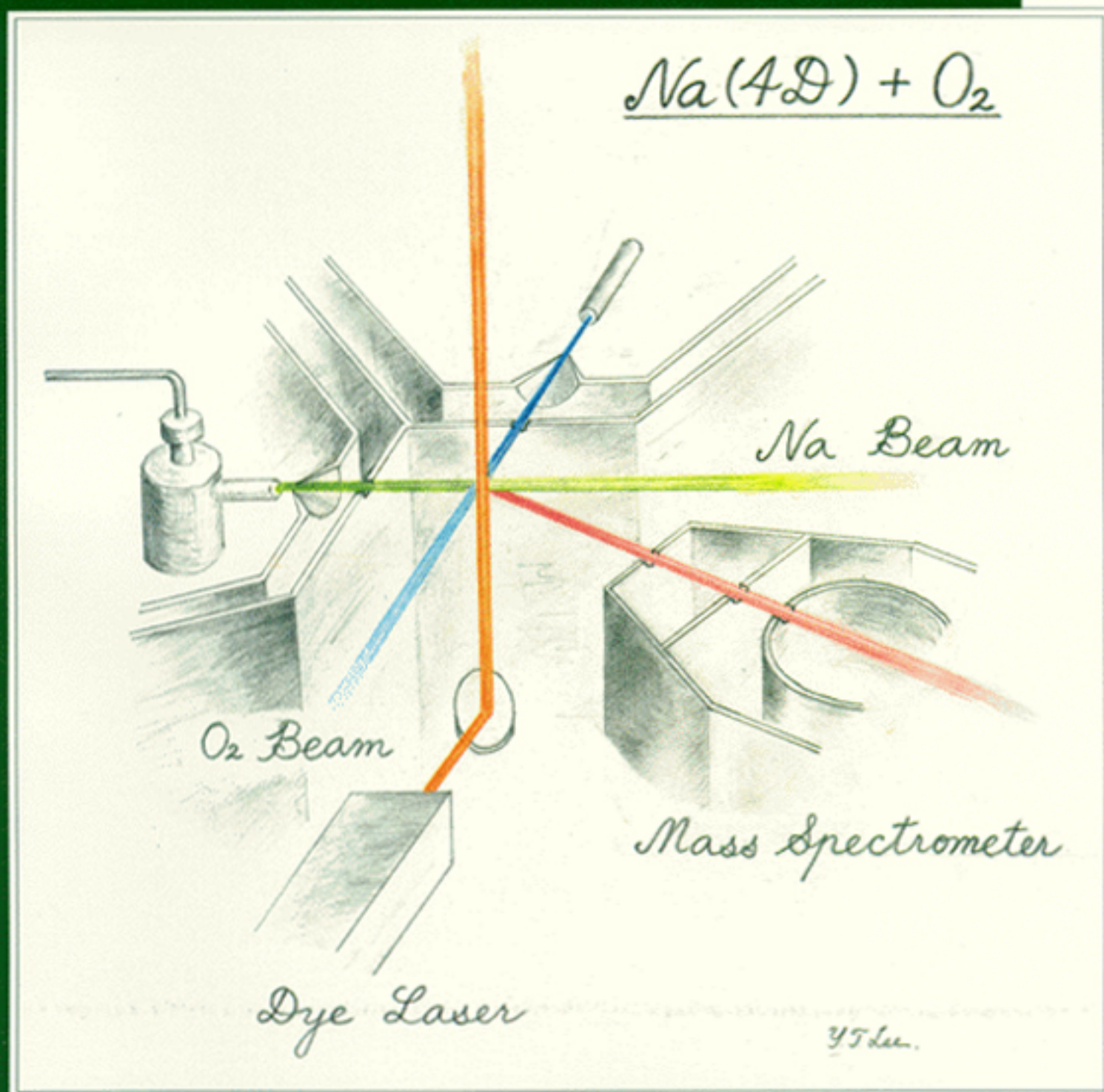


Basic Energy Sciences: Summary of Accomplishments



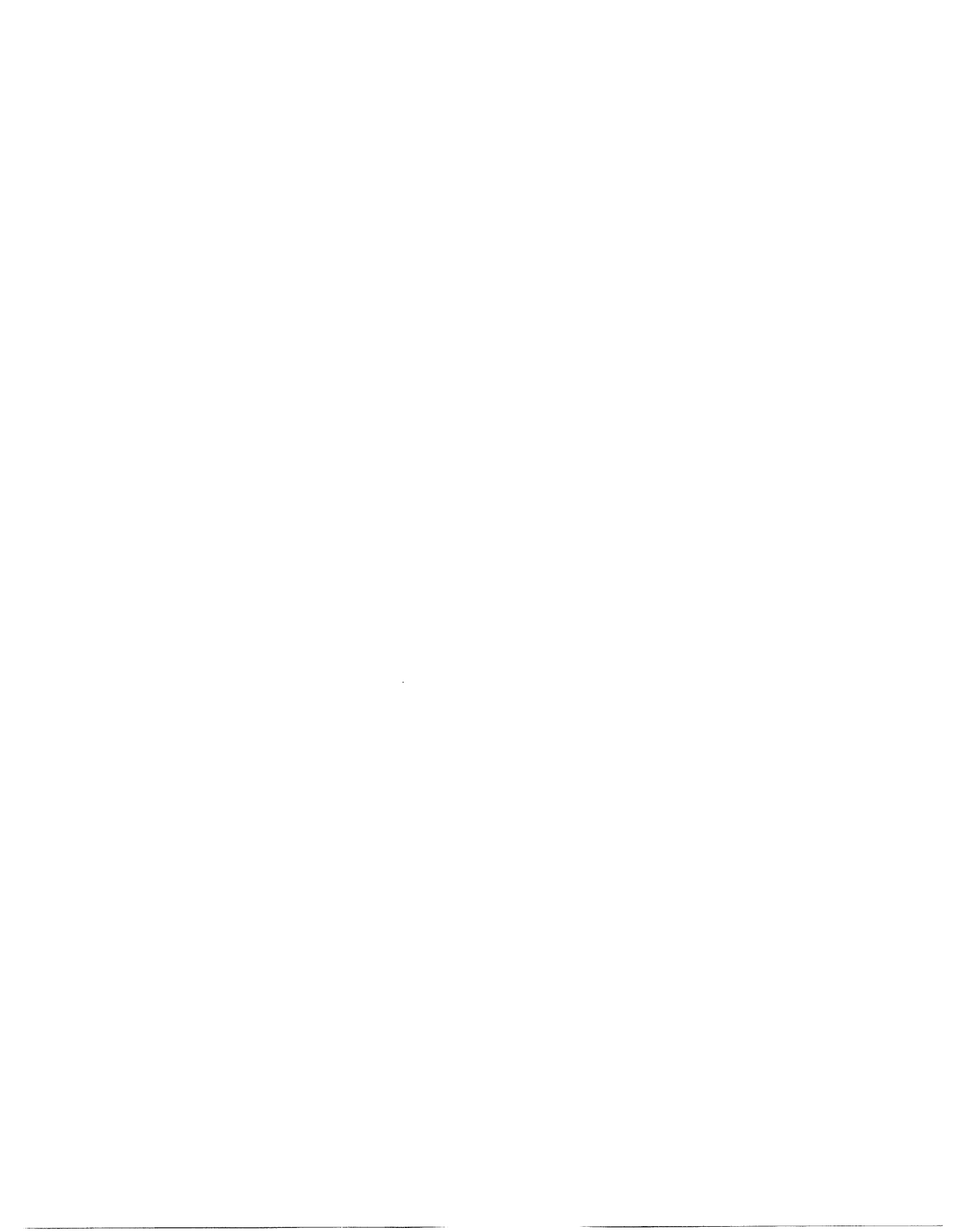
U.S. Department of Energy
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FOREWORD

For more than four decades, the Department of Energy, including its predecessor agencies, has supported a program of basic research in nuclear- and energy-related sciences, known as Basic Energy Sciences.

The purpose of the program is to explore fundamental phenomena, create scientific knowledge, and provide unique "user" facilities necessary for conducting basic research. Its technical interests span the range of scientific disciplines: physical and biological sciences, geological sciences, engineering, mathematics, and computer sciences. Its products and facilities are essential to technology development in many of the more applied areas of the Department's energy, science, and national defense missions.

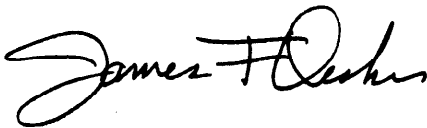
The accomplishments of Basic Energy Sciences research are numerous and significant. Not only have they contributed to Departmental missions, but have aided significantly the development of technologies which now serve modern society daily in business, industry, science, and medicine.

In a series of stories, this report highlights 22 accomplishments, selected because of their particularly noteworthy contributions to modern society. A full accounting of all the accomplishments would be voluminous. Detailed documentation of the research results can be found in many thousands of articles published in peer-reviewed technical literature.

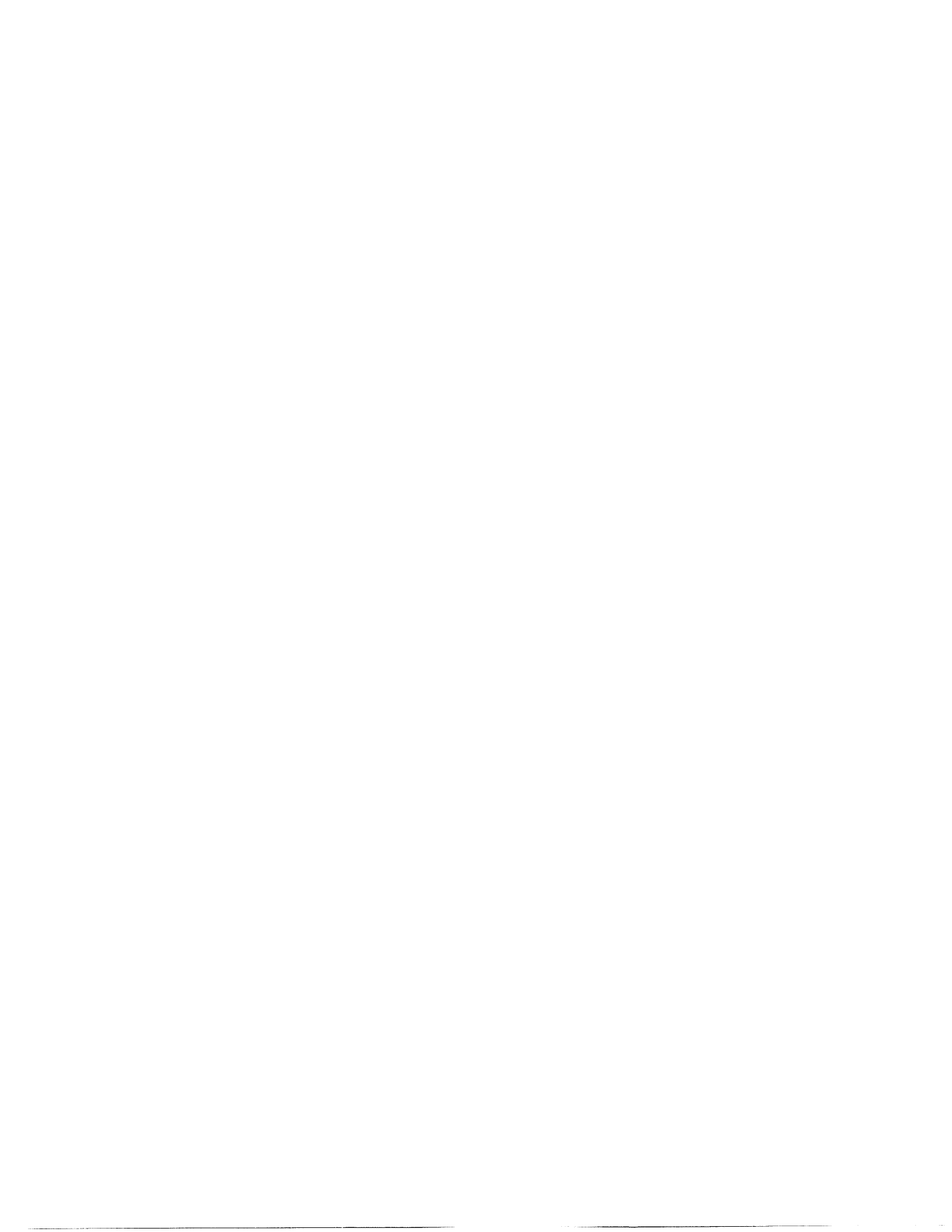
The stories are easy to read and their telling is important. In each, the link is made between the contribution of the research and its larger benefit to society.

Most of the technologies which headline these stories are fully operational. Credit for their development must be widely shared by numerous individuals and institutions. Yet, all grew out of or were aided along the way by Basic Energy Sciences research.

With this report, I invite the public to see, in part, what became of its investment. The accomplishments evidence a creative and productive record. I am confident that, with continued support from the public, Basic Energy Sciences research will contribute in the future as productively, if not more so, as it has in the past.



James F. Decker
Acting Director
Office of Energy Research



INTRODUCTION

Origins of Basic Energy Sciences

By the close of World War II, it was dramatically evident that fundamental knowledge of atomic and nuclear physics had tipped the balance of world power. The Manhattan Project, which gave rise to the atom bombs of Hiroshima and Nagasaki, vividly demonstrated the importance of basic research and its linkages to some of the most urgent national priorities.

After the War, there was a need to continue the research and development activities of the Manhattan Project and to take the opportunity to turn some of them towards non-military purposes. These were formally organized under the Atomic Energy Commission, chartered by the Atomic Energy Act of 1946.

The Commission's charter directed it, in part, to ensure continuity of ongoing activities and to carry out a diversified program of basic research. Specifically, the charter directed the Commission "to assist in the acquisition of an ever expanding fund of theoretical and practical knowledge" relating to the Commission's mission, including the peaceful use of the atom.

Basic research programs in atomic, nuclear, and radiation physics, and in related disciplines of chemistry and applied mathematics, were foremost among those brought forward from the Manhattan Project. The work was carried out in much the same way as it is today, by universities and National Laboratories, in conjunction with selected commercial and industrial collaborators.

These early basic research programs formed the origins of a body of work guided by the Commission's Division of Research. Later, the name of this Division gained some specificity as the Division of Physical Research, in part to distinguish it from an expanding program of biological and medical research in health, radiation effects, and medical uses of radiation.

In 1971, with early concerns about rising petroleum imports, the charter of the Commission was expanded to include other forms of energy and related technologies. During the period of expansion, additional focus was given to "more efficient methods for meeting the Nation's energy needs."

With a broadening emphasis on other forms of energy, many of the Division's basic research activities were collected under a new program name, Basic Energy Sciences. Although the name has stayed the same for nearly two decades, its program content has continued to evolve, punctuated by several additional historical developments.

In 1973, Arab oil exporting nations effected an embargo of shipments of petroleum to the United States and its allies, precipitating an "energy crisis." The resulting perturbations disrupted free world economies for much of the remainder of the decade.

On December 31, 1974, as part of a larger series of energy related national policy initiatives, the Atomic Energy Commission was abolished. Its functions, including Basic Energy Sciences research, were reorganized under the newly created Energy Research and Development Administration.

The Energy Research and Development Administration was chartered with an expanded research mission. In addition to research on nuclear energy, basic research responsibilities were broadened to include solar, fossil, conservation, and geothermal research.

Finally, 2 years later, the year 1977 saw the establishment of the U.S. Department of Energy. The formation of the Department gathered under one authority most of the energy-related activities which had evolved during the 1970's among a number of Federal agencies.

Included in the reorganization were not only the technical missions of the Energy Research and Development Administration and the Bureau of Mines, but also the energy policy and planning activities of the Federal Energy Administration and the regulatory responsibilities of the Federal Power Commission. The joining of policy, planning, and regulation with research and development again served to broaden the agency's basic research mission. Today, the original focus of 1946 on nuclear and related science is a relatively small fraction of a large and diversified portfolio of basic research activities. Materials sciences, geosciences, engineering, and energy biosciences, among others, have joined the portfolio. Collectively, these activities aim to maintain scientific and technical leadership across a broad spectrum of important research areas.

The origins of Basic Energy Sciences research are rooted in the history of the Nation's fervent effort to defend itself against its enemies in World War II. In this sense, the program pre-dates the establishment of the Atomic Energy Commission in 1946 and has endured continuously since then.

Current Program

In its current formulation, Basic Energy Sciences supports about 1,400 research projects in the scientific disciplines of physical and biological sciences, geological sciences, engineering, mathematics, and computer sciences. These projects are carried out at about 200 separate institutions and directly support more than 4,000 investigators. All projects are selected on the basis of scientific excellence, their relevance to meeting long-term research goals, and their contributions toward Departmental missions.

Importantly, Basic Energy Sciences supports a number of major scientific "user" facilities. These are highly specialized research facilities which individual researchers or private firms cannot afford to build and operate at their own expense. They are often called "premier" facilities, because they are either the first of their kind and capabilities, or they are among the very best and most sophisticated in the world.

Descriptions of how these facilities are used can be found among the *stories* in this document. Some of the more prominent user facilities include: the National Synchrotron Light Source and the High Flux Beam Reactor at Brookhaven National

Laboratory on Long Island, New York; the Intense Pulsed Neutron Source and the High Voltage Electron Microscope and Accelerator Facility at Argonne National Laboratory, near Chicago, Illinois; the National Center for Electron Microscopy, including the Atomic Resolution Microscope, at Lawrence Berkeley Laboratory, Berkeley, California; the Combustion Research Facility at Sandia National Laboratories, Livermore, California; the High Flux Isotope Reactor and Calutrons at Oak Ridge National Laboratory, Oak Ridge, Tennessee; the Spallation Neutron Source at Los Alamos National Laboratory, Los Alamos, New Mexico; and the Stanford Synchrotron Radiation Laboratory at Stanford University, Stanford, California.

Approximately 70 percent of the Basic Energy Sciences annual budget supports research and the operation of the user facilities at the Department's National Laboratories, including two university-based laboratories, Lawrence Berkeley Laboratory and Ames Laboratory. Another 25 percent supports research conducted at other universities throughout the country. The remainder is conducted elsewhere, including non-profit institutions and industry.

Program Accomplishments

The accomplishments of the Basic Energy Sciences program highlighted in this document were selected from more than 200 individual nominations for inclusion. The stories are felt to be representative of the program's achievements.

Each accomplishment is a success and their collective presentation here serves several purposes. One is to foster an appreciation for the work itself, for the difficulties encountered, and for the ingenious means by which problems were overcome.

A second is to convey an understanding of the process of basic research and of the environment in which it thrives. Therein lies the root of our continued leadership as a Nation in science and technology.

Finally, it serves to increase awareness of the benefits of basic research, especially as the seemingly arcane discoveries of science become transformed into practical applications.

Over the years the United States has developed a tradition of leadership in science and technology which has made it a model for nations throughout the world. All of our national goals—better health and quality of life, economic growth, environmental protection, energy, security—

involve technologies which depend on basic research.

The Department of Energy's Basic Energy Sciences program has contributed significantly to both this tradition of leadership and to the furthering of these goals, as the following stories show.

Materials Sciences

Materials Sciences research aims at increasing understanding of materials properties and related phenomena. This understanding contributes to development of new or substitute materials, to tailoring materials to meet defined needs, and to predicting materials problems and service life.

LASER ANNEALING

There was an intense flash of laser light. It lasted less than fifty one-billionths of a second. Basic Energy Sciences researchers had melted the surface of a silicon crystal. They noted its almost instantaneous cooling and resolidification. Upon closer inspection they observed near-perfect crystal regrowth.

Their subsequent investigation of the phenomenon and, more broadly, of the laser as a means to manipulate the atomic structure of silicon crystals, opened a new frontier of science in the manufacture of semiconductors—the basic components of computers.

Knowledge stemming from this research revolutionized semiconductor manufacturing. It gave rise to a widely adopted annealing process, known as rapid thermal annealing. It laid the scientific foundation for the development of photochemical processing. It also contributed to the emergence of the so-called “silicon on insulator” technology. The latter technologies are both leading contenders for making the next generation of computer chips.

The basic technology, called laser annealing, exploited the laser’s unique capability to deliver an intense concentration of energy in the form of light with blinding speed and surgical precision. Initially explored as a solution to a problem involving the repair of damaged semiconductor surfaces, the technology eventually proved to be much more than simply an annealing process.

The researchers found that the laser, when “tuned” and timed properly, could deposit a precisely measured amount of energy into the first 300 or so atomic layers of a material’s surface. This rapid energy deposition, in combination with natural processes of cooling (heat conduction and radiation), provided a means by which the crystalline lattice structure of a material’s surface and near-surface layers could be modified and adapted to serve specific design objectives.

In the presence of a thin film coating or envelope of reactive gases, for example, the melting process can be made to absorb “impurities” and induce certain electrical properties. Likewise, foreign atoms can be “implanted” through bombardments into a material’s surface layers, and laser annealing can “activate” desired properties by repairing the bombardment damage.

Further, selected atoms can be “packed” into key positions of a material’s surface structure in proportions that far exceed those of equilibrium chemistry, giving rise to new classes of man-made materials. Precision timing also makes laser annealing a powerful research tool, akin to a “stop action” camera, for studying atomic details of crystal growth and rapid solidification.

Pursuing these possibilities, Basic Energy Sciences researchers provided much of the fundamental knowledge and early understanding about laser annealing and its attendant phenomena, culminating in dozens of articles published in major scientific journals, including *Applied Physics Letters*, *Journal of Applied Physics*, *Physical Review Letters*, *Physical Review*, and *Science*. Out of these findings grew numerous and varied applications of importance to commercial manufacturers of electronic devices.

In the 1970’s, for example, one of the principal means for manufacturing semiconductors involved the “doping” of crystalline silicon with so-called “impurity” atoms of phosphorous. This was accomplished by “implanting” positively charged

phosphorous ions (phosphorous atoms with one or more electrons temporarily removed) in the near-surface region of the solid silicon crystal.

In a vacuum chamber, phosphorous ions were accelerated in an electrostatic field to the desired energy (speed) and then made to impinge on the surface of the silicon crystal. The ions would strike the surface, collide with or scatter among the electrons and nuclei of the silicon atoms, and eventually come to rest in the surface layers of the solid in a predictable way with known depth and density distributions.

Unfortunately, a major problem with this approach was that the ion implantation process caused heavy damage, wreaking havoc with the otherwise orderly lattice structure of the silicon crystal. It is estimated that, with typical ion concentrations required by commercial applications, *every* atom within the affected solid was physically displaced at least several times.

As a result, there were many lattice defects, vacancies, and clumps of unconnected atoms, known as interstitial excesses. Most of the implanted dopants were not electrically activated, because they did not occupy key positions known as substitutional sites, in what remained of the crystal's lattice structure. For most applications it was necessary to repair the damage, at least partially, and activate the implanted atoms electrically.

Conventionally, this was done by heating the doped solid in a furnace-type oven at high temperatures for 30 minutes or more. But this thermal annealing process was often accompanied by undesirable and unpredictable consequences such as incomplete repair, random precipitation of dopants in the near-surface regions, excess migration of dopants out of the desired region, degradation of other electrical properties, and warping or decomposition of the underlying substrate materials.

