic perturbations of the spiral magnetic ordering in holmium which has a length incommensurate with the atomic lattice spacing above the ferromagnetic transition at 20K. This effect gives rise to a temperature dependent modulation of the spiral length and hysteretic effects near the ferromagnetic transition.

SIGNIFICANCE: Magnetic structures and their dynamics are important to improving our scientific understanding of magnetism and the development of technologically significant magnetic materials. The usual probe of these magnetic properties has been neutron scattering where the magnetic scattering is comparable with the atomic structural scattering and of such character that the two can be resolved from one another. Magnetic scattering of X-rays is only about ten one-millionths of the atomic structural X-ray scattering -- too weak to be studied with ordinary X-ray sources. However, with the advent of very intense beams of X-rays from wiggler insertion devices on synchrotron sources such studies are not only possible but can very precisely measure some parameters difficult to determine with neutrons.

The results of this experiment, other than proving that synchrotron radiation can play a significant role in magnetic studies, has led to a modification of the successful spin discommensuration model for the magnetic structure of holmium.

Synchrotron X-rays have other properties which have not yet been exploited. It may be possible, for example, to use very intense circularly polarized X-rays to resolve the two contributions to the magnetic moments in crystals, the orbital and the spin components. (Research conducted by Drs. D. Moncton, D. Gibbs and their co-workers at Brookhaven National Laboratory. See their recent publication, Physical Review Letters 55, 234 (1985).)

METALLIC SUPERLATTICES USING THE INEXPENSIVE TECHNIQUE OF SPUTTERING

TECHNICAL RESULT: A significant advance had been made in the manufacture of metallic superlattices with relatively inexpensive technique of sputtering. Metallic superlattices are sandwich structures with atomically smooth interfaces between the two metallic components and precise uniform thickness of all layers. Metallic superlattices have been grown to more than 50 layers with interface smoothness of 1-2 atomic layers with compound pairs of carbon-tungsten, iron-molybdenum, iron-tungsten, niobium-copper, niobium-aluminum, niobium-tungsten and tantalum-molybdenum.

SIGNIFICANCE: One of the chief goals of the Materials Sciences is to be able to specifically 'design' materials with properties optimum for a particular use. For example, up to ten years ago, the approach has been to grow the most pure and defect-free homogenous semiconductor possible and use carefully controlled doping to control the electronic properties. Since that time, with the increasingly sophisticated deposit with growth techniques, incoherent multilayer films and, more recently, compositionally modulated alloy systems have been prepared. Very recently, metallic superlattices, described above, have been grown by the two gun sputtering technique, a much less expensive technique than the molecular beam epitaxy technique. Low Temperature electronic properties of superconductor-normal metal superlattices can be set to desired values by adjusting the thicknesses of the layers. A significant recent accomplishment is a 51 layer carbon-tungsten superlattice designed to operate as an X-ray mirror for wavelengths of 9.8 nanometers. This type of mirror can reflect the very intense soft X-ray beams originating from modern synchrotron radiation sources. (Research conducted by Professor C. Falco and co-workers at the University of Arizona).

EXPLANATION OF TRANSITION-TEMPERATURE OSCILLATIONS IN THIN SUPERCONDUCTING FILMS

TECHNICAL RESULT:

Controversial experiments and models have recently been presented concerning the oscillations in T_c of thin superconducting films. The behavior was formerly believed to be due to the quantum size effect (QSE) which predicts an oscillation period about half of that which was experimentally observed. The current model and experiments explains these results on the basis of a film which initially becomes continuous at about 30 Å thickness even at 15K, and which consists of a collection of small spheres that barely touch. This suggests that size quantization in a sphere is the important relationship. Utilizing this model together with Schrodinger's equation yields a new quantization condition that gives an oscillation period twice that of a homogeneous film.

Experimental observations of the nucleation and T_c of thin films show that, depending on the substrate, films deposited at 4K could be first made continuous as thin as 10Å or as high as 50Å depending on substrate conditions. This suggests that in this thickness range agglomeration may occur with spheres that are inter-connected. Quantization conditions for a sphere are applicable since an electron spends most of its time localized within a grain and scatters as much as thirty times before it transfers to the adjacent grain. This is an adequate condition for sharp levels in a particle and T_c oscillations.

