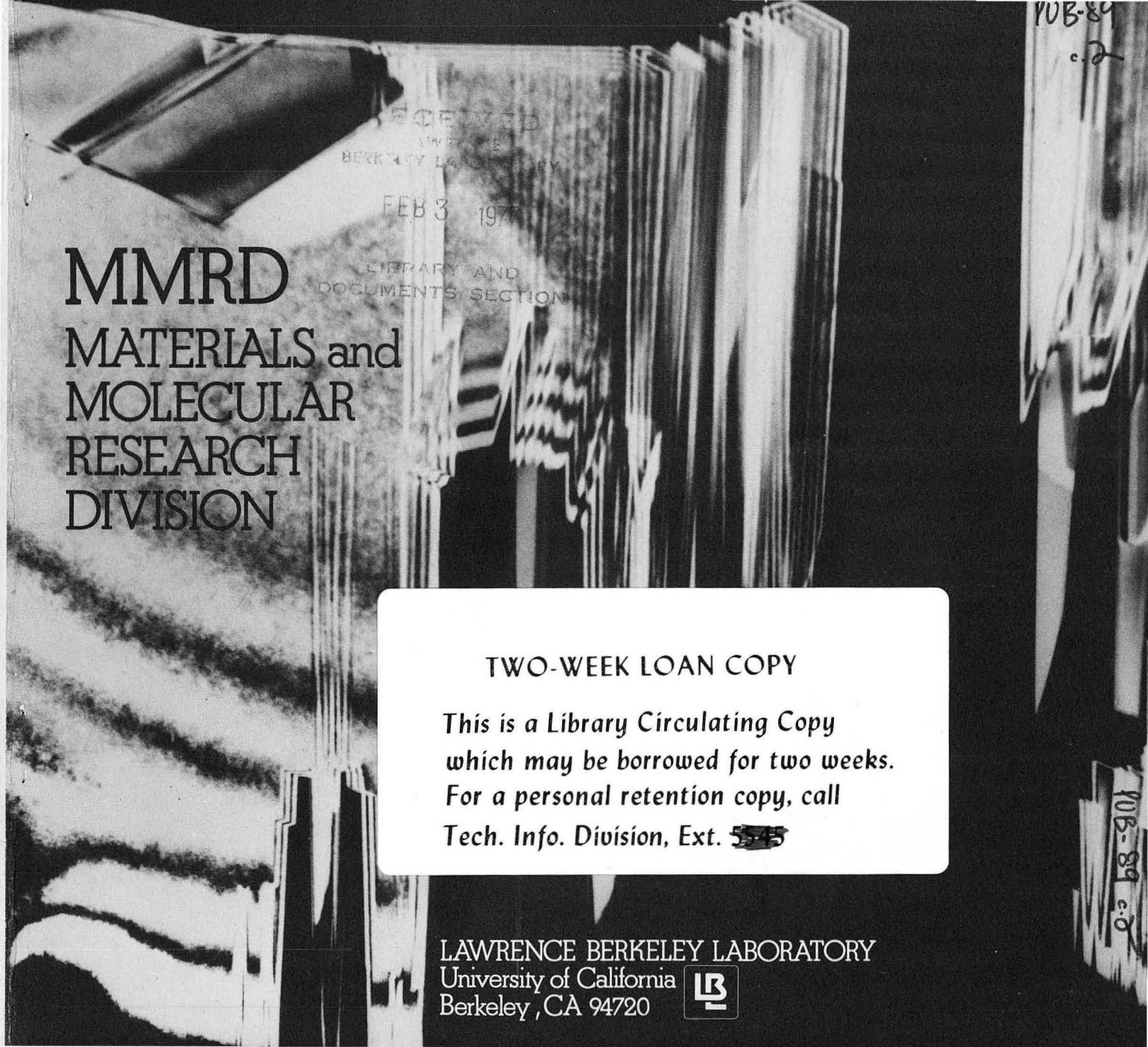
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COVER:

Electron micrograph of the complex twin and fault structure in β-silicon carbide, a refractory ceramic.