In search of a better means of repair, Basic Energy Sciences researchers pursued a report by Soviet scientists concerning the use of lasers to deposit energy on the surfaces of solids in amounts sufficient to cause temporary melting. Guided by this work and the success of related pilot projects, funded in part by the Department of Energy's Exploratory R&D program, the researchers set out to investigate the phenomenon of laser annealing, particularly as it might be compared to conventional

thermal annealing, and undertook a wide variety of experimental and theoretical studies.

Specifically, these researchers characterized the effects of various forms of lasers and their illuminating radiations, as to appropriate wavelengths, energy densities, beam diameters, and pulse durations. It was found during these studies, for example, that most samples of ion implanted silicon could be fully repaired by a single pulse from a ruby laser of approximately 50 one-billionths of a second.

Energy densities were optimized, so that the amount of energy deposited in the near-surface region was sufficient to ensure annealing, but below the thresholds for vaporization and subsurface damage. Wavelengths (i.e., energies) of the laser's light were matched to the excitation energies of the electrons in the sample's atoms, insuring minimum reflection and transmission and maximum energy absorption of the laser's energy by the surface material.

Experiments were conducted on a range of implanted ion densities (10^{14} to 10^{17} ions per square centimeter) covering the full range of interest for semiconductor device fabrication. The experiments tested ions of boron, phosphorous, arsenic, and antimony—the more important dopants for semiconductor devices in single-crystal silicon.

A full battery of instruments were used to characterize the "before" and "after" properties of the laser annealed samples. All results pointed to complete repair. After annealing, for example, highly magnified pictures of thin sections of samples made by transmission electron microscopy, showed no holes, stacking faults, or dislocations. Electron diffraction patterns showed that crystal and lattice structures had returned to normal. Diagnostic techniques, such as Rutherford ion-backscattering and ion-channeling, showed that the atoms had realigned themselves in orderly rows and columns.

More fundamentally, Basic Energy Sciences researchers characterized the phenomena which took place *during* transition. The melting front traveled from the surface to its end-depth and back again, a round-trip distance of 40 one-millionths of an inch. The sample solidified at an average speed of about 270 centimeters per second. They determined that the bulk of the near-surface material would remain in a molten state on the order of a few

hundred nanoseconds (10^{-9} seconds) or, in total, about one-third of one-millionth of a second!

Solidification of the melted region took place so fast that the silicon atoms and the dopant atoms would settle into their proper lattice positions comfortably, but the solidification time was too short to allow any dopant atoms to agglomerate (by precipitation) or escape (by vaporization). By varying the duration of the laser pulse, other desired effects could be achieved.

Additionally, by using this knowledge the researchers were able to achieve dopant concentrations that exceeded by two orders of magnitude (100 times) those allowed by normal equilibrium chemistry, greatly enhancing electrical performance. Ion implantation, in combination with laser annealing, prevented atom precipitation and migration, leading to large excesses in atom concentrations above the solid solubility limits.

This supersaturated or metastable condition had never before been possible to achieve in standard metallurgical processes. Its achievement opened a whole new realm of materials exploration and industrial possibilities.

Finally, the researchers determined that ultra-rapid surface melting had other useful possibilities. They discovered that when dopant atoms were merely deposited as a thin film on the surface and then laser irradiated, they could be made to diffuse into the temporarily melted surface and then fast-frozen there during solidification. This new process avoided entirely the need for ion implantation in certain applications.

Altogether, the results of this work contributed significantly to the emergence of modern semiconductor manufacturing and near-surface materials processing techniques. For example, while lasers were originally chosen for their ability to deliver intense energy with precise control, it soon became apparent from the theoretical and experimental evidence that certain, more conventional sources of light and heat could be substituted for lasers to obtain annealing results which were acceptable for a number of commercial applications.

Guided by this evidence, industry found that arc lamps and high-intensity halogen lamps could provide annealing nearly comparable to that obtained with conventional furnaces but with greatly increased manufacturing production efficiency.

The commercial process became known as rapid thermal annealing.

Annual sales of rapid thermal annealing equipment grew explosively, from near zero to more than \$10 million in 5 years, and to nearly \$100 million in 10 years. One leading semiconductor manufacturer set the early trend by using rapid thermal annealing to produce 10 million devices per week, with yearly sales valued at \$15 million.

Semiconductor manufacturers entering markets for ultra-high density computer memory chips incorporated rapid thermal annealing in production lines to produce a new standard size, one-megabit memory device (one million "bytes" of memory). In producing such a device, rapid thermal annealing is used for many processing steps, including the annealing of ion implantation damage, promoting glass reflow to achieve flat surfaces, annealing polysilicon to achieve lower electrical resistance, and alloying metals to semiconductors to improve the performance of electrical contacts.

Basic Energy Sciences researchers continued to make contributions to follow-on applications. In the manufacture of very large scale integrated circuits, for example, certain chemicals are introduced as gases rather than liquids, in a process known as photochemical processing. By choosing the appropriate intensity and wavelength of laser light, one can achieve localized doping of the semiconductor, or localized etching of the surface. This process makes possible the direct writing of the many fine line features that one must achieve in very large scale integrated devices, while eliminating many of the costly masking steps required in conventional technologies.

Finally, as semiconductor devices become more sophisticated and densely packed, with as many as one million transistors positioned on a chip half the size of a postage stamp, the slightest interactions between various parts of the circuit become detrimental. To eliminate such "cross talk," manufacturers pursued another new technology stemming from laser annealing, called "silicon on insulator" technology.

Silicon on insulator technology involves a layered, three-dimensional design. Silicon is deposited on an insulating substrate. This is followed by selected laser melting and crystal formation. Because the active region of the device is physically separated by the insulation from underlying areas,

silicon on insulation technology affords the capability of multi-level devices, with each part of the circuit appearing on its own island. This permits high device densities. Also, the dielectric properties of the insulation make the devices faster than devices made in bulk silicon.

In summary, Basic Energy Sciences research on laser annealing opened a new frontier of science in the manufacture of semiconductors. It contributed directly to solving one immediate problem, giving rise to rapid thermal annealing. More broadly, it provided fundamental knowledge of rapid melting and solidification phenomena, leading to other successful applications. Outgrowths of this research now occupy established positions in commercial production. Others point toward further technical advances necessary for maintaining competitive positions in this important and fast growing industry.

SUPERIOR CERAMICS

From time to time in basic research, a new insight so clearly points the way toward potentially superior products that dozens of commercial and industrial firms rush to capitalize on it. Such was the case with Basic Energy Sciences research on the processing of ceramic materials. The insight not only helped to explain why conventionally formed ceramic materials failed to live up to performance expectations, but also outlined specific methods by which such shortcomings might be mitigated or overcome.

The underlying theory, modeling and small-scale experimentation which gave rise to this insight, stemmed from Basic Energy Sciences research at the Ceramics Processing Research Laboratory of the Massachusetts Institute of Technology. The accomplishment revitalized interest in this ancient material and thrust its promise toward the forefront of a host of modern applications.

For five thousand years and more, ceramic materials have been made from a mixture of clay and finely ground minerals, such as silica (forms of silicon dioxide, SiO_2) and feldspar (forms of aluminum silicates). When wet, these ingredients can be shaped or pressed into a mold of almost any desired configuration. After drying and firing under intense heat, the ingredients fuse together in a process

called sintering. The resultant product is extremely hard, forming a dense but slightly porous solid.

Materials scientists long recognized that the physical properties of ceramics offered unique opportunities for materials design. Although generally perceived as brittle, some ceramics can be made to resist fracture. Others have useful electromagnetic properties. Many ceramics remain hard and functional at temperatures well above those that cause alternative materials to melt.

In practice, however, the fulfillment of this larger promise of ceramic materials had proven elusive. There were a number of serious shortcomings in the performance of the final products, stemming from the way they were manufactured.

In conventional methods of manufacture, ceramics are made from finely ground powders. Greatly magnified pictures of the powder particles showed that they were unevenly sized and highly irregular, appearing like broken stones from a crushing process. At the microscopic level, these shapes, in turn, led to irregular-sized pores, which could not be removed entirely during the firing and fusing process.

The resultant mass contained jagged grains and voids. This flawed microstructure gave rise to a number of undesirable properties: low strength or toughness; weak resistance to mechanical, thermal, and electrical shock; a tendency to crack and break under stress; and inconsistent electromagnetic properties.

Previously, ceramics developers had tried to overcome these problems by using different "recipes," that is, by mixing different ingredients together, changing the firing temperatures, or exerting high pressures during firing. All of these prior attempts were relatively ineffective. They failed to produce the ceramic materials required for today's high technology applications. The basic approach was largely trial-and-error. Knowledge of the underlying processes occurring at the microscopic level was limited.

Rather than alter the recipe, Basic Energy Sciences researchers took a more fundamental approach. They noted that theoretical models of ceramics often predicted strength and other properties superior to that which was found in reality. They knew that the models "idealized" the ceramic particles as densely packed, single-sized spheres.

They hypothesized that the breakdown between the models and reality occurred for two reasons: one relating to the shape and size of the particles and the other to the process of packing.

The first part of the Basic Energy Sciences research aimed at making unfired ceramic powder that consisted of tiny, uniformly sized spheres, made as perfectly round as possible. Methods for producing such spheres from titanium dioxide (TiO_2) were developed using carefully controlled *chemical* processes instead of milling. Both wet chemistry precipitation and, later, laser-heated gas-phase chemistry provided the tiny monosized powder particles with the desired characteristics. Each particle was so small, in fact, that tens of thousands of them could be lined up within a span of a single inch.

The second part of the research focused on solving the packing problem. The tiny spheres were suspended in a liquid and allowed to settle out slowly as a sediment. But even when the spheres were uniformly sized and perfectly round, they tended to clump together in a process called agglomeration. This clumping resulted in uneven densities and relatively large structural flaws.

The researchers knew that agglomeration was problematic because the tiny particles were so small. Under such conditions, the normally weak interparticle forces become comparatively strong and influenced the nature of particle dispersion in the settling process. These forces, most notably Coulomb and van der Waals forces, arise from variations in the physical distributions of atoms and their electrons on the surfaces of the tiny particles.

Building on methods borrowed from other fields, such as surface and colloidal chemistry, Basic Energy Sciences researchers recognized the importance of acidity in controlling these interparticle forces. By adjusting the acidity (pH level) of the suspension liquid, the researchers were able to prevent agglomeration during the sedimentation step. The powder was then collected as sediment from the stable dispersion.

With these two advances, the packed particles achieved nearly homogeneous density, closely approaching that of theoretical limits. This arrangement of closely packed spheres also resulted in a uniform distribution of voids. This, in turn, promoted uniform shrinkage and densification during the sintering process. Such uniformity had never

before been achieved with conventionally milled powders and less controlled sedimentation processes.

Importantly, two other advantages appeared. The sintering time required to achieve 96 percent of the theoretical density was dramatically reduced, from 120 minutes to 10. Further, the firing temperature was reduced from 1500°C (degrees Celsius) to 1060°C .

Besides providing obvious efficiency gains to the manufacturing process, the lower temperature and shorter sintering time greatly impeded the growth of fused grains in the ceramic microstructure. This is important because the physical properties of ceramics are strongly dependent on both the size and uniformity of the grains. Smaller and more uniform microstructures markedly improve the mechanical characteristics of the bulk material. The new process routinely demonstrated reduced grain growth by factors of 20 to 1, and in some cases, 50 to 1.

Finally, the lower firing temperatures led to one immediate benefit for the electronics industry. It allowed certain ceramics to be used as parts in large integrated circuits. Before, the higher temperatures of the sintering process would have melted the attached electrical solder.

The focus of the Basic Energy Sciences research was soon broadened to include other ceramic powders, such as silicon dioxide (SiO_2) and silicon carbide (SiC). As the research continued to yield new insights, worldwide enthusiasm for commercializing ceramic materials was renewed.

The simplified concepts developed through this research, expressed as paradigms for reliable manufacturing, proved to be as important as the detailed results. They enabled other research groups, especially corporate ones, to better focus their intellectual resources on further developments.

A number of major corporations formed a consortium, which provided industrial funding of more than \$1,000,000 per year to the Ceramics Processing Research Laboratory in Massachusetts. New experimental facilities were developed, and scientists with expertise in surface, colloid, and inorganic chemistry were added to the group.

Today, well over 50 companies incorporate features of these new techniques in their own ceramic processing facilities. The sizes of their in-house programs on the new processing techniques range, in some cases, to more than 100 people. Published papers and reports indicate that foreign firms are also applying these concepts.

Ceramics fabricated by these methods and their extensions are now being used in a variety of applications. These include automobile turbochargers (rotors), microelectronic circuits, high-temperature energy converters, engine parts, computers, televisions, aircraft, and vital defense weapons, among others.

More generally, many varied ceramic compositions with fine grains can now be fabricated. Major improvements in the mechanical and electromagnetic properties of ceramic formulations have been reported as a result of better processing. Previously unrecognized avenues of materials fabrication, such as layering of different ceramic materials, have been opened up, and totally new electronic components and devices are now possible as a result.

The original decision to eschew further tinkering with recipes and to proceed, instead, with more fundamentally oriented research into the chemical processing of ceramics led directly to these results. In this way, Basic Energy Sciences provided the seed money and critical initial sponsorship of a risky venture. This work, in turn, generated the concepts and the experimental verification that allowed others to appreciate the advantages of the new approach and encouraged them to pursue practical applications.

NICKEL ALUMINIDE

The continuing quest for improved efficiency in the use of combustible fuels is often limited by the properties of the materials used to make up the fuel burning engines. In theory, higher operating temperatures make possible higher efficiencies. In practice, the physical limitations of materials call for moderation to ensure engine reliability and longevity.

Recently, Basic Energy Sciences researchers contributed significantly to the emergence of a new metallurgical alloy, called nickel aluminide, which promised to combine the best of both worlds. It is

made up of nickel and aluminum, combined in a ratio of about 3 parts to 1, with trace amounts of boron added. When properly prepared, it exhibits extraordinary properties.

For example, nickel aluminide is much stronger than steel. In contrast to most other materials, it actually increases in strength with higher temperatures, up to about 1300°F. It then maintains this strength to more than 1600°F. It is also lightweight and strongly resists corrosion by oxidation.

Important for fabrication and durability, it is malleable and ductile. This makes the material easy to form into different shapes and forgiving to shock and stress. Yet, with the addition of certain other elements, it can be made to resist strongly permanent deformation and rupture at high temperatures—two common modes of metal failure.

The mechanical properties of nickel aluminide provide significant advantages over many currently available heat resistant materials in a number of important applications. These range from machine tools and boilers to parts for the automotive and aerospace industries. For example, at 1500°F, a temperature well within the operating temperature ranges experienced by most metal parts in today's gas turbines, jet engines, and diesels, nickel aluminide is four times stronger than most high-temperature speciality steels.

Because of its high strength and resistance to oxidation at these temperatures, the alloy is now being examined under exclusive license by Cummins, Inc., a major United States manufacturer of heavy diesel engines. While more expensive than most ordinary steels, nickel aluminide promises to be cost competitive with other speciality materials, such as heat resistant alloys made of nickel, titanium, chromium, and cobalt.

An initial application under investigation is its use in strengthening exhaust valves. This part of the engine, which is subjected to high temperatures, corrosive environments, and repeated pounding, is often the first part to fail. Extending valve life with an improved material would increase the engine's reliability, stretch out maintenance schedules, reduce costs of repairs under warranty, and make the entire engine more competitive in international trade. Ultimately, new designs may capitalize on the added strength, raise combustion temperatures, and improve fuel efficiency.

A more recent area of emphasis is its use in strengthening the rotor blades in so-called "turbo-charger" gas compressors. Propelled by the hot exhaust gases of combustion engines, turbochargers compress intake air and boost significantly overall engine efficiencies. Nickel aluminide not only stands up to the extreme heat of the exhaust gases, but also exhibits a much longer life before failing due to cyclic stresses and fatigue. It also costs less than competing "superalloys" and other high-temperature withstanding materials.

Because the alloy is made partly of aluminum, it is 10 percent lighter than steel. Also, because of its strength, a part made from the alloy can be designed smaller, further reducing its weight. Hence, the alloy also has potential applications in the aerospace industry as a substitute for heavier materials now required for strength, such as fasteners, rivets, and certain structural components.

Finally, another valuable property of the alloy is that once it has formed an initial, protective layer of aluminum oxide, it is nearly impenetrable to further corrosion and oxidation. Its corrosion resistance has been measured at 1,000 times better than competing steels. As a result, it is now being investigated for use in heat processing equipment subjected to fouled environments, such as steam boiler tubes and hot exhaust gas heat recovery equipment in industry.

Technically, nickel aluminide is part of a larger family of materials known as "ordered" intermetallic alloys, so named because of the precise ordering and interweaving of the atomic structures or lattices of the two metals. This particular situation, called a low "free energy" condition, makes it difficult to remove an atom from its position in the lattice, which gives the material its strength and chemical stability.

Intermetallic alloys were well known in the 1950's and 1960's for their extraordinary strength. Unfortunately, the problem with them in the past had always been that they were too brittle for most practical applications. Although single crystals of some of these alloys were known to be ductile, bulk quantities in polycrystalline form fractured, like glass.

The basic problem was with the microscopic interfaces, called grain boundaries, where the crystals which constitute the bulk material join together. It is at these interfaces where the crystals

tended to pull apart or slip against each other under stress, causing the material to break.

This problem could be solved, it was hypothesized, if means were found for increasing the adhesiveness of these surfaces. Perhaps the addition of small amounts of alloying elements, to be used as "impurities" in the larger matrix of nickel and aluminum, could somehow cause a strengthening of metal-to-metal bonding at these surfaces. Little knowledge was available to guide this search, however, and progress in solving the brittleness problem slowed.

In the late 1970's, Basic Energy Sciences researchers were working on a seemingly unrelated problem. In retrospect, this work laid a foundation of basic knowledge and improved laboratory capabilities in the use of a key instrument. Both investments later helped to explain a startling new discovery and set into motion a resurgence of research activity on ordered intermetallic alloys.

These researchers were studying the effects of neutron radiation damage on certain types of stainless steels used in nuclear reactors. They would stress the steel until it would break. Then they would study the chemical and atomic composition of the fractured surfaces.

They found that, while the steel had remained in solid polycrystalline form, certain alloying elements, such as phosphorus, tended to migrate to the intergranular fracture surfaces and concentrate there in amounts much larger than normal bulk proportions would predict. Further, they determined that other alloying elements, such as carbon, oxygen, and chromium, did not exhibit this migrating phenomenon, suggesting atomic selectivity.

Importantly, the researchers increased their capabilities in the use of one special research tool called Auger electron spectroscopy. This instrument bombards the top few layers of atoms on a given surface with low energy electrons. This temporarily disturbs the equilibrium nature of the electron shells of these atoms, ultimately resulting in the emission of an identifying spectrum of electrons, whose abundance and energies can be detected and measured. From this spectrum, the constituent elements of the top-most surface layers of a material, including their relative atomic proportions, can be accurately inferred.

Further, the instrument can "raster" the observed surface with argon ions, blasting off the top few layers of atoms like a machine gun. This then allows subsequent analyses of the underlying layers. Through repeated cycles of this process, comparative analyses of one layer after another can be made. This reveals the depth of impurity segregation on the intergranular surfaces and portrays a good picture of surface chemistry and its effects on bulk material properties.

In 1979, Japanese researchers reported a remarkable discovery. They found that the addition of small amounts of boron to nickel aluminide increased its ductility. Following this lead, researchers at Oak Ridge National Laboratory, using Exploratory R&D funds, determined that this phenomenon only worked under a highly specific condition. This was when the total number of aluminum atoms, compared to the total number of nickel atoms, was just slightly less than that dictated by its natural or stoichiometric ratio. In nickel aluminide (Ni_3Al), the natural atom ratio of nickel to aluminum is 3 to 1, or in other terms, 75 to 25 atom percents.

In 1982, Basic Energy Sciences researchers applied their earlier gained knowledge about grain boundaries, intergranular surfaces, and impurity migration to the problem of understanding what was going on. Once again, a key element of their research involved the capabilities of Auger electron spectroscopy.

In a report published in 1985, Basic Energy Sciences researchers presented their findings and offered an explanation of the ductility phenomenon. Under conditions where the relative abundance of aluminum, compared to nickel, was slightly less than the natural ratio in pure Ni_3Al , say 24 atom percent rather than 25, boron atoms migrated in droves to the grain boundaries. They accumulated there in the top two or three atom layers of the surface. They concentrated themselves in numbers far outweighing, by 60 times or more, their bulk proportion of, say, 0.1 percent.

Under these circumstances, boron acts as an electron donor in the lattice structure. This is believed to add to the electron bonding potentials of nickel atoms between the intergranular surfaces. This makes the surfaces adhesive, lending ductility to the polycrystalline bulk material.

Other impurities, by contrast, such as sulfur or phosphorous, were found to migrate strongly to open cavities and voids, and to a much lesser degree to the grain boundaries. This was fortunate, because these elements act as electron captors, believed to diminish the bonding strength between the intergranular surfaces, encouraging fracture and adding to embrittlement.

Specifically, Basic Energy Sciences researchers showed that the solubility limit of boron in Ni_3Al was about 0.3 weight percent; that ductility of Ni_3Al increased dramatically from near zero to over 50 percent elongation with the addition of boron up to about 0.1 weight percent; that boron migration to the grain boundaries was highly dependent on the existence of slight deficiencies in the relative abundances of aluminum atoms compared to nickel; that grain boundary boron segregation strongly affected grain boundary cohesion and related atomic arrangements, which affected ductility; and that distribution of other impurities remained unaffected by the existence of slight variances in alloy stoichiometry (relative atom abundances).

All of this led to a much clearer understanding of the boron-ductility phenomena which, in turn, led to more broadly-based research on other members of the family of ordered intermetallic alloys. It also provided much needed specificity to guide theoretical work on the role of atomic arrangements and electron structures in metal-to-metal bonding at grain boundaries. Finally, it encouraged engineers to pursue practical applications by lending predictability to various metallurgical procedures.

The discovery of the boron-ductility effect, accompanied by this detailed understanding, was pivotal in the development of a whole new field of research. It precipitated much follow-on and continuing research by both Government and industry on nickel aluminide. As one measure of industry's interest, over a half a million dollars in research money was provided by private companies to the Oak Ridge National Laboratory in 1985 to investigate related production and processing methods. The research earned an IR-100 Award from *Research & Development* magazine (formerly *Industrial Research*), and the alloy is now subject to extensive patent and licensing activity by industrial firms throughout the United States.

SYNCHROTRON LIGHT SOURCES

The human eye is uniquely adapted to see only a very limited form of light. Not surprisingly, this light is of a form that best illuminates the surface of the earth. Of all the light forms produced by the sun, this light, falling within the visible spectrum, is most capable of penetrating a thick atmosphere, reflecting off of, and resolving well, objects we need to see. The light and the eye are ideally matched to serve the special purposes of living organisms.

Likewise, scientists probing the physical attributes of atoms and molecules find most useful special forms of light ideally suited for "viewing" objects of this size and scale. Although technically known as synchrotron radiation, named after the early laboratory machines in which its presence was first observed, it is really just another form of light.