SIGNIFICANCE:

These results indicate that substrate conditions are vitally important in the preparation of very thin superconducting strips with optimum physical

parameters. Further, these results reveal the potential importance of corollary electron microscopy studies to confirm predicted behavior and modeling. (Research conducted by M. Strongin - Brookhaven National Laboratory and A. Paskin - Queens University, New York.)

NEW SENSITIVITY LEVEL ACHIEVED WITH INFRARED SPECTROSCOPYTECHNICAL RESULT:

A novel infrared emission technique has been developed to measure the vibrational spectra of molecules chemisorbed on clean, single crystal metal surfaces. The system tested was that of a CO molecule on a Ni(100) surface in an apparatus consisting of a liquid helium cooled infrared grating spectrometer coupled to an ultrahigh vacuum system for preparation and characterization analysis. The infrared component is capable of measuring over the frequency from 330 to 3000 cm^{-1} with a resolution of 1 to 15 cm^{-1} .

SIGNIFICANCE:

When a molecule approaches the surface of a metal and forms a chemical bond it must lose its kinetic energy and bond energy to the surface very quickly (10^{-12} sec.). By this infrared technique, the first measurement of the linewidth of a molecule-substrate vibrational mode was made. At saturation coverage, the observed linewidth of the carbon-nickel mode of CO on Ni(100) is 15 cm^{-1} and indicates that a substantial fraction of the energy lost goes into the creation of two surface phonons. The linewidth measurement is in excellent agreement with the value predicted for a two-phonon relaxation mechanism.

Measurements of the vibrational spectra of chemisorbed molecules provide data for the fundamental understanding of catalytic reactions. The experiment described here is a major advance in this area. (Research conducted by S. Chiang, D. L. Richards, and R. G. Tobin - Lawrence Berkeley Laboratory.)

HIGH RESOLUTION NEUTRON TIME-OF-FLIGHT TECHNIQUE USED TO DETERMINE COMPLEX STRUCTURES DERIVED FROM POWDER DIFFRACTIONS

TECHNICAL RESULT:

Through the recent development of high-resolution-time-of flight pulsed neutron techniques, new insights have been gained in understanding complex polycrystalline materials. The advance has been aided by the use of the Rietveld profile refinement method coupled with detailed computer programs. These important scientific efforts have had an impact on three types of materials.

SIGNIFICANCE:

In the first, type the relationship between crystal structure and ionic conducting properties in battery electrode and electrolyte materials was determined. As an example, Li-stabilized $\text{Na}^+ \beta$ "-alumina was examined for Na positions and a pathway for Na^+ ion conduction was found through the resolution of two distinct Na^+ positions that had not been observed before.

The example of superconducting ternary compounds was performed on SnMo_6S_8 where minor impurity of oxygen causes large depressions in the superconducting transition temperatures. The powder diffraction studies revealed an oxygen defect replacing a sulfur atom on the principal axis of the structure. This results in the movement of a Sn atom away from its normal position, to form a Sn-O bond, and the possible filling of the d-band levels in Mo to cause a decrease in T_c as much as 4K.

In the area of plastic deformation of alloys, powder diffraction studies of the important reactor fuel ladding material Zircaloy-2 revealed unusual effects of stress. Tensile and compression strains (produced by application and release of initial stresses of approximately 400 MPa) produce shifts in lattice planes which are reversed normal to the (0002) plane. From this

data it was determined that stresses arising from interactions between grains during the deformation process was the cause. (Research performed by J. D. Jorgensen, J. Faber, Jr., and F. J. Rotella, Argonne National Laboratory.)