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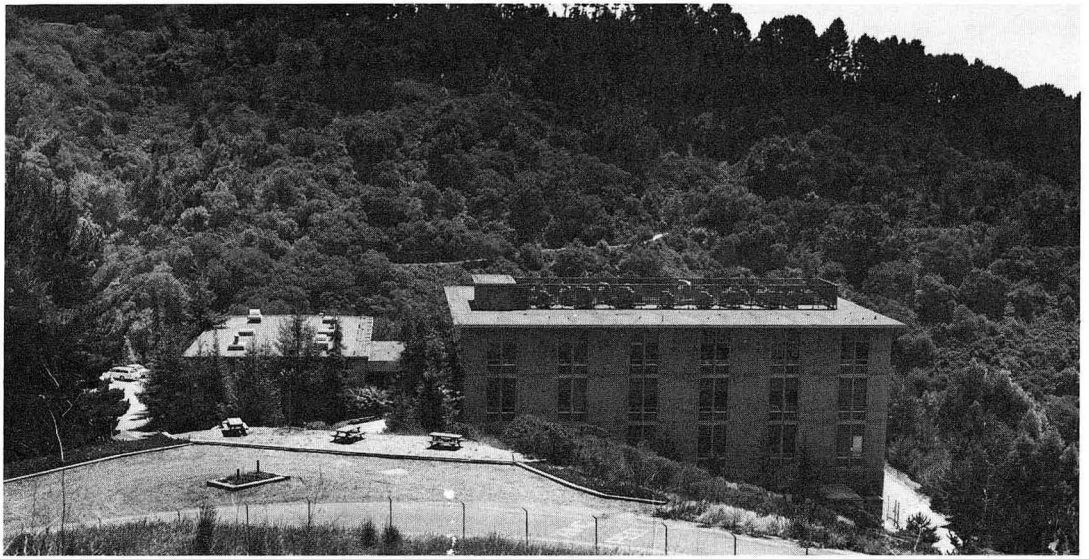

MMRD

MATERIALS and MOLECULAR RESEARCH DIVISION

David A. Shirley
Division Head

Rolf H. Muller
Assistant Division Head

Conway V. Peterson
Business Officer

LAWRENCE BERKELEY LABORATORY
University of California
Berkeley, CA 94720

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Introduction

Understanding the behavior of materials and the details of molecular processes is central to the development of new energy resources. Research conducted in the Materials and Molecular Research Division (MMRD) of the Lawrence Berkeley Laboratory is concerned with the physical and chemical aspects of the behavior of materials and of chemical processes. MMRD was created in 1975 by merging the Laboratory's Inorganic Materials Research Division—set up in 1960—with molecular sciences and actinide chemistry research groups from other Divisions. The Lawrence Berkeley Laboratory is operated by the University of California, with primary financial support from the U.S. Energy Research and Development Administration.

Development of any of the widely discussed new sources of energy requires innovations in materials as well as improved understanding of the chemical processes by which we prepare and consume fuels. For example, new ceramic materials are needed to make more efficient electricity-generating turbines, while high-temperature and catalytic chemical reactions must be better understood in order to produce clean fuels from coal.

Because materials are complex substances and their uses are diverse, a multidisciplinary approach is required to study them effectively. In MMRD, groups of researchers in various technical fields—chemistry, metallurgy, ceramics, solid-state physics, atomic physics, chemical engineering, mechanical engineering, and nuclear engineering—focus their attention on projects concerning the preparation, structure, and behavior of materials and systems. In all this diversity, there is a community of problems and techniques that unites the disciplines and leads to cooperation and interchange of ideas.