It encompasses a broad range of "colors" or wavelengths of light. In its most useful form, it cannot be seen by the human eye. Its optimum band of operating wavelengths lies just beyond the deep blue and violet end of the visible spectrum.

Aided by Basic Energy Sciences research, a number of premier facilities now produce this light with great brightness and versatility. Just as the microscope ushered in an era of new discovery, so too are the instruments of these facilities ushering in their own. Although still in a period of relative infancy, these facilities have already had major impacts on basic research programs of leading industries, universities, and Government laboratories.

Further, their value extends beyond basic research. More than a dozen major United States corporations are using these facilities for industrial research, ranging from x-ray lithography in the manufacture of computer chips to the development of catalysts in the refining of petrochemicals.

Synchrotron radiation is produced as a natural consequence of accelerating electrically charged particles, such as electrons or, in some advanced light sources, their sister particles, positrons. The simplest machines accomplish this by accelerating the charged particles to a velocity near the speed of light (186,000 miles per second) and simultaneously forcing them with powerful magnets to follow a circular or curved path in what is now known as a storage ring.

The acceleration which produces the radiation stems from the force that "holds" the particle, like a rock swung overhead on the end of a string, in its circular path and keeps it from flying away. The resulting radiation is emitted tangentially to the curved path and so-called "beam lines" of light emerge through ports or windows in the evacuated tube which encloses the ring.

What makes this light so valuable? There are at least four compelling advantages. Most importantly, the lengths of its waves, measured from crest to crest, and their corresponding energies, are about the same as the characteristic structures and features of individual atoms, molecules and the atomic lattices of solids. As a result, the interactions of light with matter in this realm are unusually strong and revealing.

A single atom, for example, may be 2 Angstroms in diameter. One Angstrom is one ten-billionth of a meter, which is about two one-trillionths of an inch. The strength of an electronic bond between two atoms is strongly determined by its length, which may be on the order of 1 Angstrom. A molecule may be a thousand times as large.

In so-called photon (light ray) transmission and scattering experiments, wavelengths of synchrotron radiation are short enough to bracket these dimensions nicely. Typically, they fall within a range of 0.01 to 3,000 Angstroms, yielding excellent resolution for a variety of needs. The wavelengths of visible light, by contrast, are too long. They range in length from 4,000 (blue) to 7,000 (red) Angstroms.

In so-called photon absorption and spectroscopy experiments, the energy levels of synchrotron radiation can be precisely tuned to match that of the desired physical interaction. This allows scientists to select special wavelengths, eliminate others, and use slight variances in wavelengths for a host of investigative purposes.

A second advantage is that synchrotron light is extremely bright. Operated essentially as a light bulb, the radiant output of energy from a synchrotron light source focused on an experimental target can be as much *10,000 billion times brighter* than that of the ordinary 100-watt variety!

This extreme brightness makes experiments go hundreds and thousands of times faster, thus allow-

ing complex experimental regimens to be undertaken within reasonable time and cost. Also, because there are so many light rays (photons) impinging on a surface, it makes certain rare experimental events occur more frequently. This increases the strength of the resulting signal and allows observation of events not possible before, given the so-called “noise” levels and sensitivity limits of available instruments.

Third, the light beam is well behaved. Because it can be narrowly focused into a beam diameter hundreds of times smaller than a pinhole, it can eliminate many experimental distractions from light reflected off of areas not part of the particular point of interest. The light beam is also nearly “coherent,” meaning that most of the waves in the beam are similar in length and propagate as cohorts, all moving in step. This enhances the predictability and usefulness of the light, particularly in experiments involving interactions with matter that occur only at precise wavelengths.

Finally, the light can be turned on and off with blinding speed, in less than one-billionth of a second, giving the experimentalist extraordinary control. Repetition of pulses, if desired, can be as frequent as a million times per second.

The fact that all these properties are found in one light source makes it a remarkably versatile tool. Once dismissed by the inventors of electron storage rings as a nuisance, synchrotron radiation is now widely regarded as a unique and highly valued scientific and technological resource.

The story of its emergence is one of vision and leadership on the part of many dedicated individuals, institutions, and agencies. Key agencies in the early development of synchrotron radiation included the National Science Foundation, the Department of Commerce’s National Institute of Science and Technology (formerly the National Bureau of Standards), and the Department of Energy’s High Energy Physics Program.

In the 1970’s, however, it was Basic Energy Sciences which took the lead. The leadership of this program sponsored the major programmatic initiatives, guided the design of the facilities, and funded the substantial costs of construction and operation of the Nation’s top synchrotron light sources.

This was no small accomplishment. The machines that produce synchrotron radiation are large and technically complex. In many respects, they resemble high energy physics particle accelerators, requiring state-of-the-art vacuum systems, powerful magnets at every step along the way, and sophisticated controls. A completed ring can be hundreds of feet in diameter. The so-called third-generation machines now being built range in cost from \$100 to \$500 million, depending upon their intended functions.

Moreover, decades of tradition within certain scientific communities had held that synchrotron radiation was, at best, marginally useful to a few and, at worst, a regrettable loss of energy detracting from other experimental objectives. In the beginning, access to synchrotron radiation was best obtained when no one else wanted to use the accelerators for other experiments.

Basic Energy Sciences researchers, however, were well positioned to appreciate the importance of synchrotron radiation. The program had long supported materials science research, which requires the probing of atomic relationships in solids—an ideal application for synchrotron radiation.

In the early 1970’s, Basic Energy Sciences helped sponsor a watershed study conducted under the auspices of the National Academy of Sciences. This study critically assessed the Nation’s need for facilities dedicated to synchrotron radiation. The resulting report, published in 1976, outlined a series of uses of synchrotron radiation, all relevant to urgent national priorities.

The Academy’s report recommended both the construction of new and dedicated facilities and the upgrading of existing and shared facilities. It specified the capabilities required and noted that demand for such capabilities was growing and would soon outstrip all available assets.

Basic Energy Sciences researchers took up the challenge, invited the scientific community to refine an earlier design proposed by Brookhaven National Laboratory, and nurtured this design and others for upgrades into a broad set of programmatic initiatives for Presidential and Congressional consideration. In Fiscal Year 1979, a new facility was funded for construction. It was named the National Synchrotron Light Source and is sited at

Brookhaven National Laboratory on Long Island, New York.

When completed in 1984, the National Synchrotron Light Source joined another major center for synchrotron radiation research in the United States, namely, the Stanford Synchrotron Radiation Laboratory at Stanford, California. It was at the Stanford facility where researchers, in collaboration with others from Lawrence Berkeley Laboratory, developed many of the key technical breakthroughs that advanced this technology to its present state of refinement.

Two new facilities are under construction. These are the Advanced Light Source, at Lawrence Berkeley Laboratory, Berkeley, California, and the Advanced Photon Source, at Argonne National Laboratory, Argonne, Illinois. The former is designed to produce light best in that part of the spectrum known as "vacuum ultra violet" and "soft-x-ray." The latter will serve a more energetic part of the spectrum, known as "x-ray" and "hard x-ray."

All four facilities fall under the auspices of Basic Energy Sciences. Through 1987, the two facilities at Brookhaven and Stanford had met the needs of more than 1,350 scientists from 100 universities, 50 private companies, and 15 Government laboratories. More than 90 separate beam lines were operating, some with multiple experimental stations. On average, one-third of the beam lines were used for proprietary purposes by industrial users.

Building on the experiences gained at Basic Energy Sciences facilities, at least one United States computer manufacturer is planning to build its own synchrotron. It will be a limited version, designed not for versatility, but for highly specialized functions in x-ray lithography, a form of fine line etching.

Using x-ray lithography a manufacturer of computer chips can make fine etchings less than a millionth of an inch wide in the surfaces of semiconductors. This capability is believed to be essential for further miniaturization and future competition in this industry. Indicative, perhaps, of their importance in this respect, foreign competitors are slated to build eight or more of these machines. Design experts from Basic Energy Sciences facilities are assisting American manufacturers to compete in this important area of future technology.

As a final example of the tangible contributions this technology is making, a large United States producer of petroleum and petrochemical products recently claimed that its use of synchrotron radiation at Brookhaven had a "major impact" on its research and development of proprietary catalysts. This same firm is continuing to apply this special form of light to solving a host of other problems including: the search for hydrocarbon resources; the development of new materials, from alloys to ceramics; the research in polymer science, surfactants, and microemulsions; and the study of lubrication and wear.

The value of synchrotron radiation as a tool for both research and industrial manufacturing is now well established. Many private, public, and institutional organizations hold a stake in the opportunities made possible by its availability.

In the early 1970's when this consensus was not so broadly shared, Basic Energy Sciences research contributed significantly to the complex process that helped build this consensus and bring to reality the Nation's most important synchrotron light sources. These light sources now serve as a wellspring of invention for a broad array of economically important industries, furthering the United States' technical leadership in many vital areas of international competition.

FAR-INFRARED DETECTORS

What curious observer of the clear night sky has not wondered, "Do planets, like earth, circle the distant stars?" The latest evidence from space, obtained with instruments whose development was aided by Basic Energy Sciences research, suggests that planets, like earth, are possibly quite common.

In 1984, the National Aeronautics and Space Administration of the United States, in collaboration with similar agencies of the United Kingdom and The Netherlands, launched a special satellite-borne telescope. Its purpose was to survey the heavens at special, heat-related wavelengths of invisible light.

The telescope, known as the Infrared Astronomical Satellite, was equipped with instruments so sensitive that they could detect the faint heat of unlit objects in the frigid cold of deep space. In this way, the telescope could "see" the unseeable, such as the cooling remnants of a darkened sun or the

presence of cold, dimly lit orbiting matter, ever so slightly warmed by a central star.

The telescope performed spectacularly. In the course of 1 year's operation, it identified 100,000 new stars, discovered 10,000 previously unknown galaxies, probed the dust-obscured heart of our own Milky Way galaxy, and spotted an unidentified comet. As it focused its eye on nearby stars, it also revealed the existence of orbiting matter, suggestive of early solar system formation.

Several of the key instruments that made these discoveries possible are called far-infrared detectors. They are capable of discerning radiant energy emissions from objects whose surfaces register temperatures hundreds of degrees Fahrenheit below zero.

Infrared radiation is a form of invisible light common to our daily lives. Although we cannot see it, we can feel it, as radiant heat given off by warm objects, or as the warm (and invisible) part of sunlight that falls on our skin. As a general form of light, it is called "infra" red (below red) because its characteristic energies and wavelengths lie just beyond the red or lower energy end of the visible spectrum. "Far" infrared refers to radiation furthest away from red.

Just as visible light comes in many colors, infrared radiation also has many variations. These variations, sometimes characterized by energy, and other times by wavelength, are closely associated with temperature. The hotter the object, the higher the energy of the emitted radiation, and the shorter its wavelength. Very hot objects, in fact, emit a spectrum of radiation with waves of sufficiently high energies and short wavelengths that some of them spill over into the visible spectrum. We see these objects as "red hot."

Although we may think of infrared radiation as "warm," all objects, even those at temperatures of extreme cold, give off detectable "heat." The emitted waves simply have lower energies and longer wavelengths.

For example, objects at room temperature emit radiation with relatively high energies and short wavelengths. Such wavelengths average about 10 microns (1 micron is one-millionth of a meter). The glaciers of Antarctica, whose temperatures may be -100° Fahrenheit (F), emit radiation with lower energies and longer wavelengths, on the

order of 15 microns. Weather satellites, which map the cold (-250° F) upper cloud decks of the stratosphere, use infrared radiation with still lower energies and longer wavelengths on the order of 25 microns.

By the mid-1970's, infrared detectors in these ranges (wavelengths shorter than 30 microns) were well developed. As a happenstance of nature, most waves at the higher energies and shorter wavelengths propagate freely through air and water vapor, allowing many practical uses. Specially designed detectors, for example, locate objects in the dark, point out leaks in building insulation, target the heat signatures of enemy equipment on the battlefield, and sense minute variations in skin temperature caused by the rapid growth of tumor cells.

Waves at lower energies and longer wavelengths, by contrast, are strongly absorbed by air and water vapor. Moreover, few objects in our natural environment exist at three or four hundred degrees Fahrenheit below zero. For these reasons, both research and practical applications at this end of the infrared spectrum lagged.

Even so, it was clear that such temperatures were important to the further advancement and better understanding of space. In anticipation of our Nation's capability to launch heavy payloads into earth's orbit, a telescope was planned which could detect the longer wavelengths, once free from atmospheric hindrances. For the temperature ranges of interest, infrared radiation had wavelengths greater than 30 microns (-285° F). No existing detector had the required capabilities. New detectors had to be developed.

The technological approach chosen for the development of these early far-infrared detectors focused on a physical phenomenon known as photoconductivity. This phenomenon takes place when an incoming ray of light, or more precisely, a photon of infrared radiation, strikes the surface of a semiconducting material laced with so-called impurity atoms. Under special conditions designed into the material, some photons will interact with weakly bound electrons of the impurity atoms, knocking them out of their positions. If a voltage is applied to the material, the freed electrons will drift toward an electrical contact, giving rise to a current. This current can then be read by a sensitive meter.

In the case of the longer wavelength radiation, however, the incoming photons are weak and ineffective when used in conjunction with the more common semiconducting materials. Even weakly bound electrons are held too tightly. Incoming photons may strike the electrons but lack the energy and momentum required to knock them loose.

The development of suitable detectors was a collaborative effort involving the National Aeronautics and Space Administration, university-based research groups, and the telescope focal plane contractor, Rockwell International, Incorporated. Ultimately, the project succeeded in meeting the requirements of the detector specifications but not without first encountering some difficult challenges.

Several technical problems faced the developers. First, they had to identify a material in which the binding energy of the electrons was suitably matched to the energies of the incoming photons. Second, they had to produce the material with the desired composition. Finally, they had to fabricate a reliable device with high electrical quality and low noise interference, so that the relatively faint stream of photons arriving from deep space could be recorded by the telescope with good resolution.

Silicon, properly doped with impurity atoms, is a material commonly used for semiconductor devices and for infrared detectors of higher temperature sources (wavelengths shorter than 30 microns). A related element, germanium, was known to bind the electrons of the impurity atoms more weakly and, thus, was known to be more susceptible to far-infrared photon interactions. Unfortunately, while there was a well-developed industry associated with silicon, no comparable capability existed for germanium. Numerous trial and error attempts produced encouraging results but fell short of the required performance.

As launch deadlines neared, word of these detector development difficulties spread to Basic Energy Sciences researchers at Lawrence Berkeley Laboratory. Here, the Basic Energy Sciences program had long supported a unique facility aimed at exploring fundamental interactions between matter and photons in the far-infrared range. Here also was located another group of researchers supported by the Department of Energy's Office of Health and Environmental Research.

Both groups of researchers had done earlier collaborative work on germanium—an element which also happens to have a number of unique advantages for nuclear radiation detectors used in health and environmental protection fields. Certain crystals grown for other purposes, in fact, were already available for testing.

Within 2 weeks, the Lawrence Berkeley Laboratory collaborators had constructed a prototype detector and successfully demonstrated its capabilities in the Basic Energy Sciences far-infrared radiation laboratory. From this success and their prior experience with radiation detectors, the collaborators could infer: (1) the optimal mix and selection of materials and impurities, (2) procedures for making high quality and well-characterized gallium-doped germanium crystals, (3) the usefulness of sophisticated ion implantation techniques for low-noise electrical contacts, and (4) detailed methods for physically constructing the tiny devices.

This information was immediately shared with the National Aeronautics and Space Administration and its project participants. Shortly thereafter, Rockwell reported success in overcoming previous development barriers. Cornell University, using Lawrence Berkeley Laboratory techniques, produced half of the focal plane's far-infrared detectors.

Launch schedules were met and the Infrared Astronomical Satellite performed as planned. Four spectral bands were used. Two employed silicon detectors. Two others used the germanium detectors whose development had been aided by Basic Energy Sciences research and laboratory capabilities.

From the images captured by these detectors, the telescope clearly recorded and made visible the presence of previously unseen matter orbiting nearby stars. In each case, this matter appeared as a thick, material-laden disk, extending in radius a distance comparable to the orbits of our own outer planets.

This evidence is consistent with and suggestive of prevailing theories about the early formation of our own solar system, planets, asteroids, and moons. Its only apparent difference is one of time. The fact that such matter was found orbiting the first few stars viewed suggested, further, that its prevalence among stars in general was likely to be

high. Given the countless billions of stars known to exist, planets like our own may indeed be quite common.

Building on this accomplishment, the Lawrence Berkeley Laboratory collaborators continued their far-infrared detector work, with an eye toward even more demanding specifications. Supported by funding from many sources, including Basic Energy Sciences, which focused on much of the fundamental work concerning the interactions of radiation with matter work, the collaborators produced improved far-infrared detectors capable of sensing radiation with wavelengths in the spectral region of 100 microns for source temperatures down to -400°F .

Further developments included an invention which extended this capability to 240 microns, or to -440°F ! Absolute zero, by comparison, is just shy of -460°F . This latter feat was accomplished by applying stress to the detector with a small mechanical clamp. Known as the "stressed germanium photoconductor," this device opened up a whole new spectral band for space astronomy.

The spectacular success of the Infrared Astronomical Satellite, combined with the promise of new spectral bands, stimulated the development of other approved or planned infrared space research projects. These included the Cosmic Background Explorer Satellite, the Infrared Space Observatory, and the Space Infrared Telescope Facility.

The designs for such projects all employed detectors sensitive to wavelengths in the far-infrared spectral bands. Refined versions of these detectors all build on fundamental knowledge and science concerning the nature of far-infrared radiation and its interactions with matter—a field to which Basic Energy Sciences researchers made numerous and substantive contributions.

GLASSY METALS

The iron age wasn't very old before weapons makers discovered the value of rapidly cooled metals. Although the scientific principals of how atoms in a metal arrange themselves were unknown to these prehistoric foundrymen, they learned by experience that when a white hot sword blade was doused in cold water, it was a tougher weapon than when it was allowed to cool of its own accord.

During the next thousand years or so, advancements in metallurgy came slowly—so slowly in fact that the most advanced metals of the first half of the 20th century were little different structurally from the sword King Richard the Lionhearted used when he fought his way to the Holy Land.

In 1959, all of this changed. It wasn't much of a change at first because the experimenters at the California Institute of Technology were working with very small amounts of metal, but what they were doing with this metal was very different indeed.

Professor Pol Duwez and his Basic Energy Sciences supported researchers at Caltech had an idea how to make new kinds of metal alloys, especially out of mixtures of metals that normally separated from each other as they cooled from the melted state. Their idea was that they could make a new arrangement of the atoms if they could develop a technique that chilled liquid metal faster than it had ever been chilled before.

The difficulty was in producing sufficiently rapid cooling. Such old techniques as those practiced by the ancient sword makers were not nearly fast enough—cooling rates hundreds of times faster were needed. Duwez' team saw that rapid cooling could be achieved if a way could be found to make liquid metal suddenly and instantaneously come into intimate contact with a cold surface. They recognized the practical limitations that made this a difficult problem. First, they had to rule out trying to make any thick layers of metal. Thick layers could not be cooled fast enough. Their final product would necessarily be thin foils. Second, a fresh cold surface must be provided for each droplet of the molten metal. Otherwise, the molten metal would quickly make the cold surface hot. Third, the liquid metal and the cold surface must be brought together at a high rate of speed so that the liquid would not have time to cool.

With determination and despite initial failure, Professor Duwez' team succeeded. In their successful experiment, they propelled droplets of molten copper and gold alloys at high velocity onto a cold copper substrate, a process sometimes referred to as "splat cooling." This simple but ingenious setup did indeed achieve the cooling rates required, over a million degrees per second, and totally new kinds of materials were produced.

While it wasn't a traditional transparent glass, the new material had the same helter-skelter atomic arrangement as ordinary window glass. The Professor and his research assistants, R.H. Willen and W. Klement, called their discovery Metallic Glass.

At first the metallurgical community wasn't impressed. While the Duwez team had made a profound discovery in materials technology, most metals researchers thought the process had no practical use. For one thing, only very small amounts of the material could be produced. For another, the first materials produced did not have obvious applications. But 10 years later, experts would call the advent of these wonder metals "one of the most exciting events in the annals of materials science and engineering."

This change in perspective was largely attributable to another set of discoveries by Duwez and his collaborators between 1967 and 1970. What they found was that alloys containing the metal iron could also be made into metallic glasses.

That these new materials exhibited novel and unexpected magnetic properties was recognized immediately by industry. It was also soon recognized that such metallic glasses, like traditional glasses, were exceptionally strong. Some were more than twice as strong as commercial high-strength steels. However, unlike traditional glasses, they were not nearly as brittle so that they could be formed into useful shapes.

The great strength and other unusual properties of metallic glasses have to do with their atomic structure. Ordinarily, the atoms in solid metals are neatly arranged in patterns to form small crystals. These crystals and the boundaries between them strongly influence the strength, resistance to corrosion, and other properties of items made of metal. The metallic glass is like frozen liquid. As such, its properties are very different from those of an ordinary metal prepared by slow cooling. When metals are melted, their atoms, like those in ordinary window glass, have no regular arrangement, but as the metal cools and hardens, its atoms become regularly ordered within the crystals.

What Professor Duwez and his team had done was to find a way to cool the liquid metal before its atoms had time to return to their regular positions. In an instant the glass-like, irregular placement of the atoms was "frozen" and a new kind of material had been made.

Other investigators discovered ways to increase the rate of production, and important commercial applications were found. Over 1,000 transformers built with metallic glass cores by General Electric were shipped in late 1985 and early 1986 to over 90 utilities as part of a 2-year field trial. In recent years, American, Japanese, and German companies have developed commercial production methods for metallic glasses with the goal of using this new material as a replacement for the traditional materials used in transformer cores and similar electrical devices associated with power distribution networks. Power losses in metallic glass core transformers are 60 to 70 percent less than in conventional core equipment.

Other examples of the application of metallic glasses include a flexible, metallic glass magnetic security strip which is fastened to merchandise in department stores. Pacific Northwest Laboratory has developed metallic glass coatings for pipes and vessels that resist corrosion by salt solutions and concentrated acids.

The recent discovery at Caltech that metallic glass can also be made if certain metals, such as gold and lanthanum, are deposited in alternating thin layers and heated, has opened the possibility that conventional powder metallurgical methods, such as those used in the manufacture of many commercial aluminum alloys for aircraft, may be used in producing these new materials.

Dr. Duwez' marvelous substance continues to find new applications in a technological world needing strong, energy efficient metals. Currently, 500 tons of metallic glasses are produced in the United States each year with plans afoot to increase this to 500,000 tons in the very near future—a considerable advance in the years since they were first created by Professor Duwez in quantities weighing only a fraction of an ounce.

ION IMPLANTATION

At the dawn of the Bronze Age 5,000 years ago, man discovered that copper mixed with tin could overcome the shortcomings of stone tools. Thus began mankind's relentless search to combine the elements of the earth in new and improved ways to better serve his needs.