EXISTENCE OF DIMENSIONAL CROSSOVER IN METALLIC SUPERCONDUCTING/NORMAL METAL SUPERLATTICES

TECHNICAL RESULTS:

Experiments have been performed utilizing the proximity effect in metallic superlattices (superconducting-normal metal pairs) to observe the existence of dimensional crossover in a number of physical phenomena. Earlier studies were made on NbGe superlattices where dimensional crossover was not observed because the coupling length across an insulator is very small. Proximity coupled superconductors, however, are controlled by long coupling lengths (100-200 Å) and in the case of metallic superlattices, allow many more interaction effects to be examined.

In the example of Nb-Cu metallic superlattices, a crossover was seen from 2D-strongly coupled to 2D-weakly coupled to 3D behavior. Where the superlattice contains equiayers, the vortex lattice, which is proportional to the coherence length, ξ , matches the superlattice periodicity, λ . The magnetic vortices are preferentially located in the normal metal, and this greatly enhances the critical field. The crossover for 2D-3D behavior occurs at $\xi=\lambda$ and the temperature dependence of the critical field varies as a function of 2D or 3D configurations. Most importantly, it has been shown that the parameter that controls both the temperature and angular dependences is the ratio of the perpendicular coherence length to the normal separator (ξ/D_{Cu}).

SIGNIFICANCE:

This is the first observation of a transition from two dimensional to three dimensional behavior in the temperature and angular dependence of the superconductivity of metallic superlattices. The sharp enhancement of the

critical field is being explored for possible application in high critical field magnet technology. (Research conducted by Ivan K. Schuller - Argonne National Laboratory.)

THEORY OF NOVEL SEMICONDUCTOR COMPOUNDS

TECHNICAL RESULTS:

Theoretical predictions of novel ternary crystalline semiconductors and of new ordered phases of alloys of binary semiconductors have been made with electronic structure methods to predict structural parameters, optical characteristics and thermodynamic stability of two novel classes comprising over twenty semiconductors.

The theoretical methodology first utilized mixed-basis band calculations on chalcopyrites, and pnictides and established the first microscopic description of ternary semiconductors. It was further found that these ternary semiconductors have an anion distortion, a bond alternation and smaller band groups. The discovery of the inherent instability of bulk semiconductor alloys led to predictions of bond alternation in 64 semiconductor alloys. By conceiving of spatial arrangements of atoms, that would allow bond alternation without exerting strain total energy, calculations could be made predicting that specific ternary alloys would be stable. Application of similar theoretical models led to the prediction of 22 new ternary semiconducting compounds, such as tellurides and antimonides, with attractive physical properties for potential technological application.

SIGNIFICANCE:

By new theoretical techniques, the prediction of new stable ternary semiconductors has been accomplished. The success of the technique offers insights into the creation of new complex semiconductor materials with vastly improved properties. (Research conducted by A. Zunger - Solar Energy Research Institute.)

FIRST RESULTS OF BOND STRENGTHS AND VIBRATIONAL STATE
DETERMINATIONS IN AMORPHOUS METALS USING RAMAN SCATTERING

TECHNICAL RESULT:

An optical method has been developed that, for the first time, allows the study of the collective motions of atoms in amorphous metal alloys. Prior to this work these vibrational motions could be studied by such optical techniques only in noncrystalline insulating glasses and amorphous semiconducting materials. This limitation is a consequence of the high reflectance of metals as well as the small depth to which light penetrates. The present optical method utilizes thin film multiple layer structures to enhance the local electric field of the laser incident on the amorphous metal. Known as interference enhanced Raman scattering (IERS), the technique has provided information on the vibrational states and bond strengths of the amorphous, transition metal-nonmetal alloys of either iron or nickel with boron.

SIGNIFICANCE:

The ability to observe the vibrational motion of atoms using Raman scattering from amorphous metals implies that this class of both scientifically and technologically important materials may now be studied in greater detail than ever before. Information about the vibrational motion of atoms in these alloys will provide a measure of the strength of the interatomic forces between metal atoms and between metal and nonmetal constituents. Since the method employs thin films it will allow a broader range of composition to be studied than previously possible, encompassing the full

alloy range from amorphous metals to amorphous semiconductors. The investigation of structural rearrangements of atoms in metastable amorphous metals will also be feasible utilizing this method. (Research conducted by J. S. Lannin, Pennsylvania State University.)