Over the years, the Division has been fortunate in having three innovative directors—all outstanding scientists and administrators. Professor Kenneth Pitzer was the first. One of the nation's top chemists, he became head of the fledgling division in 1960, setting its direction. When he left a year later to become president of Rice University, leadership passed to a versatile scientist, Professor Leo Brewer, with Professors Alan Searcy and Victor Zackay as associate division heads. The Division flourished in this period and became well-known in several fields. In 1975, after serving as division head for 14 years, Professor Brewer resigned to return to teaching and research, handing the reins over to Professor David Shirley, a leading researcher in solid-state physics and molecular spectroscopy.

With a staff of outstanding research scientists, most of whom are also faculty members of the University of California, MMRD provides a unique environment for instruction at the graduate level. Several hundred graduate students in the University's engineering and physical science departments have received part of their training in the Division's laboratories. In 1975, MMRD research programs were directed by 47 principal investigators with a staff of 116 postdoctoral and other scientists; 245 graduate students; and 66 technical, administrative, and clerical support personnel. Their work this year resulted in 297 publications in journals and books, 36 doctoral theses, and 23 master's theses.

Brief descriptions of current research interests of the principal investigators are contained in the following pages.

Contents

CONTINUED

Physical Chemistry

PHOTOELECTRON SPECTROSCOPY

Studying the structure of matter by photoelectron spectroscopy is a major research interest of Professor David A. Shirley. In this research, the positions and character of occupied molecular orbitals are determined by binding-energy and cross-section measurements. Similar studies in solids yield the densities of states of occupied valence bands – the solid-state analogue of molecular orbitals.

Many new binding energies crucial to understanding the stability, bonding, and properties of materials continue to be determined by the group. Studies cover metals, semiconductors, insulators, and molecules—even high-temperature species. The information obtained by electron spectroscopy is directly relevant to energy research and development, as is widely recognized, through its contributions to knowledge of surfaces, catalysis, and materials.

Work done under Professor Shirley's direction, plus the impressive array of various kinds of spectrometers that has been assembled over the years, have given this project a leadership position among American electron spectroscopy laboratories. Current projects include research at the Stanford electron-positron storage ring, where the group is studying the angle-resolved photoemission from metal single-crystals and the orbital structure of chemisorbed molecules on catalysts.

PHYSICAL CHEMISTRY, WITH EMPHASIS ON THERMODYNAMICS

Current research interests of Professor Kenneth S. Pitzer include theoretical and experimental investigations involving quantum and statistical mechanics and thermodynamics, as well as spectroscopy and calorimetry. The goal is a deeper understanding and more effective prediction of the thermodynamic properties of physical and chemical systems.

In an on-going program, practical equations for predicting properties of aqueous electrolytes over wide ranges of composition, temperature, and pressure are being developed; this has been accomplished with respect to properties at room temperature, and up to 300°C for NaCl. Success in using these equations has led to their recent application to problems in geothermal energy development. A major effort of the group is now directed toward predicting the chemical and engineering thermodynamic properties of geothermal brines. Such equations will also be of great value in other scientific and technological areas.

Studies of the effect of relativistic terms on the properties of heavy atoms and ions have provided some interesting results (even in the early stages of developing a relativistic quantum chemistry) in that certain otherwise anomalous properties are explained, such as the marked difference between xenon and radon fluorides. A more general and quantitative quantum chemistry for molecules containing heavy atoms is being developed and applied.

Other recent investigations have included a study of the three nuclear-spin species of CH_4, the catalysis of their interconversion by O_2, and their effect on solid-state properties down to 0.3°K, as well as studies of molecules with special internal motions, including XeF_6 which displays a two-dimensional pseudorotation.

DYNAMICS OF ATOMIC AND MOLECULAR PROCESSES WITH CROSSED MOLECULAR BEAMS

Using the method of crossed molecular beams, Professor **Yuan T. Lee's** research group is investigating the dynamics of elementary atomic and molecular processes; their work provides detailed information about interaction potentials, the nature of inter- and intra-molecular energy transfers, the disposal of reaction energy and angular momentum, lifetimes of reaction intermediates, and reaction dynamics. Most of the information on atomic and molecular processes is derived from measurements of angular and velocity distributions of molecules scattered from single collisions with well-defined initial conditions.