This search took an unusual turn in the 1950's with the advent of a potentially powerful technol-

ogy called ion implantation. Named after the method by which it is accomplished, it promised the modern metallurgist an opportunity to construct the operative surfaces of materials, literally, atom by atom.

The technology had been demonstrated in principle as early as World War II. It was already in operation in certain limited applications by the 1950's. Despite these successes, however, its further development lagged.

In the ensuing decades, from the 1950's through the present, Basic Energy Sciences researchers pioneered much of the evolving research on ion implantation. Their early results stimulated research by others and broadened considerably the scope of applications. Their continued research, along with that of others, contributed significantly to the eventual emergence of ion implantation as an established production technology.

Today, implantation is a worldwide enterprise valued at several billions of dollars per year. Thousands of ion implantation machines are at work around-the-clock producing speciality parts vital for business, medicine, science, and defense. Products range in diversity from long-lived surgical bone implants to some of the most sophisticated semiconductors for computers.

Technically, ion implantation is simply a means of inserting atoms of one kind or another into the surfaces of solids. Any species of the Periodic Table of Elements can be selected for implantation with almost absolute purity. Precisely controlled, the technique affords good reproducibility, an important feature for commercial applications.

Ion implantation is accomplished in two steps. First, sources of atoms selected for implantation, or molecules containing such atoms, are placed in a vacuum and given an electrical charge, using a number of standard ionization techniques. The charge-carrying atoms, or ions, are then accelerated in an electrostatic field to the desired energy and impinged onto the surface of the material to be modified.

Depending upon a variety of factors, the ions come to rest in the solid at predictable depths, densities, and distributions. Once embedded, the ionized atoms return to their neutral state.

A principal advantage of ion implantation lies in its ability to construct materials by design. It can position atoms precisely where one might want to have them. It can mix elements in ways otherwise unachievable. It is not subject to constraints imposed by solubility and equilibrium considerations of normal elemental chemistry. Under such constraints, for example, tin must be soluble in molten copper to form bronze, and likewise carbon in iron to form steel.

A graphic example of its unique capabilities involves the element of nitrogen. Nitrogen, as it turns out, is often an excellent element to mix into the structural matrix of certain metal alloys, giving the bulk material added toughness and resistance to corrosion. Yet, nitrogen is a gas and naturally escapes the molten metal environment of most metallurgical processes. In ion implantation, such problems are irrelevant. Atoms of nitrogen can be implanted directly into solids as easily as any other kind of atom.

In the same way, ion implantation can create materials in supersaturated and metastable states. This is done by implanting "excess" numbers of atoms, that is, more than those allowed by solubility constraints, into the atom structure of the implanted solid. The excesses cause the atoms of both to interact in new and often beneficial ways.

Such features are important in materials science, because small quantities of foreign elements, or so-called "impurities," when introduced into solids, can alter or dominate the electrical, chemical, optical, and mechanical properties of the original material. These properties, such as strength, hardness, resistance to corrosion and wear, electrical conductivity, and others, often impose the crucial constraint limiting further advances in technology.

The emergence of ion implantation as a practical technology is scientifically rooted in the early days of atomic energy research and related studies of energetic particles and their interactions with solids. This field of research, then known as radiation damage, was motivated by a need to understand the effects of radiation and their implications for reactor engineering and materials design.

The radiation damage of interest was mainly that caused by neutral particles, or neutrons. The use of ions came into being because they proved to

be more convenient for some experiments. Ions created damage similar to that caused by neutrons, but they had other advantages. They did not cause the samples to become radioactive, were cheaply produced, and easily focused and controlled using electrostatic and magnetic fields.

A pivotal point in the development of ion implantation occurred in the early 1960's. Basic Energy Sciences researchers simulated mathematically the ordered atomic lattice structure of a solid and its interactions with a penetrating particle. As an approach to particle-solids modeling, this was a departure from prevailing practices.

At the time, most experimentalists assumed that solids were satisfactorily represented as homogeneous masses, like pudding. In the pudding models, impinging particles entered the solid and slowed down, all in the same way, through a series of collisions with atoms in the solid in a process called scattering.

By introducing the concept of ordered lattices, the researchers predicted that some particles, if they entered the solid from certain angular directions, would behave much differently. Their penetration depth, called range, might be as much as one or two orders of magnitude (10 to 100 times) greater than that predicted by the pudding models.

This phenomenon was called channeling. It was tested experimentally and proved to be correct. This one success, widely repeated at many laboratories, changed the course of future research. It drew attention to the need for more sophisticated analytical approaches and demonstrated convincingly the usefulness of theoretical simulations.

With renewed interest, Basic Energy Sciences research on ion implantation began to diversify and evolve. With continued model development and experimental evidence, it became possible to predict accurately end points, locations, distributions, and damage effects of implanted ions of varying species, energies, and impinging angles.

Conversely, it also became possible to control the implanting process in such a way so as to achieve specifically desired results. Gradually, as knowledge and capabilities expanded, it became clear that surface structure modification using ion implantation, rather than "damaging" materials, could actually "improve" materials in ways not possible using other means.

Throughout the 1960's, these developments were followed closely by private industrial laboratories involved in manufacturing semiconductors, the basic components of computers. The introduction of impurity atoms, such as phosphorous, into a crystalline substrate material, such as silicon, is an essential step in this process. Ion implantation was one of several competing methods for accomplishing this, and Basic Energy Sciences research provided much of the basis for evaluating its capabilities.

In one notable discovery, Basic Energy Sciences researchers, in collaboration with the University of Alabama at Birmingham, found that implantation of nitrogen atoms in the surface material of surgical bone implants made of titanium, aluminum, and vanadium, increased longevity 400-fold. Prior to this, implants were not generally advisable for patients with 10 years or more to live, because the implants would succumb to the corrosive effects of body fluids, breakdown, and would cause internal poisoning.

This discovery was actively pursued by private laboratories, whose follow-on research ultimately brought the application to fruition. Tens of thousands of nitrogen implanted hip prostheses are now in use in human patients, and this number is growing rapidly. The potential market is significant. Hip and knee joint replacements are estimated to occur at the rate of 200,000 per year.

In the 1980's, applications of ion implantation grew explosively. Their diversity is worth noting, even though their links to Basic Energy Sciences research are more removed. The United States Navy, for example, used ion implantation to develop hardened metal bearings for high performance jet aircraft engines. Implantation in common steel of atoms of chromium, molybdenum, and boron, or alternatively, titanium and carbon, was found to more than double bearing longevity, as well as make their manufacture more uniform.

Other surface hardening applications were pursued to improve the performance of metal working dies, punches, and cutting tools. One interesting example is the tool used to stamp out the precision cuttings in the top of a soft drink can to make the pull-tab work.

Spinnerets, which are nozzles used to extrude glass or organic polymer fibers, are made of cobalt superalloys or chromium carbide. These have been

treated by ion implantation with silicon, titanium, boron, and other elements, to reduce deformation under pressure and retard oxidation—two common modes of failure. Even organic polymers have been modified by ion implantation to give them certain electrical properties, making possible the advent of plastic electrical wires.

The list of applications of ion implantation is long. Even so, its dominant uses remain firmly established in the semiconductor industry. With ongoing research by Basic Energy Sciences, the technology continues to evolve to increasing levels of sophistication.

Today, industrial laboratories worldwide conduct research and development on ion implantation. These and many other individuals and organizations must be credited with state-of-the-art contributions to its continued advancement.

The story of this technology's emergence, from radiation damage to metallurgical tool, is one that spans more than three decades. Also, it is illustrative of some of the key elements of the process of technological innovation.

Systematic and sustained investments in basic research pursued interesting atomic phenomena. The results of such work, in turn, opened new avenues of exploration. Eventually, basic research filled out a body of scientific knowledge in sufficient detail to lend confidence to insight and speculation, which motivated applied research by others. Private laboratories sensed opportunities, built on the foundation of prior work, and successfully labored to bring the technology to fruition. The end result was a cascade of benefits for society.

SQUID

Imagine a device so sensitive that it can locate hot areas of the earth's interior by measuring tiny changes in the earth's magnetic field, or measure the faint magnetic signals given off by the human brain while thinking! Superconducting Quantum Interference Devices, or SQUID, can do all of this and more. Seldom does a new invention hold so much promise for physical research as do these tiny devices measuring less than a tenth of an inch on a side and operating at temperatures just a few degrees above absolute zero.

SQUID are based upon a device made from two pieces of superconducting material separated by a very thin insulating layer. These low-temperature "sandwiches" are called Josephson tunnel junctions after Brian Josephson who won a Nobel Prize in 1973 for predicting their properties. The most sensitive type of SQUID consists of two Josephson tunnel junctions incorporated into a conducting loop of wire that senses magnetic field. The key feature that makes the junctions so useful when employed in a SQUID is that their electrical characteristics change significantly when a weak magnetic field is applied. SQUID convert a tiny change in the magnetic field, which is a difficult quantity to measure directly, into a change in voltage which can be easily measured by conventional electronic equipment.

Sensitivity of early models of the two-junction SQUID was limited by intrinsic electrical noise. In the mid-1970's, Basic Energy Sciences researchers at the Lawrence Berkeley Laboratory developed a systematic theory that showed how the intrinsic electrical noise depended upon the size, shape, and other design parameters of the two-junction SQUID. Primarily, what they found was that "smaller is better" and that if it were small enough, a two-junction SQUID was potentially much more sensitive than alternative designs. Fortunately, the development of their theory coincided with the availability of thin-film technology, then under development at IBM. With this new technology, film "wires" less than one-thousandth of an inch wide could be deposited onto a glass or ceramic surface. This process made the miniaturization of SQUID a straightforward production technique and their commercial manufacture soon followed.

The group at Lawrence Berkeley Laboratory as well as other researchers have made steady improvements in the fabrication of ultra-small SQUID. They are now about 10,000 times more sensitive than the ones made prior to 1980. The most sensitive SQUID produced to date was developed at Lawrence Berkeley Laboratory in the early 1980's and is very close to the theoretical limits of sensitivity.

The SQUID's incredible capabilities first proved useful in the laboratory for measuring tiny voltages and current. Their role has diversified in recent years to include, among others, sensing brain waves and the detection of subterranean resources and collapsing stars.

Medical

In the sixteenth century, William Gilbert thought magnetism was “the soul of the world;” we now know that humans have magnetic properties too. The strength of our magnetic signals is roughly a billion times weaker than that of Earth and are not measurable with conventional instrumentation. SQUID, however, are capable of detecting the magnetic signal generated by groups of nerve cells in the brain. This means they have the potential to become a major clinical tool in the diagnosis and treatment of ailments that are characterized by abnormal brain signals such as epilepsy, schizophrenia, Alzheimer’s disease, Parkinson’s disease, and alcoholism.

Current interests in neuromagnetism include the determination of the location within the brain of both the responses to external stimulation and the source of spontaneous signals. Researchers studying brain response are using multiple SQUID to determine where the processing of visual and aural signals takes place. A very important aspect of these instruments is that they are entirely noninvasive and do no damage to tissue. By contrast, the alternative methods are invasive requiring the placement of electrodes on the surface of the brain itself.

Using SQUID, New York University scientists have studied the response in the brain’s auditory cortex to musical tones. In the early 1980’s, they showed that the location of the brain response changes as the musical frequency is changed.

University of California at Los Angeles scientists have used multiple channel SQUID to study human subjects with focal epilepsy, a disease in which abnormal brain tissue responsible for seizures is confined to a small region called the epileptic focus. The fact that the epileptic source is localized makes surgical removal possible when the exact position of the focus is known. Using SQUID, the UCLA research team detected the magnetic signals generated when the seizures occurred and were able to pinpoint the epileptic focus to within a few millimeters.

SQUID have been used to identify the brain’s response to pain, eye movement, and drugs. With these kinds of studies, SQUID are aiding in the production of a detailed map of the functions of the human brain. They also provide physicians with

greatly improved means to test the brain itself for malfunction.

Geophysics

John Clarke and his co-workers at Lawrence Berkeley Laboratory employed SQUID for use in the field of magnetotellurics, a scientific word denoting methods of examining the earth’s interior by measuring differences in the electrical resistance of the earth. Small electrical currents and changes in the magnetism of the earth occur in response to the naturally fluctuating magnetic fields propagating to and through the planet’s surface from the magnetosphere. The magnetosphere is the electrically charged region above the earth that varies continually due to the interaction of Earth’s magnetic field and the solar wind.

The process works well for finding geothermal energy sources. It is also effective in exploring for those minerals that affect rock magnetism and electrical conductance. Virtually all magnetotelluric surveys made throughout the world use SQUID and the procedures that were developed at Lawrence Berkeley Laboratory.

Astrophysics

Nearly 100 years ago the German scientist Heinrich Hertz demonstrated the existence of electromagnetic waves. Today astrophysicists are attempting to demonstrate by measurement a different kind of radiation—the gravitational waves that were predicted by Albert Einstein in his general theory of relativity in 1916.

The search has been unsuccessful so far because equipment must detect motions that are ten million times smaller than the size of an atomic nucleus! At present there are a dozen research groups worldwide trying to detect the pulse of gravitational radiation that is believed to be generated when a dying star collapses. The most popular type of detector for this work is a 5-ton aluminum or niobium bar cooled by liquid helium to within a few degrees of absolute zero. When the waves from the distant star (if there are any) pass by the bar, they are expected to cause the bar to vibrate and these oscillations would be detected by a SQUID. If this experiment proves the existence of gravitational waves, astrophysicists will have confirmed yet an-

other aspect of the theories that describe how the universe works.

Recent Developments

One drawback in the use of SQUID is the requirement for superconductivity, which before recent advances in high temperature superconductivity was known to occur with predictability only in the presence of super cold (4.2° Kelvin) liquid helium. With the advent of high transition temperature (T_c) superconductors, however, our thinking on the applications of SQUID has expanded dramatically.

Recently, workers at IBM fabricated SQUID from yttrium- and thallium-based high- T_c materials that operate at much higher temperatures, around the boiling point of liquid nitrogen, or 77° Kelvin. While these types of SQUID are somewhat less sensitive than those fabricated from low- T_c materials operating at 4.2° Kelvin, they are still satisfactory for many useful applications.

The chief virtue of the higher temperature operation is not so much that liquid nitrogen is cheaper than liquid helium, but rather that the amount of cooling it provides is roughly 60 times higher. Consequently, a highly insulated container of liquid nitrogen could be expected to function unattended

for very long periods, perhaps as long as 1 year or more.

This long running time makes it possible to undertake a large number of new measurement activities, which had been previously impractical, such as geophysical surveying operations with SQUID magnetometers in remote areas of the world where it is out of the question to use liquid helium cooled devices. It may now be possible to field magnetometers for long-term studies of geophysical phenomena, such as the change in magnetic field along earthquake-prone fault lines. Such studies could conceivably lead to new methods of earthquake prediction. The availability of liquid-nitrogen cooled devices makes them far more tractable for use in everyday measurements of physical qualities such as voltage and magnetic field as well as for instructional purposes in universities and high schools.

While the benefits to society of research are not primarily reflected by counting product sales, it is important to note that SQUID have also moved from the laboratory to commerce. For example, biomedical research now requires a production schedule of roughly 10 biomedical systems per year each containing many SQUID at a cost of 22 million dollars. The SQUID is an excellent example of how basic research can lead to wide ranging commercial applications in science, medicine, and technology.

Chemical Sciences

Chemical Sciences research cuts across a broad front of basic studies in chemistry and atomic physics. The knowledge gained is essential to understanding key processes which form the basis for future energy technologies.

DYNAMICS OF CHEMICAL REACTIONS

The benefits of modern chemistry so profoundly affect our daily lives that it is difficult to imagine a world without them. Yet, despite all this progress, man's basic understanding of the most fundamental aspects of chemical reactions is just beginning to yield to the scientists' probes.

In 1986, the Nobel Prize in Chemistry was shared by three physical chemists. Two, Dudley R. Herschbach and Yuan T. Lee, were supported in their research by Basic Energy Sciences. The Prize was awarded for discoveries that helped to explain the physical dynamics of chemical reactions.

Specifically, Basic Energy Sciences research revealed how two molecules undergoing a chemical reaction collide, combine and transform themselves, step by step, into very different resultant products. Although the reactions studied were comparatively simple and straightforward, the insights gained revolutionized prevailing thought.

From the point of view of chemical reaction dynamics, the 19th century way of writing down chemical reactions, using arrows and symbols, is misleading. The equations obscure which aspects of chemical reactions are important and which ones are not. If one looks at the reactions in a different light, as did Herschbach and Lee, focusing instead on particular structures of certain atomic electrons and orbitals, the pieces of the puzzle begin to fall into place.

Striking similarities stand out among their experimental data. These form a relatively small num-

ber of "rules" which govern chemical reactions and their dynamics. These, in turn, can be generalized to other molecules and other reactions. With this knowledge, it may be possible ultimately to manipulate, using a variety of control mechanisms, the timing, speed, sequence, extent, and very nature of chemical reactions, attended by virtually unlimited variations and possibilities.

The specifics of the Basic Energy Sciences contribution may be appreciated by visualizing a chemical reaction. Imagine, for a moment, an immensely enlarged, slow motion picture of one atom, potassium (K), and one molecule, methyl iodide (CH_3I), hurtling toward each other through the vacuum of a laboratory chamber on a collision course set by the scientists to result in a glancing blow.

In some cases, the expected chemical reaction takes place with the explosive formation of two by-products, potassium iodide (KI) and an incomplete methyl group (CH_3), flying off in opposite directions. In other cases, the collision results in no chemical reaction, with the original constituents, called reactants, simply bouncing off each other in a physically expected distribution of random directions.

By varying the velocities and angles of the incoming reactants, and by measuring and determining the distributions of the resulting products, Basic Energy Sciences researchers were able to infer the necessary and sufficient conditions under which the reaction would take place. In the case studied, the incoming potassium atom had to strike the opposing methyl iodide molecule on the iodide end, and then bounce backward.

Over the years, the experimental devices used to analyze the reactions became more sophisticated and the kinds of reactants and reactions studied became more complex. Gradually, the data began to reveal patterns and similarities, even though the molecular structures of the varying reactants appeared to be quite different.

This led to what Herschbach called the "harpoon" model of reaction dynamics. One molecule sneaks up on the other, uses a very specific valence electron orbital as its harpoon, spears its target in one selective and vulnerable spot, and hauls it in. Once these mechanisms are known, many of the other potentially obscuring complexities of molecular shapes, bonds, and electron potentials, fall away as being irrelevant.

The experimental technique used in these studies, developed by Herschbach and Lee, is today known as "crossed-molecular beam" research. The facility recently constructed at Lawrence Berkeley Laboratory, under Lee's direction and with continued support from Basic Energy Sciences, is widely acclaimed as the best molecular beam instrumentation facility in the world.

In recent years, this facility enabled Lee to study more complex molecules, such as those having long hydrocarbon chains. Pioneering exploration was begun in two key areas of pressing national interest—hydrocarbon (oil and natural gas) combustion and atmospheric chemistry.

With these advances, understanding chemistry from first principles is now a practical goal. Its applicability extends beyond fuel burning and ozone depletion. Insights gained using crossed-molecular beam research may yield new models of how catalysts operate in specific chemical reactions. Because the velocities of molecular collisions, which determine reaction potentials, are related to temperature, the nature of reaction rates is now a subject of detailed and quantifiable research.

Perhaps more importantly, crossed-molecular beam research permits a better understanding of reaction intermediates, the short-lived arrangements of atoms and molecules that are the first results of a molecular collision, but which soon decay to some other or more stable forms. Manipulating the reaction intermediates offers one of the best hopes for precisely controlling chemical reactions and, thus, determining the nature of the final reaction products.

For Herschbach and Lee, more than two decades of fundamental research culminated in the Nobel Prize. They envisioned and devised a productive experimental approach, built and perfected the necessary hardware and instruments, gathered data with sufficient variety and scope to yield robust conclusions, and presented the scientific com-

munity with a wholly new view of chemistry and the dynamics of reactions.

Crossed-molecular beam research is now firmly established as a fundamental research tool. With continued support from Basic Energy Sciences, it is being used in a growing number of inquiries. With expanding knowledge, focused more on applications, improved understanding of reaction dynamics and, perhaps, the ability to control the reactions themselves, move closer to reality.

Despite all the wondrous advances of modern chemistry, new frontiers remain to be explored. Crossed-molecular beam research lies at the forefront of this endeavor, with great potential for continuing contributions to industry, health, and environment.

ENERGY FROM PHOSPHATE ROCK

Phosphoric acid, used primarily to make agricultural fertilizers, ranks in total economic value among the most important industrial chemicals manufactured in the United States. By a happenstance of nature, much of the phosphate rock which serves as the raw material also contains a trace amount of uranium—the elemental source of energy which fuels the Nation's nuclear power and research reactors.

Basic Energy Sciences research provided the scientific knowledge and the patented methods which subsequently enabled the efficient extraction of uranium as a valuable byproduct of the phosphoric acid manufacturing process. In recent years, large manufacturing plants in Florida and Louisiana, representing about half of the industry's phosphate rock processing capacity, recovered uranium using methods based on this original work.

The incentive to separate and recover uranium was recognized early in the 1950's. Concentrated primarily in Florida, Louisiana, North Carolina, Idaho, Montana, Utah, and Wyoming, the natural reserves of phosphate rock were estimated to contain over 600,000 tons of uranium. However, because the uranium typically appeared in weak concentrations of about only 1 pound for every 4 tons of phosphate rock, these reserves were considered to be too poor for economic extraction of uranium alone.

On the other hand, the idea of simply adding on an extra step or two to an already existing process of manufacturing phosphoric acid was tempting. Prodigious amounts of phosphate rock are mined and processed each year, producing over 10 million tons of phosphoric acid.

In the most commonly practiced "wet" process, the rock is digested by sulfuric acid, during which the uranium is dissolved in the solution. At this point in the process the uranium is, in effect, mined and dissolved "for free." Hence, its recovery as a byproduct is potentially economic. All that was required was an efficient separation process.

The key to an efficient separation process was the development of a special chemical, called an "extractant," which had a strong preference for the uranium atoms as found in the acid solution. To be effective, the extractant's attraction had to be sufficiently strong to cause the uranium to separate from its unwanted neighbors in the acid solution and chemically bond to it. The extractant then had to be easily removed from the solution and persuaded under different conditions to let go of the uranium, so that it could be recycled to pick up another load. Finally, it had to be prepared at an acceptable cost and remain stable for many repeated cycles of gathering and releasing.

At Oak Ridge National Laboratory, the study of uranium chemistry had long been a topic of research. This experience uniquely positioned Basic Energy Sciences researchers there to tackle this problem.

Earlier research had demonstrated, for example, that the strength of chemical bonding between uranium and certain types of extractants is highly sensitive to the number of electrons uranium shares with other elements. It was well known that these electrons can number either six or four, and that uranium can be made to favor one form or the other through interactions with certain chemical agents.

An agent that converts uranium to a form that shares four electrons (the tetravalent form of uranium) is called a reducing agent. An agent that converts uranium to a form that shares six electrons (the hexavalent form) is called an oxidizing agent.

Given this knowledge, the researchers hypothesized that one or more extractants might be found that bonded strongly to one form, and weakly to the other, providing a means to first attract, and then

release the uranium. One such extractant had been developed in the 1950's, but proved to have a number of operating difficulties, including low stability and insufficient affinity for uranium. This resulted in recovered products of poor quality. Even so, the research showed some promise, and the researchers began in 1967 to experiment with similar approaches.

The concept of extracting a valuable mineral from solution by adjusting its valence was novel to the commercial extraction industry at that time. It was a logical step for Basic Energy Sciences researchers, however, with years of experience working with uranium chemistry.

Five years later, in 1972, these researchers announced that they had developed a combination of two stable extractants with improved capabilities for stripping uranium from the phosphoric acid production process. Together, they were known by the acronym, DEPA-TOPO, after the two extractants, *Di 2-Ethylhexyl Phosphoric Acid* and *Tri-n-Octyl Phosphine Oxide*.

The actions of the two extractants were found to be synergistic in that they worked together much more effectively than either did individually. So well did they work as a team that almost 90 percent of the uranium originally in the phosphate rock solution was recovered when the process was used.

As the Basic Energy Sciences researchers had hypothesized, it was the hexavalent form of uranium that DEPA-TOPO preferred. The phosphoric acid solution was first treated with an oxidizing agent, such as hydrogen peroxide or oxygen gas, to convert all the dissolved uranium to the hexavalent form. Then a kerosene solution containing the DEPA-TOPO extractants (kerosene was chosen because it does not mix well with acids) pulled the uranium into the kerosene solution and left behind the uranium-depleted phosphoric acid.

In the second or stripping step, the extractants were persuaded to let go of the uranium by bringing them into contact with a small amount of acid to which a reducing agent had been added. This reducing agent converted the hexavalent form of uranium back to the tetravalent form, which DEPA-TOPO extractants did not favor. This allowed the uranium to be stripped from the kerosene solution containing the extractants and put back into a new separated stream of acid solution.

The stripped uranium was thus concentrated by a factor of 50 to 100. At the same time, the DEPA-TOPO kerosene solution was cycled back to the first step, ready for reuse. The two-step uranium extraction operation was then repeated on the concentrated product stream in a similar but smaller-scale process designed to further purify the uranium and isolate it for sale.

Several United States phosphate companies consulted closely with Oak Ridge National Laboratory while developing specific versions of the process tailored for their plants. Commercial use began in late 1978. By 1983, in addition to having been installed in five commercial plants in the United States, commercial recovery operations, based on this technology, were put in place in Belgium, Canada, and Taiwan.

A patent was awarded in 1973 to the Basic Energy Sciences researchers, F. J. Hurst and D. J. Crouse, who developed the process. They were later honored for their seminal efforts by being selected as finalists for the prestigious Kirkpatrick Chemical Engineering Honor Award in 1979. They also received an "IR-100 Award" in 1980, as winners of the annual competition for the 100 industrial research prizes sponsored by *Research and Development* magazine.

NON-PROLIFERATION

Since the first awesome use of the atomic bomb as a weapon of war on August 6, 1945, the specter of the spread of nuclear weapons has haunted civilization. So it is, then, that more than 135 nations, including the United States and the Soviet Union, joined together and signed the Treaty on the Non-Proliferation of Nuclear Weapons.

This Treaty both encourages the peaceful use of nuclear power and nuclear research activities and deters the further spread of nuclear weapons. Upon ratification, each country which did not already possess nuclear weapons, agreed not to develop or acquire them. In return, all signatories, including the so-called "weapons states," were encouraged to share more freely their nuclear expertise. Importantly, each "non-weapons state" agreed to allow on-site inspection and monitoring of all nuclear-related operations to prove compliance.

The Treaty's mechanisms of enforcement are aimed at safeguarding special "fissionable" nu-

clear materials, primarily plutonium and enriched uranium. Both are used in or generated by nuclear reactors. If such materials were not carefully controlled, they might be diverted to make a bomb or otherwise be used illegally.

Basic Energy Sciences research developed a practical technology that now serves as an important method for keeping track of these special nuclear materials and validating reports of their movements. This technology, known as resin bead technology, is used by the United Nations' International Atomic Energy Agency, headquartered in Vienna, Austria, to maintain an accurate accounting balance on material flows. Any discrepancy in this balance would signal a possible diversion and alert the authorities.

Of particular concern today is the fact that maintaining this material balance is more complicated than simply counting the fuel assemblies that go in or come out of a reactor site. A growing number of nations now recover plutonium and enriched uranium by "reprocessing" the highly radioactive spent fuel from nuclear power plants.

In reprocessing, the spent fuel is cut into little pieces and dissolved in an acid solution. The plutonium and uranium are then chemically extracted from this solution and refined.

Once the spent fuel is cut up and dissolved in acid, the methods for monitoring plutonium and uranium must shift from item counting to chemical analysis. By knowing the volume of each batch and measuring the concentrations of all relevant species (isotopes) of plutonium and uranium in solution, the material balance can be inferred. To detect cheating, concentration measurements are performed independently at laboratories operating under the auspices of the International Atomic Energy Agency. In the past, this procedure required a large sample from each batch of acid solution. The sample, like the spent fuel, was intensely radioactive.

The heavy shielding required for safe transport to the laboratories in Vienna was expensive. With thousands of shipments per year anticipated, the cost of transport alone would amount to millions of dollars. Moreover, compliance with all local and international restrictions on the shipments of highly radioactive materials was becoming increasingly complex.

Motivated by these considerations, Basic Energy Sciences researchers looked for new techniques that might reduce the need for shipping large samples. Based on earlier work, these scientists were familiar with methods for separating and purifying plutonium and uranium. They were also aware of a unique and highly sensitive process used to test for the presence of trace amounts of plutonium and uranium in waste water effluents at separation and purification plants in the United States. Such effluents are routinely tested to ensure public safety.

The technique used a quantity of granular material through which a sample of the effluent water was required to pass. Each grain, called a resin bead, was no larger than a grain of sand, but had the unique ability to adsorb (attract and attach to its surface) selectively a variety of different chemicals from the solution flowing by it.

The resin beads were known to work for the water effluent sampling process. The question was whether or not they could be modified and made to work in the acid solution of reprocessing.

Researchers hypothesized that under the right conditions the resin beads could be made to adsorb selectively a minute but fully representative sample, consisting mainly of the special materials of interest—plutonium and uranium. If so, the amounts adsorbed would not only be infinitesimally small, but would also consist mainly of elements which by their nature exhibit low levels of radioactivity. Other elements, collectively known as “fission products,” exhibit high levels of radioactivity. These would be left behind in solution.

The resin beads could then serve as a proper substitute for the bulk sample. They could be safely shipped for analysis with little or no shielding. In fact, the amount picked up by each tiny bead would be so minute and its radioactivity so slight that the bead could be legally and safely sent through ordinary mails.

Technically, in order for the resin bead to serve as a proper substitute, it had to be both analyzable and contain a full array of information on the relative abundances of all the atomic species of plutonium and uranium found in the original solution. Basic Energy Sciences researchers developed and certified the laboratory methods that would ensure systematic and reproducible results.

At the point of adsorption, such as would be the case at a reprocessing site, the researchers obtained completely satisfactory results by adjusting the acidity of a small part of the reprocessing solution into which a number of resin beads were immersed. These adjustments affected the rate of uptake and the degree of selectivity for the elements of interest.

The adjustments achieved essentially complete separation of plutonium and uranium from the other highly radioactive species in solution. Left behind were not only the fission products, but also the highly radioactive heavier elements. Small amounts of the elements of thorium and neptunium were adsorbed, but these were not highly radioactive, and both elements could be easily distinguished and ignored in later analyses. The entire adsorption process took about 20 minutes.

The researchers verified that the amount adsorbed for each isotope was proportional to its original concentration in the solution. The total quantity of plutonium and uranium adsorbed by each resin bead was less than *three billionth's of a gram!*

At the point of analysis, such as would be the case at the safeguards laboratory, the researchers used a highly sensitive mass spectrometer. In this instrument, the bead was heated on a filament of wire until the adsorbed plutonium and uranium were driven off as electrically charged atoms, or ions. By analyzing and counting the ions, the spectrometer identified and quantified the relative abundances of all isotopes of plutonium and uranium atoms present.

When this technology was first developed, instruments sensitive enough to analyze the tiny samples were found only in a few sophisticated nuclear energy-related laboratories. This tended to limit the technology's application. However, instruments with the requisite sensitivity soon appeared on the commercial market in response to the demand. The manufacturers of these spectrometers also built in special tools and fixtures for handling the tiny resin beads.

Oak Ridge National Laboratory researchers trained staff members of the international program in resin bead technology and installed a high-sensitivity mass spectrometer at the safeguards laboratory in Vienna. Indicative of its success, the resin bead technology is now an important method for

monitoring compliance and is being considered for adoption as the standard method.

Research closely associated with this work resulted in other important applications of resin bead technology. These include: measuring plutonium and uranium concentrations in the environment, quantifying accidental human exposure through urinalysis testing, characterizing radioactive discharges and effluents, and measuring radioactivity in reactor cooling water in the event of an accident.

Resin bead technology also provided a simple method for accurately determining the amount of fuel used up in a reactor. The method is also used at Oak Ridge National Laboratory to determine the proportions of transuranium elements—plutonium, americium, curium, californium, and einsteinium—produced in a special reactor there. These elements increasingly provide important services to the public.

While there are growing numbers of applications for resin bead technology, one of the most important remains its use in monitoring compliance with the Non-Proliferation Treaty. Its use is straightforward, economic, and reliable. As reprocessing activity expands throughout the world, resin bead technology will play an increasingly important role in detecting the unauthorized use of special nuclear materials, thus helping to deter the further spread of nuclear weapons.

POSITRON EMISSION TOMOGRAPHY

Nearly one person in three eventually suffers some disease or disorder of the central nervous system—usually the brain—in his or her lifetime. Unfortunately for the afflicted, the more rapid development of successful treatments is hampered by incomplete knowledge of neurological function, physiology, and biochemistry.

These barriers are beginning to yield, however, with the help of a powerful new diagnostic tool for medical research, called positron emission tomography, or PET. Its development, stemming from three fields of research, namely nuclear chemistry, mathematics, and high energy physics, was aided significantly by support from Basic Energy Sciences.

During most of the 20th century, the brain and its associated network of nerves remained shrouded in a fog of clouded x-rays. Although dissection, exploratory surgery, and enhanced methods of x-ray photography were able to define certain aspects of nervous system *structure*, some of the more insightful physiological details of *function* laid beyond the reach of all available probes.

With the advent of PET, medical researchers can now observe selectively specific biological functions important to understanding the causes and cures of brain disease and other organ disorders. Further, a growing number of major hospitals and medical centers now use PET daily in clinical applications to diagnose illnesses and guide the treatment of patients.

In a related technique, known as CATSCAN (for computerized axial tomographic scan), x-rays are used to produce cross-sectional views of the structural aspects of human anatomy. In PET, by contrast, faint emissions from specially prepared drugs are used to chart the chemical activities of the body's life processes.

With PET, for example, it is possible to focus on biochemical reactions that pinpoint which brain cells trigger a patient's epileptic seizure or locate which muscle cells were damaged in a heart attack. Schizophrenia, depression, Alzheimer's and Parkinson's diseases, heart disease, and tumors of the brain are also being explored by PET. The findings are helping doctors prepare better treatments, in many cases before external symptoms become apparent.

The natural elements involved in human metabolism are carbon (C), nitrogen (N), oxygen (O), and hydrogen (H). The genius of PET is that its technology makes use of relatively rare and short-lived species of these elements, called radioisotopes. These radioisotopes have atomic weights that are different from the atomic weights of the natural elements: the radioisotope of carbon, for example, has an atomic weight of 11 and ordinary carbon has an atomic weight of 12. Using atomic symbols and their unusual atomic weights, these radioisotopes are labeled ^{11}C , ^{13}N , ^{15}O , and, by substituting fluorine for hydrogen, ^{18}F .

These radioisotopes can be chemically combined with other elements to form small molecules which, in turn, can be attached or "tagged" to sugars, proteins, steroids, or other probes. Once

tagged with the radioisotopes, these organic compounds become known as radiopharmaceuticals. Each is designed to seek out a unique area or bodily function. They are typically introduced into the human body intravenously and carried along in the bloodstream to that area or organ requiring observation.

Radioisotopes are inherently unstable and give off unique and detectable signals (energetic particles) as they transform themselves into more stable and non-radioactive forms. For the radioisotopes used in PET, all undergo the same type of transformation. They emit positively charged particles, called positrons. Important to PET, a positron tends to annihilate itself in the presence of a nearby electron. This final destructive event broadcasts two oppositely-traveling gamma rays, which can be observed by PET outside the body.

In this way, the location, concentration, and rate of disappearance of tagged, metabolizing sugars, for example, can be quantitatively observed. Positrons combine with electrons from nearby molecules in surrounding tissue, releasing gamma rays. These are precisely recorded and counted by a large ring of detectors in the PET instrument. The signals are processed by a computer to reveal a high resolution picture of the phenomena.

The short life of the radioisotopes used to tag the sugars and other carriers means that the associated radioactivity is brief and relatively harmless to the patient. Typically for these radioisotopes, half their number disappear within minutes. This also means, however, that they must be created, chemically combined with other elements into small molecules, attached to carriers, purified, and made ready for injection into the patient, all within the brief period of time before their usefulness disappears.

For all these steps to take place quickly, two scientific advances were necessary. The first was a practical means for locally producing the short-lived positron-emitting radioisotopes. The second was a detailed set of procedures, or chemist's protocol, for creating the small molecules to be attached to the larger organic structures of the carriers. Both successes stemmed from Basic Energy Sciences research.

Concerning the first advance, positron-emitting radioisotopes are atoms that are short-lived and

unstable because they have too many positively charged nuclear particles, called protons, relative to the number of neutral particles, called neutrons. Although the process for creating them is indirect, it usually involves bombarding ordinary atoms with protons in order to create this imbalance. This is accomplished by accelerating protons in special laboratory machines known as a cyclotrons.

Before the invention of the compact cyclotron, these machines were typically large and expensive. They were operated by scientists and housed in special research facilities. These requirements were not easily accommodated by the physical, technical, and budgetary constraints of most hospitals.

Using the larger machines, Basic Energy Sciences researchers derived the data on radioisotope production rates under a variety of conditions. These data made practical highly accurate predictions of production rates, which led to optimum methods for maximizing production yields. These data and methods, in turn, laid the foundation for the subsequent development of the smaller, less costly, compact cyclotrons more suitable for use by hospitals.

Concerning the second advance, the process of creating radioisotopes in this way gave rise to a number of unique conditions under which the chemical reactions in the next step of the overall process would have to take place. Specifically, the energy and momentum of the incoming proton was imparted to the new atom, causing it to "recoil," either from the initial collision or from the spontaneous ejection of one or more other nuclear particles. The high energy of the recoiling atom, referred to as a "hot atom," can lead to unusual chemical interactions with other atoms, especially those with which the hot atom collides in the process of slowing down.

Basic Energy Sciences researchers focused on understanding and characterizing the chemistry of these "hot atoms" and their interactions. Gradually, an extensive base of knowledge was established. This was important to predicting how the newly formed radioisotopes would react chemically immediately after being created.

Ultimately, this knowledge led to the development of precisely controlled procedures for producing small, labeled "building block" molecules, known as intermediates, such as carbon dioxide

(CO₂), carbon monoxide (CO), the cyanide radical (CN), and others. These intermediates are then attached to the larger organic molecules, thus forming radiopharmaceuticals used as biological carriers or probes. No human biochemical system can be studied with PET without an appropriately labeled probe for that system in its normal or diseased state.

The compact cyclotron and hot atom chemistry provided the means for locally producing the positron-emitting radiopharmaceuticals. Today, these two advances are fully incorporated into modern and commercially available medical cyclotrons. More than 35 such machines are in use throughout the United States, usually associated with hospitals. They are not only reliable but simple to operate. Several private companies manufacture PET units. Although each unit costs more than a million dollars, five to ten units are sold annually, and sales are expected to increase as new uses for PET are developed.

Highly specific biological probes are needed for each situation. Building on the base of knowledge created by Basic Energy Sciences research, these are proliferating. The early success of measuring regional brain glucose metabolism, for example, was achieved with a special probe named ¹⁸F-FDG (¹⁸F-fluorodeoxyglucose).

Likewise, the ability to measure brain oxygen utilization and blood flow was made possible with two other probes, ¹⁵O-O (oxygen) and H₂¹⁵O (water). More recent and notable innovations include the use of ¹¹C-labeled amino acids for evaluating protein synthesis or tumor metabolism, and ¹¹CDG (¹¹C-deoxyglucose) and ¹⁸FDG for evaluating patients with Alzheimer's disease.

Encouraged by these successes, medical researchers worldwide are discussing applications of other new compounds. Amino acids for pancreatic and liver tumors and ¹⁸F-labeled steroids for breast tumors are just two of the many new areas under study and development. At Brookhaven National Laboratory, a new method for quantifying enzymes in the brain using ¹¹C-labeled compounds is under development in order to relate the enzyme levels to diseases such as Parkinsonism.

In summary, Basic Energy Sciences research played a key role in creating the knowledge underlying these advances and facilitating their application. Less directly, but importantly, Basic Energy

Sciences research also contributed by providing the seminal education, training, and experience for many of the scientists who are now actively engaged in PET-related work today.

In 1986, the National Institutes of Health recognized these contributions by conferring upon Basic Energy Sciences principal investigator, Dr. Alfred Wolf, a mechanistic organic chemist, and his colleagues at Brookhaven National Laboratory, the Javits Neuroscience Investigator Award. Also in 1986, Dr. Wolf received the prestigious George von Hevesy Memorial Medal from the Fourth World Congress of Nuclear Medicine, in acknowledgment of his "pioneering work—recognized worldwide—in the field of radiochemistry and radiopharmacy for the nuclear medicine community."

Although cures for the most serious neurological and organ disorders still remain beyond the grasp of modern medicine, positron emission tomography has opened the door to new frontiers of medical research.

RARE EARTHS

As a result of splitting large atoms into smaller ones during the process of nuclear fission, an unusual family of metals began to appear inside America's first nuclear reactors. Reactor designers needed to know what effects, if any, these metals, called rare earth elements, had on reactor performance. Their designs depended on it.

Research aimed at obtaining this knowledge required significant quantities of rare earth elements in highly purified form. Unfortunately, this was a problem. Chemically, the 15 naturally occurring rare earth elements are virtually indistinguishable from one another. As a result, they are found co-mingled in rare earth-bearing ores and are difficult to separate. In pure form they are truly rare, as their name implies.

Ultimately, Basic Energy Sciences researchers provided the key to solving this problem. They developed sophisticated rare earth separation technologies, described below, which produced the quantities required. Reactor designs proceeded and nuclear technology was advanced.

More profoundly, however, these technologies provided for the first time easy access to rare

earths in pure elemental form. Subsequent discoveries of each element's unique electrical, optical, magnetic, and fluorescent properties, to name a few, and their associated behavioral characteristics, led to a virtual explosion of new and advanced applications.

Rare earths, when combined with certain other elements, form metal alloys having unusual magnetic properties. The resulting products pervade modern society. The red elements of color television pictures, for example, emanate as colored light from rare earth phosphors. Compact starter motors in automobiles make use of powerful rare earth magnets. Such magnets also make possible the miniaturization of magnetic tape readers, popularized in the so-called "walkman" audio cassette players. Some rare earth lasers are used to cut steel. Others surgically repair tissues of damaged or diseased eyes. Rare earth materials are used as well in advanced defense warning systems to detect submarines at great distances.

Today, 17,000 tons of rare earths are used annually in the United States to manufacture such products. Global consumption is far greater. Producers worldwide use separation methods, or extensions thereof, of the basic technologies originally developed by Basic Energy Sciences researchers.

Rare earth elements, such as ytterbium, praseodymium, dysprosium, and gadolinium, represent a class of metals, numbered 57 through 71 in the Periodic Table of Elements. They were once so obscure that for a hundred years after their discovery they were little more than laboratory curiosities. Although originally named "rare," the scarcest of their kind is now known to be considerably more abundant than silver and gold combined.

When first confronted by the needs of the nuclear research community, Basic Energy Sciences researchers attacked the problems of separation and purification by seeking improvements in existing processes. These processes had proven successful in separating small quantities of rare earths.

One process in particular called for a column of "absorbent" material to be packed inside a vertical tube. A liquid solution containing dissolved rare earths was poured in at the top of the column and "soaked up" by the absorbent material. Once full, a second "washing" solution was then introduced at the top of the column. It was allowed to flow

continuously down through the tube, slowly passing through the absorbent material.

Because of its special properties and varying chemical affinities for the different rare earth elements, the washing solution tended to attract some rare earth elements slightly more strongly than others. Hence, different rare earths moved down the column and out the bottom of the tube at different rates. Those that moved more easily came out first, and so on. This resulted in enhanced concentrations of certain rare earth elements at different stages in the process.

Although this process worked, it was slow and tedious. The process had poor selectivity, in that there was only partial separation of the rare earths with each pass down the tube. This required repeated processing of the output in successive stages. Recovering minute quantities at high levels of purity took months.

Basic Energy Sciences researchers hypothesized that the key to improving this process was to increase the selectivity of the washing solution. This might be accomplished by adding a chemical called a "complexing agent."

The researchers were familiar with a large class of such agents as a result of their work on other separations having to do with fuel for nuclear reactors. They knew, for example, that each molecule of a complexing agent is shaped in such a way that it forms a "pocket." This pocket, depending upon its particulars, can attract and physically "hold" certain types of atoms.

With this knowledge, the researchers selected several agents, each with a pocket believed to be well matched to the physical attributes of certain groups of rare earth atoms. The results were dramatic. The affinity between the washing solution and the targeted rare earth atoms rose significantly, leading to faster trips down the tube, higher selectivity, and more concentrated separations.

Building on this advance, the researchers further improved the process by becoming adept at optimizing the conditions, such as the acidity and temperature of the washing fluid, under which the complexing agents performed. In this way, they produced practical processes for separating commercial amounts of all of the rare earth elements in reasonable time periods. Purity levels of 99.9999

percent could be achieved, if and when applications demanded it.

Today, the center for rare earth chemistry and related technology is located at Ames Laboratory, Iowa State University, just north of Des Moines, where these discoveries were first made. Since then, refinements continue to be made to both these processes and others.

The Laboratory provides a full array of technical services to research laboratories and commercial and industrial firms throughout the United States. Within this technically supportive environment, applications for rare earth products continue to expand, finding uses important to commerce, industry, science, medicine, and the national defense.

Besides color televisions, rare earth phosphors are used in high-efficiency fluorescent lights, achieving not only a 30 percent reduction in energy consumption, but also yielding a more appealing and natural spectrum of light. These lights are popular in Europe and are becoming more so in the United States. Recently, rare earth phosphors were also heralded as a boon for medical science, because they amplify x-ray signals, cutting patient exposures by 97 percent.

The rare earth neodymium made possible some of the world's most powerful and versatile lasers. The neodymium laser's pure and coherent light beams serve countless purposes in manufacturing and research. One of the most versatile research lasers is the so-called neodymium-YAG laser (yttrium aluminum garnet), employing two rare earth elements, the former in extremely high purities.