Research problems include the chemistry of hydrogen, deuterium, and halogen atoms; fast reactions of oxygen with species involved in combustion processes; and the properties of electronically excited metastable and high-Rydberg state rare-gas atoms.

With the collaboration of other research groups, Professor Lee is also actively engaged in the investigation of atmospheric chemistry, surface chemistry, and electronic and ionic processes, using the molecular-beams method. Recently, the group has begun to use this method as a tool to synthesize new radical molecules. They also are developing efficient laser-molecular beam isotope-separation schemes.

CHEMICAL DYNAMICS STUDIES WITH ION-MOLECULE COLLISIONS

The research goal of Professor **Bruce H. Mahan** is to derive fundamental and practical information about chemical kinetics from the study of collision processes that involve ions and molecules in the gas phase. Emphasis is on simple systems where the interaction of experiment and theory can lead to effective methods of predicting the behavior of complex reacting systems. Among the systems studied are those important as impurities in hydrogen plasmas; thus experiments and theoretical models lead to information of practical value in assessing energy transfer and loss processes, and impurity generation and removal in controlled thermonuclear devices. In addition, a more general fundamental understanding of reaction dynamics is achieved.

Recently completed are studies of the N^+-H_2 and CO_2^+ - H_2 systems. Comparison of results with the predictions of electronic state correlation diagrams proves this method to be a fast and accurate way of anticipating the nature of the detailed dynamics of chemical reactions.

Crossed molecular beam equipment is used to study the dynamics of chemical reactions.

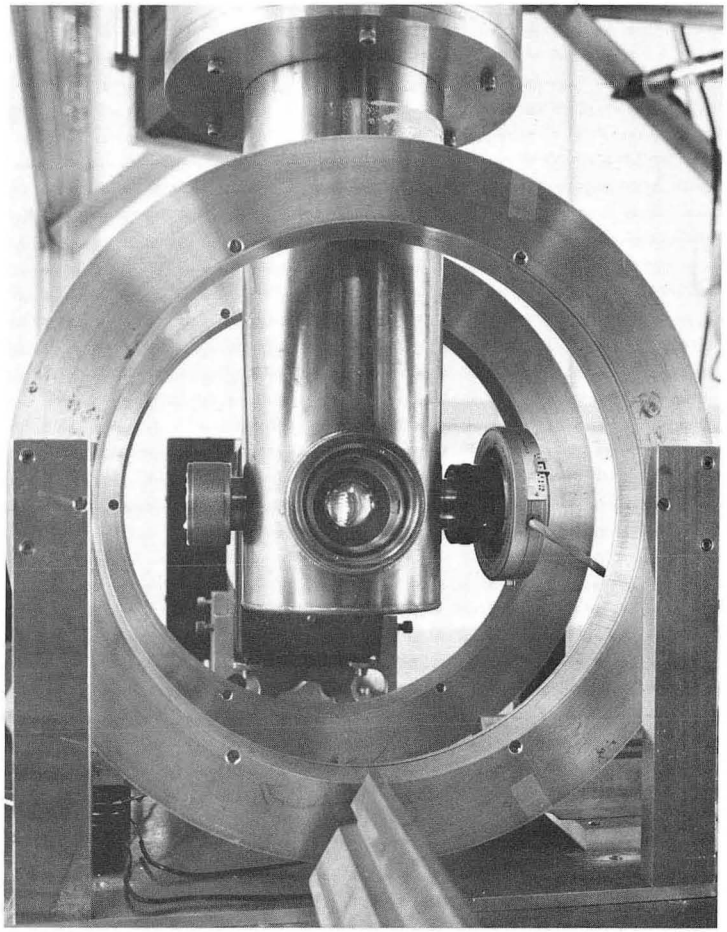
PHOTOCHEMISTRY OF MATERIALS IN THE STRATOSPHERE

Understanding the environmental impact of aviation in the stratosphere is the goal of research undertaken by Professor **Harold S. Johnston.** Ozone, an exceedingly unstable chemical substance, is chemically destroyed by a large number of molecular species including some derived from jet-fuel combustion. In several instances, this destruction is catalytic so that one part of stratospheric pollutant per thousand parts of ozone may be considered a large amount. Laboratory investigation and computer modeling both are being applied to studying the role of chemical catalysts in the destruction of atmospheric ozone.