The high magnetic strength of the rare earth magnets enabled motors to have higher efficiency and lower weight than more conventional motors. In a unique and highly visible extension of this application, General Motors used them in an experimental solar-powered racing car, called Sunraycer. Sunraycer propelled itself by electric motors employing these magnets, winning a 2,000-mile endurance race across Australia's sun-baked interior.

Finally, rare earths have also found many other useful, albeit less glamorous, applications. These include polishing compounds, petroleum refining

catalysts, and alloying materials for the iron and steel industry.

These examples underscore a common theme relevant to the support of basic research. Basic Energy Sciences researchers did not invent, nor even foresee, all of these applications of rare earth technology. Yet, their fundamental work on separating rare earth elements in highly purified form, combined with their continued theoretical work on rare earth properties and their interactions with other elements, provided the essential foundation upon which all of these applications were built.

HAFNIUM-FREE ZIRCONIUM

In December 1957, a nuclear reactor at Shippingport, Pennsylvania, first began to produce electricity for public use. Ever since, nuclear power has contributed to growing portions of the world's electric energy supply. Today, about one-fifth of the electricity used in the United States is generated by splitting the atom, and this fraction is even larger for Japan, South Korea, the Soviet Union, and several European countries.

Bringing this achievement to reality involved scientific and technological accomplishments on a grand scale. Basic Energy Sciences research made numerous contributions to this effort, particularly in the development of special materials used in the internal construction of nuclear reactors.

These special materials had to endure prolonged exposure to adverse conditions of a unique operational environment. Most importantly, they also had to be physically compatible with the nuclear activities required for efficient and controlled nuclear fission.

In the process of nuclear fission, a large atom, usually uranium, is split into two smaller ones by a relatively slow moving "collision" with one of the basic constituents of matter, the subatomic particle called the neutron. As the atom splits, a large release of nuclear energy is carried off by the two fission products. It is this energy that ultimately turns water to steam, drives the generating turbines, and produces electricity.

Usually two or three fast moving neutrons are also produced when each atom splits. The fate of these neutrons is important to the design of a reactor because if not lost by escape or otherwise

absorbed non-productively, these neutrons can be slowed down, reflected back into the fuel, and used to carry on the chain reaction. The efficient sustaining of the fission process requires the maintaining of a delicate balance between neutrons produced and lost, with as few neutrons lost as possible.

Unfortunately, for the early designers of nuclear reactors, the preferred structural material for withstanding the corrosive and high temperature environment inside a reactor was stainless steel, which has a high propensity for absorbing neutrons. This was a particularly unacceptable situation in the metal jackets, called cladding, used to contain the small, compressed pellets of uranium fuel.

In a typical sequence of reactions, a fast moving neutron is produced by fissioning fuel. It travels out of the fuel, passing through the cladding. It enters the surrounding water, where it is slowed down or moderated by a series of collisions with hydrogen nuclei in the water molecules. It then randomly drifts or diffuses back into the fuel, passing a second time through the cladding.

In sustained operations, nearly every neutron makes two, or more typically, numerous passes through the cladding before causing another fission. Given this, it was clear that a new cladding material, one that had a very low propensity for absorbing neutrons, needed to be developed. Like clear glass is transparent to light, suitable metals, with high strength, ductility, durability, and resistance to corrosion in high temperature environments, needed to be, as well, transparent to neutrons.

Basic Energy Sciences researchers were aware of one metal, zirconium, which seemed to have most of the desired properties. In certain elaborately prepared experiments, these researchers confirmed that zirconium in rare and purified form absorbed very few neutrons.

Moreover, when zirconium was combined with tin, an alloy named *zircalloy* was formed. This material was found to be not only highly transparent to neutrons, but also capable of performing well at even higher temperatures than the stainless steels of the day.

Only one major barrier stood in the way. In all natural ores where zirconium was found, it was intricately mixed with another metal, hafnium. Un-

fortunately, hafnium exhibits just the opposite neutronic properties.

Hafnium's propensity for absorbing neutrons is 600 times larger than that of zirconium. The presence of even a minute amount of hafnium would have an overwhelmingly defeating effect on reactor performance by drastically reducing neutron population. The separation of hafnium from zirconium was essential, but the two metals were chemically very similar.

Before interest developed in using zirconium as a cladding material in nuclear reactors, several tedious and expensive hafnium separation processes were developed, but none had been used to make more than a few ounces of purified zirconium and its compounds. When the usefulness of purified zirconium was first confirmed, Basic Energy Sciences researchers at several laboratories, most notably Ames and Oak Ridge National Laboratories, began to look for more efficient and practical separation methods suitable for large scale operations.

The first major advance came with the discovery at Ames Laboratory that an absorbent material, called silica gel, selectively removed hafnium from a solution of the tetrachlorides of zirconium and hafnium in methyl alcohol. The purification process also removed several other undesirable elements, yielding a zirconium oxide product well suited for further processing. Although this was a "batch" process, which was not readily adaptable to large scale operations, the finding produced valuable technical insights.

Building upon these insights, Basic Energy Sciences researchers at Oak Ridge National Laboratory modified an existing process, called the Fischer thiocyanate process, and applied it to the zirconium separation task. As in other ore refining processes, it used continuous flows of extracting liquids, which were better suited to large scale operations.

This modified process, known generically as a solvent extraction process, was similar to another method used by other Oak Ridge researchers to extract uranium from plutonium. This other effort happened to be undergoing development and refinement at the same time, and a useful collaboration ensued.

In its simplest form, the process worked by gravitational mixing of chemicals in a long (greater

than 50 feet), narrow (4-inch diameter), vertical tube filled with a column of liquid. An aqueous (water based) solution containing dissolved zirconium ore salts, along with its hafnium contaminants, was fed slowly into the middle of the filled tube. A suitable solvent—one having an affinity for both hafnium and zirconium, but with a slight preference for hafnium—was fed in at the bottom. Such solvents, like liquid ether, are lighter than water and float towards the top. At the same time, an acid—one having the ability to strip both hafnium and zirconium from the solvent, but with a slight preference for zirconium—was fed in at the top. Concentrated acids are slightly heavier than water and sink towards the bottom.

In this way a system was created where there were two slowly moving, counterflowing, and partially mixing currents of liquids. The solvent tended to carry the zirconium and hafnium elements up the column, with increasing concentrations of hafnium. As the liquids passed through each other, the downward flowing acid solution tended to strip the zirconium and hafnium elements from the solvent, with increasing concentrations of zirconium.

The net result was an increased concentration of hafnium in the solvent, which was drawn off at the top, and an increased concentration of zirconium in the acid, which was drawn off at the bottom. The zirconium-enriched output stream could be further refined simply by adding more length to the tube. Using pumps and a series of connected tube lengths, Basic Energy Sciences researchers achieved their highest purities with 120- and 150-foot lengths.

The commercialization of this process depended on two unrelated areas of basic research. First, the researchers had to find a good solvent. Guided by years of fundamental research on separations technology, this turned out to be a chemical known as methylisobutyl ketone. The acid was a common one used in such cases, namely, hydrochloric acid (HCl).

Second, they had to experiment with the system and determine the optimum conditions under which the process would work. The key variables concerned the concentrations of the salts, acid and solvent, and their respective flow rates, and the diameter, length, and possible internal configurations of the tube. The successful accomplishment of this tedious second step was significantly accelerated by an innovative approach employing radioac-

tive tracers to tag and elucidate the behavior of all the key process constituents.

This process was then scaled up to a pilot plant, and eventually to a commercial production facility, capable of producing about 1 million pounds of purified zirconium per year at the Northwest Electrodevelopment Laboratory. The technology was subsequently transferred to Teledyne Wah Chang and Western Zirconium.

Today, the two firms together produce about 2,500 tons of purified zirconium and 50 tons of hafnium per year. About 50 percent of the United States' total metallic zirconium production is used as cladding material for new or replacement fuel rods in nuclear power reactors. The remainder, with hafnium left in, is used as a constituent of magnesium alloys and superconducting magnet wire.

The hafnium separated from the zirconium also has important applications. The very quality that makes hafnium a poor material for cladding—its high propensity to absorb neutrons—is ideal for use in control rods inserted into a reactor to slow down the chain reaction.

Other desirable characteristics of hafnium include good ductility, machinability, and hot water corrosion resistance. Most of the U.S. hafnium production is used for control rods in naval reactors for nuclear powered ships and submarines. Other uses for hafnium include additives in high-strength materials, corrosion-resistant steels, cutting tool alloys, and optical glass.

Three decades have elapsed since Basic Energy Sciences advances first made zircalloy production practical on a large scale. In the intervening years, no better material has been found for the key applications, such as cladding inside reactors, and the special benefits of zircalloy continue to accrue.

If stainless steel had been used instead of zircalloy, the task of maintaining that delicate balance between neutrons produced and lost would have been accomplished much less efficiently. The level of uranium enrichment in reactor fuel would have had to be raised significantly. It is estimated that, due to the increased enrichment requirement, the nuclear power produced in the United States, without zircalloy, would have cost \$800 million more in 1987 alone. These savings continue to accumulate with each passing year and are likely to

expand as more reactors nearing completion come on-line and begin to add to the Nation's power production.

ENRICHED STABLE ISOTOPES

During the height of World War II, the United States' fervent effort to develop the atomic bomb employed 25,000 people in Oak Ridge, Tennessee, to build and operate more than 1,100 huge, strange-looking machines, each weighing 8 tons or more. Code-named after a progenitor, the California University Cyclotron, these machines were known as "calutrons."

Their purpose was to enrich the concentration in uranium of one particular atomic species of the uranium family, namely the isotope ^{235}U . Although the calutrons were successful, other technologies proved to be more efficient for enriching uranium. After the War, all calutrons were scheduled to be dismantled.

In a fortuitous twist of history, however, 76 of these machines, born of a *war* effort, were spared, modified, and adapted over the years, to a point where a portion of these now lie at the heart of some of the United States' most sophisticated *life-saving* technologies. At what is now known as the Oak Ridge National Laboratory, calutrons hold a very special, though unheralded, place of importance for thousands of Americans who suffer from heart, kidney, brain, and bone diseases, and other organ disorders.

Supported for many years by Basic Energy Sciences, calutrons today produce and maintain inventories of approximately 200 enriched *stable* (non-radioactive) isotopes useful to science, industry, commerce, and medicine. Enriched stable isotopes are used as research materials, intermediates in the preparation of radioisotopes and radiopharmaceuticals, and non-radioactive tracers. Inventories are maintained for both sale and loan, and these are periodically replenished in accordance with demands, priorities, and available resources. Statistics on medical applications hint of the growing importance of enriched stable isotopes. Sales of radiopharmaceuticals alone exceed \$150 million per year. Products derived from enriched stable isotopes are used in 600,000 medical procedures each year. Every hospital in the United States is required to have nuclear medicine capabilities in order to become an accredited institution.

As a supplier of enriched stable isotopes, the Oak Ridge calutrons constitute the world's premiere source. Although originally designed to separate isotopes of only one element, uranium, by 1960 the calutrons had demonstrated the full range of their versatility by producing enriched quantities of more than 240 stable isotopes.

The value of enriched stable isotopes may be appreciated by understanding a little about their nature and how they are used. An isotope is one type, or species, of atom found among two or more species, all belonging to the same elemental family. Chemically, all isotopes of the same element are virtually identical. They differ only by their atomic weights.

Most elements found in nature appear as mixtures of several isotopes in almost unvarying proportions. The element iron (Fe), for example, appears as a mixture of four stable isotopes. Shown with their atomic weights, these are symbolically identified as ^{55}Fe , ^{56}Fe , ^{57}Fe , ^{58}Fe , with natural abundances of 5.8, 91.8, 2.1, and 0.3 percents, respectively.

Enriched stable isotopes are those whose abundances have been artificially increased above natural levels, say, for example, from 5.8 to 97.2 percent in the case of ^{54}Fe . Extreme levels of enrichment are attainable, if required, having impurities measuring less than one part per billion. The calutrons of Oak Ridge produce enriched isotopes by separating the naturally occurring isotopes atom by atom. Mechanically, this is achieved by applying the principle of centrifugal force. Isotopes of one elemental family are introduced into a vacuum, vaporized, given positive electrical charges (ionized), and accelerated along curved paths in a carefully focused electromagnetic field. The heavier isotopes fly more to the outside, cutting wider arcs. Although separations at the end of the arcs are small, they are sufficient to allow compartmentalized collections.

Early in their post-War history, the calutrons' principal purpose was to provide research materials crucial for fundamental studies in nuclear physics and atomic energy. These activities resulted in many spectacular scientific achievements and are still important. As the technologies of science and medicine advanced, however, other needs for enriched stable isotopes came to the fore.

Today, some of the more publicly visible of these are found in nuclear medicine. After a heart attack, for example, cardiologists need to know the location of coronary artery blockages and the extent to which heart tissues may have been damaged. A standard clinical procedure, called thallium scanning, is used to reveal such information.

The calutrons make thallium scanning possible in the following way. They produce purified quantities of thallium-203, a stable isotope which appears with thallium-205 in natural abundances of 30 and 70 percents, respectively. Thallium is of interest because it behaves chemically in the body much like the element potassium, which is essential for proper heart functioning. Pharmaceutical companies, in turn, bombard the purified thallium-203 with subatomic particles (protons) in specially designed equipment. This sets off a series of nuclear transformations. Thallium-203 is transformed momentarily into an excited and unstable form of lead-204. Through a series of almost instantaneous particle emissions (radioactivity), lead-204 becomes lead-201. Within minutes, lead-201 transforms itself into the radioisotope thallium-201, which has a useful shelf-life of several days. The prepared tracer, thallium-201, is shipped promptly to user hospitals and clinics.

There, thallium-201 is injected into the circulatory system of the patient. As a substitute for potassium, the thallium is drawn naturally to the heart. Cardiologists observe its uptake with special cameras, which detect the slight radioactivity emitted by the thallium-201. Blank or deficient images reveal blocked or damaged tissue areas.

Thallium scanning also enables cardiologists to confirm electrocardiogram tests, evaluate drug therapies aimed at dilating arteries and increasing blood flow to diseased tissues, and gauge the success of coronary bypass operations. Only minute amounts of thallium are required, which soon disappear from the body by natural decay.

Likewise, the Oak Ridge calutrons supply the basic feedstock materials for a broad range of other radiopharmaceuticals. These include zinc-68 (transformed to gallium-67) for soft tumor scanning and Hodgkin's disease, selenium-74 (to selenium-75) for pancreas scanning, strontium-84 (to strontium-85) for bone scanning, and tin-112 (to indium-113) for detection of lung cancer.

More uses include, cadmium-112 (transformed to indium-111) for detection of brain and spinal fluid leakages, tellurium-124 (to iodine-123) for thyroid scanning, mercury-196 (to mercury-197) for brain scanning, and mercury-202 (to mercury-203) for kidney scanning. Altogether, at least 36 enriched stable isotopes are used as precursors for radiopharmaceuticals for medical diagnostics and treatment.

Apart from radiopharmaceuticals, direct use of enriched stable isotopes, which require no nuclear transformations, is growing in importance. These are particularly useful in cases where radioactive isotopes cannot be used safely on certain groups of patients, such as the newborn, young children, and lactating mothers, due to the dangers of absorbed radiation.

Researchers at Washington University and the National Institutes of Health, for example, discovered the utility of calcium-46, a stable isotope, in the monitoring of the effectiveness of vitamin D-fortified milk in nurturing premature infants. Their findings provide quantitative data which can guide nutritional planning for these tiny patients.

In a similar application, millions of older people suffer from a bone-weakening condition, known as osteoporosis, where calcium loss leads to higher risks of hip fractures and broken bones. How or why calcium loss is part of the aging process remains a mystery. Scientists at the National Institutes of Health are learning more about the process, however, by charting calcium flows through the body with the aid of stable calcium isotopes.

Beyond medicine, there are numerous other uses of enriched stable isotopes. Magnesium-26 performs as a biological tracer in agricultural studies. Chlorine-37 serves as an identifier in studies of atmospheric ozone. Rubidium-87 functions as a precise standard for measuring time with atomic clocks. Cadmium-114 is used in the manufacture of commercial lasers. Ytterbium-168, a precursor of ytterbium-169, makes possible a portable source of x-rays for engineers inspecting pressure tank and pipe system welds.

In archaeology and earth sciences, the ages of materials can be determined by calculating the extent of radioactive decay found among the natural constituents of the samples. One method (rubidium-strontium) for dating rocks, for example, involves a technical procedure known as isotopic

dilution. This procedure calls for the introduction into the sampling chamber of a known amount of a highly enriched, but normally rare, stable isotope of strontium, ^{84}Sr .

Basic Energy Sciences, through sustained support over four decades of the stable isotope separation program and related research, provided the means by which these and other applications were made possible. The calutrons, spared from certain demise, produced and maintained inventories of stable isotopes not elsewhere available.

The existence of these inventories, accompanied by supportive policies governing access, both enabled and encouraged scientists of all disciplines to investigate isotopic properties and explore their possibilities. By so doing, Basic Energy Sciences and the Oak Ridge calutrons gave birth to a wondrous array of benefits to society.

Over the years, other technologies have evolved which can produce some enriched stable isotopes more efficiently than the calutrons. For many important applications, however, and particularly for the continuing scientific quest of the unexplored, the Oak Ridge calutrons remain the only steadfast and reliable source of enriched stable isotopes in the free world.

TRACE ELEMENT ANALYSIS

For many years, a chemist testing a mixture for traces of contaminants had a problem. There were no dependable and convenient techniques for doing this in complex mixtures and combinations where trace elements are most often encountered. Today, more than 5,000 research facilities worldwide routinely use unique and powerful analytical instruments for detecting minute amounts of contaminants in water, air, and other samples from our environment. The origins of these instruments can be traced to an innovation pioneered at Ames Laboratory by Basic Energy Sciences-funded research.

Called *inductively coupled plasma spectroscopy*, and embodied since the early 1980's in several versions of rapidly selling commercial instruments, the new methods can measure individual elements in rapid sequence or simultaneously by selected groups. Previously, some approaches could measure one element at a time; others could measure elements in sequence but only with sub-

stantial changes in experimental conditions from one element to another. Many tests could not show how much of the elements were present. Several methods could measure a limited number of elements and others required lengthy sample preparation and separations to reduce interferences between measurements of different elements.

Some of the new instruments can measure 55 elements simultaneously, providing a computer display of the results in a matter of minutes. In 1985, an inductively coupled plasma instrument was used to analyze more than 80 aqueous samples for 26 elements—more than 2,080 analytical chemical determinations—in an 8-hour period.

The research at Ames Laboratory advanced chemical analysis by greatly increasing the range of two proven methods for elemental analysis, namely light spectroscopy and mass spectroscopy. Both had been long recognized as having the most potential for identifying and measuring amounts of materials at low concentrations.

Light spectroscopy capitalizes on the phenomenon that each of the elements of nature emits or absorbs a characteristic pattern of colors, or *wavelengths*, when it is heated to high enough temperatures. The pattern of wavelengths is a unique signature of the element. In contrast, mass spectroscopy separates materials on the basis of their weight. It not only distinguishes one element from another, but also distinguishes isotopes of the same element. (See *Isotopic Geology*.)

Specifically, the researchers at Ames Laboratory first solved longstanding problems associated with preparing samples for light and mass spectroscopy. The first step in any spectroscopic analysis is transforming gases or aerosols generated from liquid and solid samples into free atoms, excited atoms, ions, excited ions, molecular ions, and molecular fragments. This is done by heating the gases or aerosols, and the hotter they are heated, the better.

Existing flame, arc, spark, and other excitation sources used in the early 1960's didn't perform this vaporization, atomization, excitation, and ionization step entirely satisfactorily. They also tended to introduce contamination from the fuels used to combust the sample material or from erosion of the electrodes used to create the electric arcs or sparks in which the sample material was heated. Contamination is the bane of any chemical analysis,

but especially of such an exquisitely sensitive measurement as testing for trace elements.

Velmer A. Fassel, a chemist at Ames Laboratory (concurrent with Stanley Greenfield in the United Kingdom), wondered whether it would be possible to develop a satisfactory *electrical* flame—a plasma—to start off the spectroscopic analysis. This would be a way to get an even hotter gas to tear the molecules apart and excite the free atoms and ions without the contamination of combustion or electrode materials.

Fassel's method for heating the sample came not from chemistry, but from physics. Such a cross-fertilization is not surprising in the environment of a multidisciplinary laboratory. At the heart of an inductively coupled plasma device, argon gas flows continuously through the core of a copper coil carrying an electric current. Here the electricity flowing through the coil creates an alternating magnetic field that induces an electric current to flow through the gas. This then heats the argon to such high temperatures, 10,000°C, that it becomes ionized and forms a plasma. In scientific jargon, the electricity in the coil is *inductively coupled* to the plasma.

A liquid aerosol from material to be analyzed is sprayed into the argon plasma. The intense heat of the plasma evaporates the solvent and vaporizes all of the chemicals in the sample. As the sample rapidly becomes even hotter, the molecules of the sample separate into fragments and individual atoms, electrons are stripped from many of these and raised to different orbits in others, thus transforming them into excited ions and excited atoms.

Because argon is an inert gas and will not react with the elements in the sample, the materials being analyzed can remain in the plasma longer and be heated even hotter. Once the materials from the sample are heated in this manner, they are ready to be fed to light, mass, or other types of spectroscopic devices to have their elemental content identified and quantified.

Higher temperatures, a less active chemical environment, and operation at atmospheric pressures lead to vast improvements in test material formation and excitation and allow precise control of movement of the test material to the spectroscope. The argon plasma can be sustained under low power conditions that are safer and more comfortable for analytical chemists, while sample mate-

rial is handled in the convenient form of liquid aerosols.

Having solved the problem of how to prepare the sample material, Fassel and his team turned their attention to wedding their inductively coupled plasmas to light and mass spectrometers. Optimizing the design parameters of the plasma and making the electronics of the spectrometers compatible with the plasma were difficult tasks. It would take more than a decade to develop practical instruments.

The first new approach, and the goal of the original research, emerged in the mid 1970's. It took the form of various laboratory instruments for *inductively coupled plasma atomic emission spectroscopy*. The approach is particularly well suited to rapidly finding many elements in a single mixture and measuring the concentration of each. Scientists call this process fast multi-elemental analysis.

Emission spectroscopy instruments analyze the light emitted directly by the hot ions and excited atoms in the sample material. A component of each instrument, called a spectrometer, separates the light of different wavelengths and measures the intensity of each. Light intensity indicates the amount of material present in the sample.

In a second approach first reported in 1979, inductively coupled plasma atomization cells were made part of *atomic fluorescence spectroscopy*. In this technique, light of a wavelength known to be absorbed by a specific element is shined into the plasma. Only the atoms of this specific element absorb this light, and they re-emit it almost immediately. The patterns and intensities of the re-emitted light, separated by a spectrometer, indicate the presence of the target element and its concentration.

Atomic fluorescence spectroscopy by its nature, provides a higher degree of selectivity in identifying trace elements because the signal from the underlying background is rejected. In the past, combustion flames had been used as a means to convert the sample into free atoms. Inductively coupled plasma brought to atomic fluorescence spectroscopy a more efficient way to generate free atoms from sample material and a greater freedom from interferences between elements in the atomization process.

Many of the properties that vaulted inductively coupled plasmas to supremacy for preparing sample material in light spectroscopy also were found to make them desirable as an ion source for mass spectroscopy. In *inductively coupled plasma mass spectroscopy*, only the desired ions of sample material in the plasma are "sucked out" or extracted into the vacuum of a mass spectrometer. There, the elements and isotopes present are identified and their abundance is measured.

Initially funded by the Environmental Protection Agency but supported by Basic Energy Sciences for the last 6 years, the research at Ames Laboratory found a solution to a longstanding problem in mass spectroscopy. With precise control of the ions from the plasma, chemists could dramatically reduce the introduction of undesired impurities into the super-sensitive mass spectrometer. Chemists now could measure both elemental content and isotopic abundance, from liquid or solid samples, without inserting the bulk sample itself into the high vacuum environs of the mass spectrometer. Plus, they gained an analytical tool for accurate analysis, whether the material being tested was present in the sample materials at trace or major constituent levels.

Currently, there are nine United States vendors of commercial inductively coupled plasma instruments and an estimated six vendors in foreign

countries. In recent years, inductively coupled plasma instruments led all other major analytical instruments in percentage growth of sales, amounting to over 20 percent annually.

For 1985, the estimated domestic sales volume totaled \$55 million while the world market is estimated at \$100 million. Approximately 500 more facilities at universities, government research institutions, and private analytical laboratories, adopt inductively coupled plasma technology each year.

Sales of these instruments are projected to continue to increase at a rapid pace over the next decade. It is estimated that the 2,000 instruments sold during the past 4 years will reduce the costs for chemical analyses by \$500 million over the lifetime of the instruments.

Individually, or collectively, the methodologies developed at the Ames Laboratory revolutionized the way trace elemental analysis is performed. They made fast and reliable analysis of mixtures possible, and the inventor and his colleagues transformed the methods from a laboratory curiosity into a practical tool for research and industry. It was appropriate that *Spectrochimica Acta*, the international journal of spectroscopy, dedicated its first special issue honoring an American to Velmer Fassel, the inventor of inductively coupled plasma spectroscopy.



Applied Mathematical Sciences

Applied Mathematical Sciences research aims at advancing knowledge of mathematical and computer sciences and computing techniques related to energy research, production, and distribution. It also manages high performance supercomputing facilities.

EISPACK AND LINPACK

Reinventing the wheel is generally recognized as a waste of time. But, for many years, a practice much like reinventing the wheel was the order of the day in scientific and engineering computation. Engineers or scientists seeking to solve commonly encountered mathematical equations had to write their own computer programs to perform the necessary calculations.

EISPACK and LINPACK, two pioneering collections of subprograms created by a team of Argonne National Laboratory and university researchers, ended much of this waste. Engineers and scientists could solve commonly encountered mathematical problems by simply calling on these "canned" subprograms. Thus, this accomplishment significantly increased productivity in a number of different fields—from electronics to structure analysis to molecular physics. Not only have these pacesetter packages been widely used themselves, but they have become standards of excellence against which other mathematical software is compared.

The use of mathematics in all fields of science, engineering, and economics naturally divides into two parts. The first part involves the construction of a theoretical or engineering mathematical model for the phenomena being investigated, that is, setting up the equations to be solved. The second part involves solving the equations. If that requires finding **eigenvectors** and **eigenvalues** of a mathematical operator, EISPACK can be used. If the model involves the solution of a system of linear equations,

LINPACK is called for. The scientist or engineer can use EISPACK and LINPACK with confidence that computations will be done accurately and efficiently, and he or she can concentrate on parts of the problem requiring creative thought.

EISPACK is a contraction for "Eigensystem Package." EISPACK routines are used to solve what is known in the mathematical literature as a **matrix eigensystem problem**. Matrix eigensystem problems are encountered in many otherwise unrelated fields. They appear, for example, in studies of molecules, atoms, and the fundamental constituents of matter. They also appear in investigations of natural modes of vibration, whether the vibrations of interest are the swaying of a bridge or steel-framed building, the flutter of an airplane's wings or airframe, or the transient oscillations of an electrical network or electromechanical device. Some problems require computation of quantities called **eigenvalues** and **eigenvectors**, which together comprise an **eigensystem**.

In the physics and chemistry of molecules, atoms, and fundamental particles, each eigenvalue corresponds to one of the energy levels of a molecule, atom, or particle. Together with its eigenvector, each eigenvalue gives information about the form of matter that is present, its energy level, and its readiness or suitability to be involved in a reaction or interaction.

In mechanical systems such as an airplane wing or automobile suspension, each eigenvalue corresponds to one of the vibration frequencies that occur. Each eigenvector identifies the shape of the vibrating structure and magnitude of the vibration associated with one specific frequency. The first eigensystem corresponds to the base or fundamental frequency, the second to the first overtone or harmonic that is present, and so forth.

Solving matrix eigensystem problems is one of the most challenging tasks faced by scientists and engineers. Thus, it is one of the few areas where mathematical purists **do not** recommend avoiding

“canned” software. On the contrary, textbooks on numerical analysis are written to give the practitioners some appreciation of what is going on inside canned computerized routines so that they can make intelligent choices about choosing them and intelligent diagnosis when things do not turn out as expected.

This is where EISPACK came in; it made reliable “canned” software a reality. Emerging from research in software engineering, with a parallel goal of creating a useful product, it is the original, and many believe still the best, package of general use routines for solving matrix eigensystem problems. It was born in a prototype effort to create highly reliable software from innovative mathematical concepts.

EISPACK developers took stable numerical analysis methods, or **algorithms**, which previously had been inaccessible to the great majority of scientific computer installations, and made them easily usable and widely available. Algorithms for matrix eigensystem solution, which were summarized in a handbook published in 1971, were said to be **stable** because of the way they handle an inherent difficulty in numerical computation—the accumulation of round-off errors. With earlier methods of computation, errors accumulated and overwhelmed the answers, making the results not only wrong but dangerous if used in critical applications.

The project involved organizing these stable algorithms into categories related to various user problems and writing them in the popular programming language **FORTRAN**. The result was extremely reliable subprograms that researchers could readily incorporate into larger computer programs. The EISPACK software was then tested extensively at some 20 sites and “certified” for reliability by the research and development team which included scientists from Argonne National Laboratory, the University of Texas at Austin, and Stanford University.

By mid-1972 EISPACK was ready for public distribution. Arrangements were made to distribute EISPACK for a handling fee. Documentation describing the use of EISPACK accompanied the software and was extended and published in 1974 and republished in 1977 to accompany a second release of EISPACK containing additional subprograms.

Within 2 years, work began on a package of mathematical software to solve classes of linear systems. The pattern of collaborative work established for EISPACK had proved so successful that it was taken as a model for the new package, to be called LINPACK. Again, computationally sound algorithms were known, and the effort was to organize them in reliable software.

LINPACK is a contraction for “Linear Systems Package.” Systems of linear equations—or, as they are called in elementary algebra, **simultaneous equations**—describe, for example, the distribution of electrical currents or voltages in electrical networks, such as electricity distribution systems. They represent the distribution of the mass flow rate of water in complex hydraulic systems, such as city water systems. And, they provide a way to approximate solutions of otherwise unsolvable equations describing the forces surrounding the nucleus of an atom.

In experimental studies, linear systems of equations enable investigators to summarize a mass of data in order to obtain formulas for interpolating between observed values or to deduce calibration curves. In this role, they provide a means to confirm or refute a theoretical relation, to compare several sets of data in order to ascertain if they can be represented by the same sets of equations, or to choose a theoretical model.

In psychology, sociology, and economics, a technique based on systems of linear equations, called multiple regression analysis, is one of the most widely used of all statistical tools. It ascertains the relation between three or more quantitative variables so that one variable can be predicted from all of the others. Multiple regression requires that extensive systems of linear equations and large arrays of data be denoted compactly and be operated upon efficiently.

LINPACK is designed with large systems in mind. In studying problems of the type encountered in modern science and engineering, it is frequently necessary to solve 150 or 200 simultaneous equations. This task presents practically insurmountable difficulties if undertaken with other than the best numerical methods.

With the algorithms in LINPACK, the computation to solve such a system may be reduced to only thousands of multiplications—a task a supercomputer can accomplish in fractions of a sec-

ond. Suffice to say, the algorithms in LINPACK are very stable. The computational results are accurate to within the precision of the machine itself.

LINPACK, like EISPACK, goes to great lengths to minimize computer resources required to solve a specific problem. Routines for the various tasks are provided in versions corresponding to the most common ways that the user's problem might be formulated. In technical terms, LINPACK contains subroutines corresponding to the form of the input coefficient matrix: symmetric, triangular, banded, positive, and so forth. Users can take advantage of the increased efficiency provided by these different routines and not just use the form provided for general matrices.

More than 1,400 copies of EISPACK and 500 copies of LINPACK have been distributed to computer centers worldwide. Because a major computer center may have hundreds or thousands of users of these packages, the distribution numbers tell only a small part of the story. Indeed, it is rare to find a program that requires eigensystem or linear system calculations that does not use some variant of EISPACK or LINPACK, or a scientific computer user who does not know of them.

But probably the greatest long-term scientific and commercial benefit of both projects is the way in which they have influenced how we think about sub-programs for basic computations. The scientific debates in the 1960's about whether or not reliable canned programs could be produced have been settled: we now build and use them exclusively, greatly increasing the reliability and efficiency of scientific computing.

AUTOMATED REASONING PROGRAMS: Enabling a Computer to Think Deductively

Computers have become an integral part of modern life. In the home and in the workplace; in hospitals, supermarkets, and schools; computers provide man with valuable assistance in performing many complicated and mundane tasks involving numerical calculations and the processing of information.

Until fairly recently, however, computers have not been able to *reason* or to think *deductively* about a problem situation. *Reasoning* is an activity that requires one to approach a set of facts regarding a problem in a certain way and to draw conclusions that logically follow from those facts until a

solution to the problem is found. Human beings reason continually as part of everyday life, often without realizing it. Imagine how valuable it would be to humans if computers—with their speed, accuracy, and ability to handle large quantities of complex information—could be used to assist in solving problems by reasoning.

One could envision a computer program that could schedule a day's activities at home and at work so as to avoid conflicts, analyze the consequences of proposed decisions, prioritize tasks to be completed, and help find misfiled or misplaced information.

Although such applications sound futuristic, research supported by the Department of Energy's Office of Basic Energy Sciences is yielding results that represent progress toward making such a scenario possible. Researchers at the Argonne National Laboratory near Chicago, Illinois, have developed the theory, methodology, and computer programs that have made it possible to harness, for the first time, the power of computers to perform difficult and important tasks that require deductive reasoning. Using these computer programs—known as automated reasoning programs—researchers have obtained proofs for difficult mathematical problems that have eluded experts for years, designed electronic circuits for computers, and verified that other computer programs will achieve their stated purposes. These valuable research tools are now in the hands of mathematicians, computer scientists, and logicians in more than 100 universities, research institutes, and industries throughout the world.

Virtually all fields of science and engineering can benefit by applying automated reasoning to the design of better systems and the control of those systems. Eventually, all applications that involve computer programming will benefit as well. Particularly, as computer programs are used to perform more and more complex and critical procedures, it becomes increasingly important to develop formal methods for determining the reliability of those programs. Automated reasoning offers a means of doing so.

Automated reasoning is a branch of computer science that studies how the computer can be used to assist in that part of problem solving requiring reasoning. Reasoning in this sense refers to the process of drawing conclusions rigorously and logically, as opposed to probabilistic or common-sense

reasoning. Much of the work of automated reasoning is involved with trying to prove or disprove assumptions using techniques such as generating models as counter examples. Each conclusion that is reached must follow inevitably from the facts from which it is drawn. When an automated reasoning program draws a conclusion, as in the spirit of high school geometry, it cites the specific and immediate facts from which it drew the conclusion, enabling one to check its work. Therefore, one advantage of using an automated reasoning program is its ability to reason without error. No implicit assumptions accidentally occur and no conclusions are drawn that fail to follow from the given information. A result obtained with a reasoning program—a proof of a theorem, a design of a circuit, a verification of a computer code—can generally be accepted.

Another advantage of using a reasoning program is its capacity to examine large numbers of paths in search of a solution. Its effectiveness is not decreased even when the information is very complex, as occurs when processing very long formulas from mathematics or very complicated logical expressions from circuit design.

Fewer than 25 years ago, scientists considered remote the possibility of using a computer program to reason about diverse and unrelated fields. The obstacles of representing the problem to the program, of forming sufficiently general ways of reasoning, and of adequately controlling the reasoning were truly formidable. Nevertheless, because of the potential and appeal of such an idea, research began in 1963 at Argonne National Laboratory under the support of the Department's first predecessor, the Atomic Energy Commission. At the time, the field of research was known as "automated theorem proving," because its early inspiration was to develop computer programs that could prove mathematical theorems (claims for which a proof is not yet known or for which a proof may not yet exist—formulas, propositions, or statements deduced from other formulas or propositions). As it became apparent that the techniques and programs being developed could be applied to other fields of work as well, the name of the research was changed to automated reasoning.

The Argonne researchers adopted a three-pronged attack upon the study of automated reasoning. Simultaneously and with equal concentration, they began focusing on the theory and methodology to be used in an automated reasoning

program, the writing of the program itself, and the application of the program to different problems in different fields of work.

One of the major contributions of the Argonne research to the theory and methodology of the field was the introduction of the notion of *strategy* to automated reasoning. This notion changed the entire course of direction of this area of computer science. A strategy is an approach to a problem-solving situation that allows one to better manage information and to reach a conclusion without examining all possible alternatives. Humans employ strategies all the time when playing cards or games, such as poker or chess, when solving puzzles, or simply when accomplishing a particular task. Strategy, as applied to automated reasoning, is used to guide the overall attack on a problem by specifying such things as the order in which certain facts are to be examined, how to recognize and simplify equivalent information, what information is to be retained, and what information is to be discarded. Without such strategies, reasoning programs, as would humans, typically wander aimlessly through an enormous set of possible conclusions and may, after far too much time, fail.

Basic Energy Sciences-supported research at Argonne resulted in the development of several key strategies for automated reasoning programs. These strategies have been adopted as fundamental methods by other program developers in this rapidly expanding field. One such strategy, called the *set of support* strategy, directs a reasoning program to focus intensely on the important specific information about a problem under consideration, and to largely ignore extraneous background information of a more general nature. The set of support strategy is regarded by scientists in the field as the most powerful strategy currently available and is heavily in use today by almost all researchers involved with automated reasoning or automated theorem proving. Many problems in abstract mathematics, for example, cannot be solved without employing the set of support strategy. With it, some of these same problems can be solved in seconds. Without the strategy, a program can draw 20,000 conclusions and yet fail to find a solution, but, with it, the program may require drawing only 200 conclusions before solving the problem.

In addition to strategies, the Basic Energy Sciences-funded research developed several key *procedures* to help direct reasoning. One such procedure, *demodulation*, directs the program to re-

write information into a standard form to cope with the problem of alternate and redundant ways of expressing the same meaning. As an example, the terms "my father's brother" and "my uncle" refer to the same person. Using the demodulation procedure, the program would rewrite such information in a standard form, simplifying and consolidating the data.

Researchers also formulated *inference rules*, or small scale strategies, as ways the program can be instructed to reason. One such inference rule, called *paramodulation*, enables the program to understand equality; in particular, various properties of equality, such as transitivity (deducing that $a = c$, knowing that $a = b$ and $b = c$) need not be stated explicitly. The use of this inference rule permits a program to complete assignments in a few seconds that would otherwise require many minutes or hours. Other inference rules developed include *negative paramodulation* and *negative hyperparamodulation* which aid in coping with the problem of reasoning from inequalities, and *hyperparamodulation* which directs the program to avoid taking insignificant steps in reasoning through a problem.

Using these inference rules, strategies, and procedures, the Argonne researchers designed and implemented several very powerful automated theorem and automated reasoning programs. One such program, AURA (Automated Reasoning Assistant), developed in conjunction with Northern Illinois University, is considered the most powerful automated reasoning program to date. The program has been used to evaluate nuclear power plant systems designs to assist in proving that a sequence of potentially dangerous events will not result in the failure of the backup system. Another program, ITP (Interactive Theorem Process), can be used on different machines and is considered the most flexible and portable automated reasoning program available.

Over the past decade, these programs have been used to solve a number of practical problems faced by scientists and mathematicians in research and in industry. For example:

- General Motors Corporation has collaborated with Argonne scientists in applying automated reasoning techniques to the problem of sequencing cars with different options on the assembly line. The collaborative work resulted in the design of a system that permits the user to experiment with alternative methods for sequencing cars in the most efficient manner. The system combines total reliability with the flexibility to incorporate possible future improvements in assembly line functioning.

- Scientists at the Illinois Institute of Technology have used an automated reasoning program to verify the correctness of the design of a computer circuit used to add two 16-bit numbers together. The logical nature of the arguments supplied by such a program, coupled with the complete history justifying each conclusion, makes reliance on the assistance of a reasoning program most attractive for this application.

- Engineers at Hanford Engineering Development Laboratory have used the Argonne-developed software to select operation modes for the Fast Flux Test Facility (an experimental nuclear reactor).

- Draper Laboratories has collaborated with Argonne on applying automated reasoning techniques to the verification of fault-tolerance properties of the design of an instrument that will enable additional years of service to be obtained from the Department of Energy breeder reactor facility operated by Argonne in Idaho.

Automated reasoning has become one of the fastest growing and most significant branches of computer science. The number of applications for the techniques developed are multiplying daily in many different disciplines. Other countries are devoting substantial national resources to further the development of this field and to search for new applications. In Japan, for example, automated reasoning is the major thrust of the supercomputer development program. The Basic Energy Sciences-supported research at Argonne has contributed significantly to bring progress to its current state and, with continued effort and support, promises exciting new developments for the future.



Engineering and Geosciences

Engineering and Geosciences research aids the development of tools and knowledge essential for improved understanding of our physical world. This gives rise to improved engineering practices, better control over heat and fluid systems, and efficient searches for energy-related resources.

ISOTOPIC GEOLOGY

Who would think that measuring the age of geologically “young” rocks would prove that the world’s continents and its associated seafloors are actually drifting like gigantic rafts on oceans of semi-molten rock? Such was the connection, however, between Basic Energy Sciences research focused on sensitive measurements of the relative abundances of certain atomic species, called isotopes, and the idea of continental drift, today known more formally in the field of geology as plate tectonics.

As a curious observer of a world globe might wonder, the shapes of South America and Africa appear to fit together like pieces of a jigsaw puzzle. Important geological features of both continents, such as rocks of identical age and certain geological uplifts, faults, and mountain ranges, also seem to line up when fitted together.

These observations led to speculations that the two continents long ago were joined as one. Resistance to such notions, however, ran high. There was no known process which could credibly explain how this might have happened.

Then, in the mid-1960’s, the theory of plate tectonics gained almost immediate worldwide acceptance. Compelling evidence emerged from several sources, aided by an instrument developed by Basic Energy Sciences, that confirmed the phenomenon of continental drift.

The theory of plate tectonics holds that the continents and their associated undersea land masses form enormous crustal plates, which collectively “tile” the surface of earth. They float on underlying “oceans” of hot, viscous rock, believed to constitute much of the earth’s interior volume. Convective currents in the upper reaches of this regime are believed to cause the plates to move slowly and continuously.

According to theory, earthquakes evidence the bumping and grinding of plate edges as they rub past each other. Where leading edges collide, one plate may thrust over or dive under another, creating mountain ranges or deep ocean trenches. At trailing edges, where plates drift apart, upwelling molten rock, or magma, forms new crust to fill the spreading gap.

Proponents of this theory felt that the latter phenomenon, called seafloor spreading, might be susceptible to scientific testing. The formation of new crust should be observable, leaving behind a large geologic feature, such as a mid-ocean ridge, thousands of miles in length.

Further, seafloor spreading would exhibit three testable characteristics. First, the youngest rocks would lie closest to the ridge where the new rock was believed to be forming. Second, the age of the seafloor rocks would increase with distance from the ridge. Finally, the age-related patterns observed on one side of the ridge would tend to mirror those on the other.

Credence to this hypothesis was added when oceanographers using sonar located and confirmed the existence of mid-ocean ridges. As the data continued to gather over the years, maps began to trace out long, continuous ridges, rising about 8,000 feet above the seafloor, running along the approximate center of all the earth’s oceans. Curving up and down the globe, joining one ocean with another like seams on a baseball, its total length was eventually determined to be 38,000 miles—more than half again the length of the earth’s equator.

Although the existence of mid-ocean ridges suggested that the seafloor was spreading, persuasive evidence remained elusive. Conclusive proof rested with the task of dating the mid-ocean rocks.

Unfortunately, this task confronted two problems. First, the methods used to gather mid-ocean rocks were rudimentary and unreliable. Second, rock dating instruments at the time were incapable of differentiating among the minute age-related differences in rock properties found among geologically "young" rocks.

In essence, these rocks had aged so little that they were nearly indistinguishable from one another. Existing instruments were better suited to dating rocks 1 to 2 *billion* years old. The mid-ocean ridge rocks, by contrast, were predicted to be less than 5 *million* years old.

Solutions to these two problems arose independently from several sources over a period of many years. Basic Energy Sciences research provided a crucial breakthrough in both.

Concerning the first problem, Basic Energy Sciences research produced the means for accurately dating geologically young rocks with its development of a highly sensitive instrument called a static mass spectrometer. This instrument also contributed to solving the second problem by eliminating altogether the need to recover rock samples from the mid-ocean floor. The age of these rocks could be inferred through the use of a special technique.

Before describing how this technique was applied, an appreciation of the Basic Energy Sciences contribution may be gained by understanding the basic principles of age dating and the capabilities of the static mass spectrometer. Both involve measuring the relative abundances of isotopes, that is, of the various atomic species of the same elemental family.

The principles of dating rocks and other materials by measuring the relative isotopic abundances of elements trapped within are well established. They are based on the fact that certain naturally occurring, but unstable, atomic species systematically transform themselves into elements of more stable forms (daughter products) at precisely known rates. This process, called radioactive decay, acts as an internal source of (daughter product) atom formation.

Since the decay modes are well known, the new atoms add uniquely to the abundance of one or more particular isotopes. This then skews the relative abundances among the isotopes away from their naturally occurring proportions. By measuring these proportions, figuring their variances, chemically analyzing and inferring the amount of parent atoms originally present, and knowing the rates of atom decay and new atom formation, the age of the material can be determined.

Isotopic dating of ancient rocks, those more than 1 billion years old, was routinely accomplished with available mass spectrometers using potassium as the unstable parent and argon as the daughter product. In the case of young rocks, however, nature was not so cooperative. Potassium (^{40}K) decays by one-half its original amount to argon (^{40}Ar) every 1.3 billion years. In young rocks, one-thousandth this age, precious little ^{40}Ar was produced, making reliable measurements difficult.

Existing instruments simply did not have the sensitivity to date rocks which had solidified recently in geologic time. When measuring such minute amounts, contamination by particles inside the instrument was a primary limitation to the sensitivity of a mass spectrometer.