Recent studies made by the group on the distribution and persistance in the stratosphere of carbon-14 from 1961-62 nuclear bomb tests, have provided verification of models of stratospheric motion that had been used to calculate the effect of supersonic transports on ozone.

ENERGY TRANSFER PROCESSES IN ORGANIC SOLIDS

Professor **Charles B. Harris's** research group has been studying the various mechanisms important in the transfer of energy in the band states of molecular solids, and interactions important in redistributing the energy in photoexcited states of aromatic hydrocarbons to surface states of metals and semiconductors. In their work they utilize various types of experimental techniques such as optically detected magnetic resonance and picosecond laser spectroscopy, and are developing new methods for studying bulk and surface states of molecular solids.



Low-temperature apparatus for optical microwave double-resonance experiments to study energy transport in molecular crystals. The emission seen at center is phosphorescence from an exciton band.

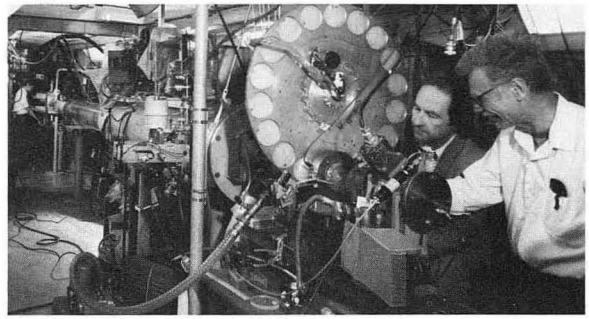
MOLECULAR AND ELECTRONIC STRUCTURE

Professor Rollie J. Myers is using electron paramagnetic resonance and other spectroscopic and magnetic techniques to determine the molecular and electronic structure of molecules; investigations are made on solids down to 1°K and on liquids and gases near room temperature. Particular attention is being paid to transition-metal complexes and compounds that are important as catalysts for industrial and biological processes. Examples are the iron-storage protein, ferritin, as well as compounds that are potential catalysts for production of methane from CO.

Investigation of the magnetic interaction between hydrated transition-metal ions has shown that the interaction falls into a simple pattern which can be explained by the bonding orbitals of ions. In addition, the accuracy of the group's molecular field model was confirmed by fundamental calculations.

RADIATION CHEMISTRY

Dr. Warren Garrison's program in radiation chemistry examines the mechanisms of chemical reactions initiated by the absorption of ionizing radiations in systems containing biologically-important organic compounds. Studies are confined to the simpler biochemical species that are well-defined in the physicochemical sense and which can be prepared in a high state of purity. Substances under investigation include amines, acylamines, amino acids, oligopeptides, and polypeptides. Most of the work to date has been concerned primarily with γ-ray induced reactions in such compounds. These investigations have been expanded to include parallel studies of the radiation chemistry of heavy-ion beams from the 88-inch cyclotron and from the Bevalac facility.



Experimental arrangement for the study of heavy-ion radiolysis at the 88-inch cyclotron.

THEORY OF LOW-ENERGY ATOMIC AND MOLECULAR COLLISIONS

An understanding of atomic and molecular collisions at the molecular level underlies all gas-phase chemistry and molecular physics. A major research interest of Professor William H. Miller is the development of a "semiclassical mechanics" for describing collision phenomena, which include rotational and vibrational excitation, tunneling in chemical reactions, electronic energy transfer, and collisional excitation. The semiclassical approach is the most natural descriptive formalism because atomic and molecular dynamics is largely classical even though quantum effects are frequent. It also is much more amenable to numercial calculation than is the full quantum-mechanical treatment.

Semiclassical scattering theory has already been usefully applied to atomic scattering from crystal surfaces, and preliminary work in the area of atomic and molecular scattering from solid surfaces suggests that the semiclassical approach also may be a simple and more reliable way to analyze low-energy electron diffraction (LEED) measurements. Very recently, the group has made some fundamental breakthroughs in the semiclassical description of eigenvalues of

multidimensional systems, such as vibrational states of polyatomic molecules.

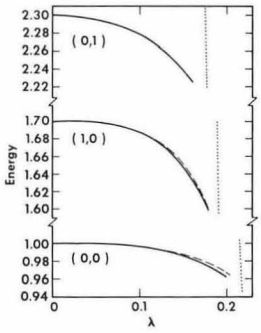
POTENTIAL ENERGY SURFACES FOR CHEMICAL REACTIONS

The goal of the research program of Professor Henry F. Schaefer III is to continue the needed development of theoretical techniques relating to electronic structure and to apply these to problems such as chemisorption on metal surfaces and the reliable prediction of potential-energy surfaces, which are far too complex to be studied by routine theoretical methods.

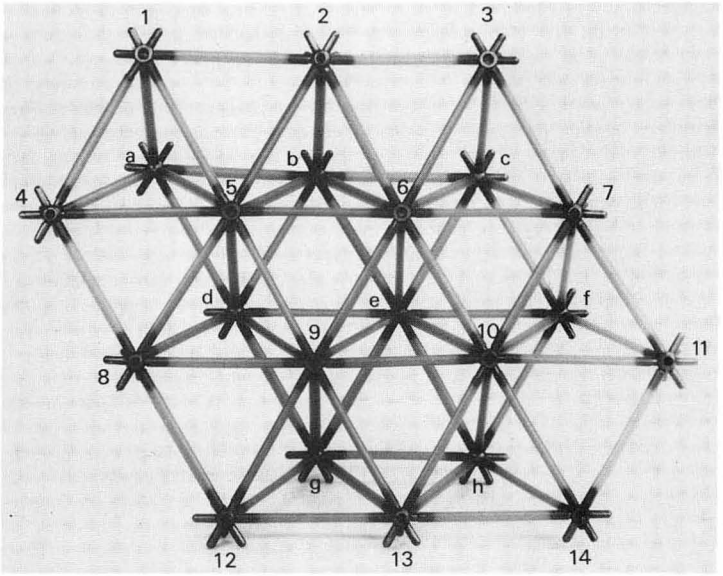
In work on the H_2 - F_2 chemical laser system, a potential-energy surface has been obtained for the exchange reaction H + FH → HF + H. The remarkable feature of this surface is the unavoidable existence of a very large potential barrier, which establishes that atom exchange plays little role in the vibrational relaxation of HF by hydrogen atoms. This barrier does not show up in less rigorous determinations of the surface.

Recently, new research projects have been initiated that involve problems of biochemical interest and the electronic spectroscopy of moderate-size organic molecules.

Model of the Be_{22} cluster used in theoretical study of chemisorption. Distance between adjacent atoms within a layer is 2.2866Å; distance between adjacent atoms in different layers is 2.2255Å. Surface atoms are labeled 1 - 14; second-layer atoms are labeled a - h.



Very little difference can be seen between the semiclassical approximation for three multidimensional systems (broken curves) and the full quantum mechanical treatment (solid curves). In the figure, eigenvalues (energy) are plotted against the strength (λ) of the nonseparable interaction.



Solid State Chemistry

HIGH-TEMPERATURE CHEMISTRY

Professor Leo Brewer's research has centered about the study of materials at high temperatures extending to several thousand degrees Kelvin. The objective is to develop chemical models that will provide predictions of the thermodynamic properties of high-temperature materials, which in turn can be used to predict materials behavior under a wide variety of conditions. The main emphasis in his current work is on the characterization of the thermodynamic properties of binary and ternary transition metal systems.