Knowing this, Basic Energy Sciences researchers focused their efforts on building an ultraclean, self-contained instrument capable of making repetitive measurements indefinitely on the same sample, with no moving parts, once the sample had been introduced. Hence, it was given the name "static" mass spectrometer.

The concept that enabled very low contamination to be achieved was an all-glass instrument capable of securing an ultrahigh vacuum that could be completely baked at high temperature, valves and all, to drive off the contaminants. Once the sample (argon gas boiled out of the rock) was introduced, the sealed glass instrument operated continuously on this initial sample, thereby avoiding contamination from pumps and other mechanisms that are normally required to keep argon gas flowing continuously through more conventional, non-static instruments.

In the sealed glass spectrometer, atoms of the sample gas drift randomly into "ionization" chambers in the instrument where, as in conventional spectrometers, they are bombarded by an electron beam and become electrically charged, or ionized.

The resulting ions are accelerated by an electric field, collimated, or restricted to a narrow beam, and the beam is then bent by a strong magnetic field.

In this magnetic field, the heavier ions (^{40}Ar) are bent in a slightly larger arc, owing to their greater momentum than the lighter ions (^{36}Ar). In this way isotopes of differing masses are separated from one another. A detector downstream of the bending magnet signals the counts of each isotope, allowing the determination of the relative abundances.

This new instrument achieved high detection sensitivity by measuring the same gas sample over and over. It was this concept and realization of design, which paid such meticulous attention to reduced contamination, that enabled the extremely small amount of argon gas contained within the young rocks to be measured accurately.

With this instrument, geologists ingeniously solved the problem of dating rocks near the spreading seafloor. They also exploited the fact that molten rock, as it solidifies, retains a remnant magnetism that records the direction of the earth's magnetic field at the time of its solidification.

The earth's magnetic field is in constant motion reversing itself at irregular intervals as many as a dozen times in the geologically short span of 5 million years. A plot of the reversals over time would show a highly unique and distinctive pattern.

Using the Basic Energy Sciences instrument, researchers sampled young rocks of volcanic (molten) origin from lava flows all over the world, dated them precisely, and recorded the remnant magnetism of each dated sample. They meticulously charted over time the changing direction of the earth's magnetic field. This research progressively built up, with increasing resolution as more samples were added, a time-sequenced plot of magnetic field reversals.

For the time period of interest—the last 5 million years—this research produced, with some missing segments, a diagram with unmistakable patterns. This diagram would serve as the reference. Any series of magnetic field reversals which matched these patterns, or a portion thereof, could thus be linked to the diagram and accurately placed on the scale of geologic time.

All the while, oceanographers continued to map the mid-ocean ridges. Using ship-towed magnetometers, they recorded the direction of the remnant magnetism of the seafloor rocks below. They, too, discovered distinct patterns of magnetic field reversals. Importantly, they formed mirrored images on both sides of the ridge.

Hampered by geologic faults and large discontinuities in the rough terrain of the mid-ocean ridges, the patterns which the researchers had hoped might be linked to the time-sequenced diagram were at first inconsistent and inconclusive. Eventually, however, perseverance yielded data with sharper resolution—and one surprise. A previously hidden, unusually brief, magnetic field reversal appeared like a distinctive, identifying “spike” in the magnetometer data from the seafloor. As perversity would have it, the geologic period during which this spike had occurred was one of the few missing segments in the time-sequenced diagram developed by the lava samplers.

Eventually, the lava sample which contained the “spiked” reversed field was found in the Jemez mountains of northern New Mexico, near a creek named Jaramillo. The magnetometer maps from the seafloor had suggested where to look—in lava flows of a certain age—with remnant magnetism pointing in a certain direction. The Basic Energy Sciences instrument confirmed the hunch by accurately dating the Jaramillo rock sample and placing it precisely in the expected position on the time-sequenced diagram of field reversals.

The diagram in this most crucial area was now complete. The data were conclusive. The irregular patterns of magnetic field reversals from the seafloor matched exactly those from the lava samples whose ages had been accurately determined. The identical patterns fixed the ages of seafloor rocks, proved that the youngest rocks were closest to the mid-ocean ridge, and showed that the age of all rocks increased with distance from the ridge. The magnetometers had already revealed the mirrored images on both sides, thus completing the three-pronged proof.

Based on this evidence, the conclusions were irrefutable. The continents, indeed, are adrift. Years later, improved drilling and coring of seafloor rocks independently confirmed these conclusions and extended their validity. With this crowning achievement, the broader theory of plate tectonics

was widely accepted and earth science was revolutionized.

Basic Energy Sciences research, focused on a seemingly unrelated endeavor, provided the crucial instrument that contributed to this advance. Moreover, technical applications of the combination of isotopic studies and geology, known as isotopic geology, are blossoming.

Today, this technology underpins studies of deep portions of the earth's crust, identification of precursors to earthquakes and volcanic eruptions, definition of geothermal reservoirs, and prediction and monitoring of toxic waste migration in aquifers and other geologic formations. Modern geology, in turn, is now returning dividends to energy technology, improving the search for oil, natural gas, uranium, and other minerals.

GAS-LUBRICATED PISTON RINGS

Because of their fuel efficiency and long life, diesel engines have long been chosen over gasoline-fueled spark-type engines for use in heavy-duty trucks. Despite their higher cost and weight, diesels have even made modest inroads into the automobile engine market. A recent invention that promises to bring about major reductions in diesel engine weight and complexity, as well as improvements in efficiency and reliability, may make the diesel an even more solid choice.

The invention involves a radically different concept for the lubrication of piston rings. Piston rings perform the critical job of sealing the hot gases within an engine's combustion chambers. The invention by a Massachusetts Institute of Technology researcher sponsored by the Basic Energy Sciences program is a piston ring that is lubricated by combustion gases blowing between an engine's rings and its cylinders rather than by an independent oil supply as in conventional internal combustion engines.

The reason the engine becomes so much simpler is that much of the cooling system water pump, water lines, thermostat, and radiator can be eliminated. Cooling requirements of internal combustion engines are set by the need to prevent the lubricating oil near the combustion zone from burning up. When oil is no longer needed there, the engine need no longer be cooled by water flowing

through an elaborate system of ducts within the cylinder walls.

Because the rings ride on a cushion of gases that have much lower viscosity than lubricating oil, engine friction—a major contributor to fuel inefficiency at high speeds—is also greatly reduced. Without the lubricating oil limiting its temperature, the engine can also run hotter, thereby improving its fuel efficiency. New ceramic materials that will permit major increases in engine temperature are also being developed by the Department of Energy.

The scientific principles of thermodynamics that show that efficiency increases at higher engine temperatures apply equally to both diesel and gasoline engines, but gasoline engines have a major practical limitation. That is, gasoline would be ignited by hot engine parts before it could get to the proper place in the engine. Thus, the focus has been on engines using various types of diesel fuel, which better resist ignition by hot engine parts.

Recently, however, gas-lubricated piston rings have been considered for another reason—air pollution control. Careful studies of the combustion inside an engine show that pollutants tend to be generated most near relatively cold metal surfaces. By reducing the need to cool the cylinder walls, it appears that gas-lubricated piston rings will permit engines to run cleaner.

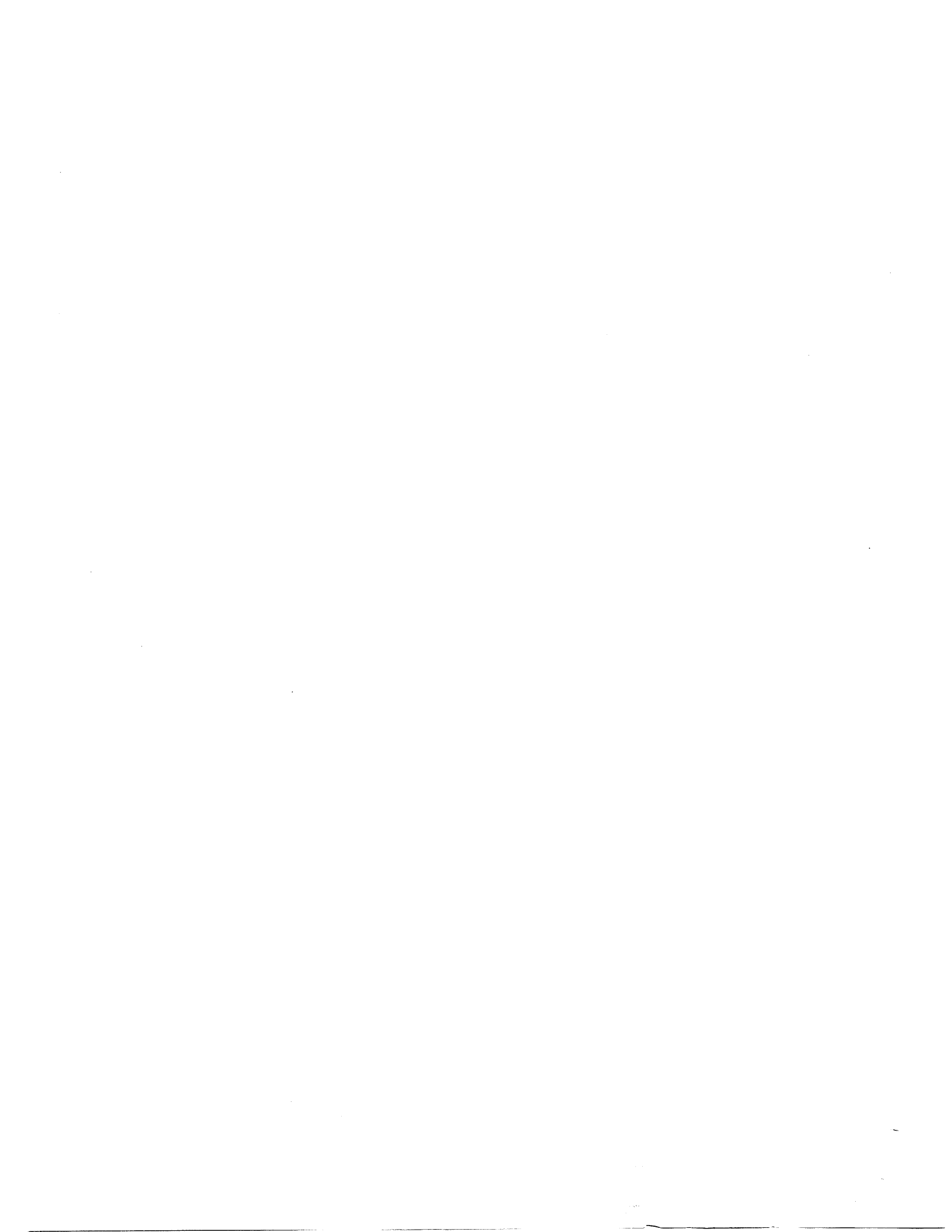
In the patented MIT design, the piston ring has a cross-section like a mushroom, with the stem part extending into the piston grooves. When this oddly-shaped ring twists under load, the rounded mushroom head maintains the curved, lifting surface close to the cylinder wall and allows a thin layer of combustion gases to flow between the two surfaces. The tolerance of the design is tight. The ring must ride close to the wall in order to prevent excess gas leakage, yet must not expand to seal the gap between piston and cylinder. The amount of gas required for lubrication is very small so that no more combustion gas leakage occurs than with oil-lubricated rings.

Many engineering hurdles remain before gas-lubricated piston rings are commercially feasible, but the idea of an engine lubricated by something other than oil with its relatively high friction and associated cooling systems is so attractive that the Cummins Engine Corporation has proceeded into a design and test program for heavy-duty diesel engines. NASA is also interested. The very low fric-

tion attainable with such rings may have applications for equipment operating in space.

If the commercial development is successful, it will be possible to make diesel engines smaller and

lighter than current spark ignition engines to go along with their already superior fuel efficiency and longevity. These improvements could produce major savings in the cost of auto and truck transportation.



Advanced Energy Projects

Advanced Energy Projects explore the feasibility of novel, energy-related concepts as they emerge from basic research. Through such research, new ideas acquire better definition and proven potential, facilitating their transition into the applied technology realm.

PLASTIC BATTERIES

Until 1987, the billions of batteries that had been marketed in myriad sizes and shapes all had one thing in common. To make electricity, they depended exclusively upon chemical reactions involving metal components of the battery. But today a revolutionary new type of battery is available commercially. It stores electricity in plastic.

Plastic batteries are the most radical innovation in commercial batteries since the dry cell was introduced in 1890. Plastic batteries offer higher capacity, higher voltage, and longer shelf-life than many competitive designs. Companies are testing new shapes and configurations including flat batteries that can be bent like cardboard. Researchers expect that the new technology will free electronic designers from many of the constraints imposed by metal batteries such as limited recharging cycles, high weight, and high cost.

The development of plastic batteries began with an accident. In the early 1970's, a graduate student in Japan was trying to repeat the synthesis of polyacetylene, a dark powder made by linking together the molecules of ordinary acetylene welding gas. After the chemical reaction took place, instead of a black powder, the student found a film coating the inside of his glass reaction vessel that looked much like aluminum foil. He later realized that he had inadvertently added much more than the recommended amount of catalyst to cause the acetylene molecules to link together.

News about the foil-like film reached Alan McDiarmid of the University of Pennsylvania who was interested in non-metallic electrical conductors. Since polyacetylene in its new guise looked so much like a metal, McDiarmid speculated that it might be able to conduct electricity like a metal as well. McDiarmid invited the student's instructor to join his team in the United States, and this collaboration soon led to further findings. The University of Pennsylvania investigators confirmed that polyacetylene exhibited surprisingly high electrical conductivity.

Scientists recognize that various materials can conduct electricity in different ways. In metals, electricity is simply the manifestation of the movement of free electrons that are not tightly bound to any single atom. In semiconductors, like those that make up transistors and other electronic devices, electricity is the drift of excess electrons to form a negative current or, alternatively, the drift of missing electrons or positive "holes" in the opposite direction to form a positive current. Typically, the excess electrons or the holes are donated by impurity or dopant atoms.

McDiarmid's team reasoned that the ability of polyacetylene to conduct electricity was probably promoted by trace impurities contributed by the catalysts involved in the Japanese student's process. In their laboratory, McDiarmid's team confirmed that it was possible to chemically dope polyacetylene to create either mobile excess electrons or holes. That these electrons and holes could move explained how polyacetylene was able to conduct electricity.

When polyacetylene was exposed to traces of iodine or bromine vapor, the thin polymer film exhibited still higher electrical conductivity. The researchers discovered that by purposefully adding selected impurities to polyacetylene, its electrical conductivity could be made to range widely—behaving as an insulator, like glass, to a conductor, like metal. The discovery that plastics can behave

like metallic conductors and semiconductors was a chemistry first.

The key breakthrough leading to practical application as batteries occurred in 1979 when one of Professor McDiarmid's graduate students was investigating alternative ways for doping polyacetylene. He placed two strips of polyacetylene in a solution containing the doping ions and passed an electric current from strip to strip. As expected, the positive ions migrated to one strip and the negative ions to the other. But when the current source was removed, the charge remained stored in the polyacetylene polymer. This stored charge could then be discharged if an electrical load was connected between the two strips, just as in a conventional battery.

Chemically, the plastic battery is different from conventional metal-based rechargeable batteries in which material from one plate migrates to another plate and back in a reversible chemical reaction. In a conducting plastic battery, only the stored ions of the solution move—the plates are not consumed and reconstituted. Since conventional battery life is limited by the number of times the plates can be reconstituted, this difference portends a longer recharge-cycle lifetime for the plastic batteries.

One potential application for polymer batteries is in battery-powered automobiles. Two key measures of a battery's suitability for automotive application are the power density, which determines acceleration and hill-climbing ability, and the energy density, which determines the number of miles that can be driven between charges. Polyacetylene's power density is 12 times that of ordinary lead acid batteries. Its energy density is also higher—about 50 watts-hours per kilogram versus

35 for lead acid batteries. Although plastic batteries are competing against other advanced development batteries with similar capability for this application, they have the unique potential to be made of low-cost, environmentally-benign materials. Supporters feel that a polymer battery can be part of the battery-powered car of the future.

Polyacetylene, however, is not an ideal battery material. It degrades in air, is chemically stable only in liquid solutions, and is brittle and not amenable to injection molding methods used for forming plastic parts in production. The University of Pennsylvania team, along with industrial associates licensed to use their technology, searched for conducting polymers of greater structural strength, thermoplasticity, flexibility, and lower costs. Allied Corporation synthesized a new material, polyparaphenylene, a black powder capable of being formed into plates by hot pressing, that could be doped to conduct electricity. Several other potentially suitable plastics were discovered thereafter.

One such material was polyaniline. In 1984 and 1985, the University of Pennsylvania group received patents on the use of this material for rechargeable batteries. It is inexpensive, and, unlike polyacetylene, it is stable in both air and water. Polyaniline is the material used in the plastic batteries that first became commercially available in 1987.

In just 8 years, plastic batteries went from laboratory discovery to commercial availability, a remarkably fast evolution. With advances continuing at a rapid pace, there are great opportunities for increasingly important applications of this new technology.

Energy Biosciences

Energy Biosciences research aims at providing scientific knowledge and improved understanding of biological principles, mechanisms, and organisms. It helps guide the development of renewable energy systems, bioconversions of organic matter to fuels and chemicals, and supplies background genetic and biochemical information in support of future energy technologies.

OLIGOSACCHARINS: PLANT CELL MESSENGERS

The genetic material within each cell of a garden plant is the source of the directions on how that cell develops. But it is well known that this genetic material is the same in practically every one of the multitude of cells that make up a plant. How then does it happen that cells develop differently, so that plants have roots, stems, leaves, and flowers? The answer is that different portions of the genetic material are "turned on," or expressed, in the various cells. A system of chemical messengers turns on the genetic material for forming leaves in some cells and for forming roots in others.

Basic Energy Sciences researchers at the University of Georgia shed considerable light on the identity of one family of chemical messengers. The findings are causing a significant amount of rethinking about plant growth. The accomplishment was an astonishing result of two Basic Energy Sciences studies of the plant cell, neither of which was originally related to the ultimate outcome. One study had to do with the structure of the plant cell wall, and the other was related to a plant's defense against disease.

Probably the best known component of the plant cell wall is cellulose. Chemically, it is a long chain of a single kind of molecular unit called glucose, one of the family of sugar molecules. Cellu-

lose chains form fibers that make the cell wall strong and stiff.

But as it came to be learned, the cell wall has components structurally more interesting than cellulose. The cellulose fibers are embedded in a matrix of other polysaccharides. Compared to cellulose, the matrix is more complex. For example, molecules of the matrix not only form chains, but also have branches of various lengths connected to the chains at any of a number of possible positions. And, unlike cellulose which is formed by many repeats of a single sugar, glucose, the matrix polysaccharides are each composed of between five and ten different sugars. The variety of combinations of the sugars in the matrix polysaccharides is large.

The discovery of the chemical complexity of the cell wall matrix led to questions about the functions that it might perform. By coincidence, the same research group was working on a seemingly unrelated Basic Energy Sciences project that suggested the direction for the answers. This research was aimed at elucidating the signal that informed the plant when it was being infected by a fungus, for when a fungus infects a plant, molecules akin to antibiotics, called phytoalexins, are produced by the infected plant. What feature of the fungus is recognized by the plant cell to trigger the production of the phytoalexins? The researchers found the answer among the fungus cell wall's matrix molecules.

In one series of experiments, a mixture of oligosaccharides (short chains of glucose units) taken from the cell wall matrix of the fungus was applied to plant cells. It was determined that oligosaccharides fragments of infecting fungal cell wall caused the plant to begin making phytoalexins. Although oligosaccharides had been studied for many years, it had not been suspected that some of them could signal such plant cell reactions. Oligosaccharides with biological regulatory activity have been called oligosaccharins.

The next task was to determine which specific oligosaccharide from the fungus cell wall caused plant cells to make phytoalexins. Because the number of different arrangements of oligosaccharides in the fungal cell wall material under investigation is so great, the subsequent project—the search for the active oligosaccharide—proved to be extremely challenging.

First, the oligosaccharides were separated according to the number of glucose units they had. It was determined that the smallest fungus oligosaccharide capable of stimulating the synthesis of phytoalexins was made up of seven glucose units. But the fungal cell wall matrix had more than 300 seven-glucose oligosaccharides, that is, the seven glucoses were arranged in more than 300 different patterns. The much more thorny question, then, and one which would require almost 10 years and great advances in analytical instrumentation to answer, was which one of these 300 different oligosaccharides activated phytoalexin production in the plant cell.

This task was particularly difficult because the oligosaccharides, though different structurally, are very similar chemically. Several of the oligosaccharides had a backbone chain made up of five glucose units with two single glucose branches attached. These oligosaccharides differed from one another only in where the branches were attached to the backbone.

Beginning in 1974 and continuing until 1983, researchers attempted to isolate and purify the oligosaccharide that stimulated the phytoalexin response. Finally, in 1983, 50 millionths of a gram (about one-tenth of a grain of salt) of the active oligosaccharide—the oligosaccharin—was successfully purified. Thanks to advances in analytical instrumentation, this small amount was enough to decipher the structure of the oligosaccharin molecule—an accomplishment that was impossible with 1974 technology, which demanded much larger samples.

The results established that a plant (in this case soybean) recognizes and responds to a specific oligosaccharide structure. The branch positions determine which oligosaccharide is capable of stimulating a response in plant cells. The presence of only a billionth of a gram of the active form is enough to

cause the plant to synthesize phytoalexins which then inhibits the growth of the fungus from which the oligosaccharide originated. The plant cell is thus protected from further effects of the fungus.

Once it was recognized that oligosaccharides play a key role in eliciting defense responses, the possibility that they might stimulate the development of the various parts of plants was also addressed. Several different mixtures of oligosaccharides were added to slivers of tobacco-plant stems, called explants, growing in a tissue culture medium. One mixture was found to inhibit flowering and stimulate prolific budding for new leaves. In the presence of a different mixture, other explants that normally formed buds for new leaves formed flowers instead. Still another oligosaccharide mixture caused explants that would ordinarily have formed buds for new leaves to form prolific roots. It was found that the oligosaccharides were effective in impressively low amounts and that oligosaccharides with very specific structure were required to observe the regulatory activities. The oligosaccharin that induces flowers has been purified and structurally characterized. The small active molecule in this case consists of 10 sugars.

Thus, Basic Energy Sciences research revealed that oligosaccharides obtained from the plant cell wall can serve as a powerful family of chemical messengers. Although similar chemically, they exhibit broad structural diversity with different structural forms delivering different messages that turn on or express the genetic material that regulates plant function. The functions include growth, defense against disease, and cell differentiation in the course of development; i.e., whether to form roots, stems, leaves, or flowers.

While the mechanism by which oligosaccharins influence expression is not yet fully resolved, researchers are already exploring applications of important potential benefit. One day it may be possible to spray specific oligosaccharins on plants to tell them to flower; to form seeds, fruits or tubers; to become resistant to a disease or an insect; to drop their fruit; to grow faster; or to become bushier. Oligosaccharins may eventually have a profound impact on agricultural productivity and on the production of renewable resources for fuels and chemicals.