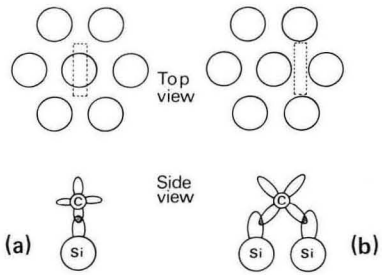
In research designed to improve understanding of the factors that determine the structure and thermodynamic stability of intermetallic phases, a high-temperature solid-electrolyte cell has been constructed; it measures the Gibbs energy of dilution as a function of concentration for strongly interacting transition metal alloys. The results are being related to a general theory of metallic structure and stability which describes the strong interaction between transition metals of the left side of the periodic table with those of the right side in terms of Lewis acid-base interactions. The measurements are designed to provide a titration curve of the activity of a metal as a function of the titration ratio.

As an application of this theory of metallic bonding and structure, the thermodynamics of the 102 binary systems of molybdenum with the other elements from hydrogen to lawrencium has been evaluated and used to calculate the 102 binary phase diagrams. In view of the refractory nature of molybdenum metal, these diagrams should be useful for the adaptation of molybdenum as a structural or container material in many high-temperature applications.

CATALYSIS AND SURFACE REACTIONS ON SOLIDS

Professor Gabor A. Somorjai's research centers on the general field of surface science. Surface studies are carried out using single-crystal surfaces and make extensive use of ultrahigh-vacuum techniques. Surfaces are probed either by electron beams or by beams of neutral atoms or molecules; chemical surface reactions are monitored by means of mass spectrometry or gas chromatography.

His work on the structure of metal, insulator, and molecular crystal surfaces, and of adsorbed gases, presently emphasizes platinum and iron surfaces and organic single-crystals such as naphthalene and amino acids. Another area of interest, catalytic reactions, includes studies of the mechanism of catalysis of hydrocarbon reactions by platinum, and the catalysis of surface reactions involving carbon monoxide,

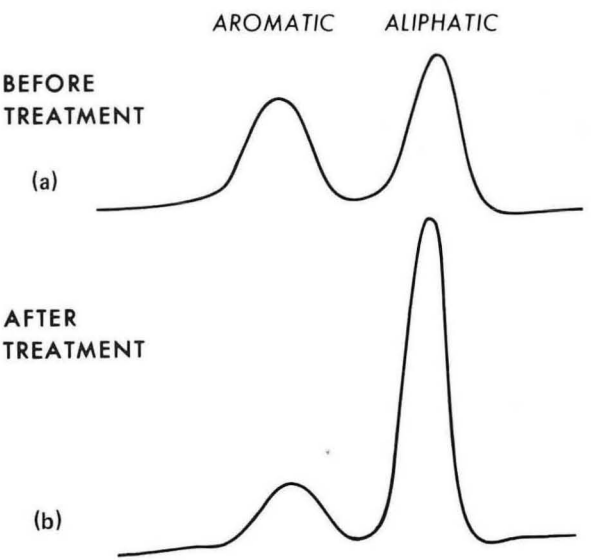


Models of acetylene orientation on the silicon single crystal surface. (a) Acetylene molecule sits on top of the silicon surface atom. (b) Acetylene molecule sits in a bridge position between two silicon surface atoms.

hydrogen, and nitrogen on other metal surfaces (iron, rhodium, and alloys). Auger electron spectroscopy and uv photoelectron spectroscopy are used to examine surface composition and valency, including determination of the surface composition of alloys and the electronic structure of various molecules when they are adsorbed on silicon and platinum surfaces. Also in progress is work toward the development of low-cost silicon photovoltaic cells using heteroepitaxially grown silicon, and studies of light-assisted production of hydrogen from water on oxide catalyst surfaces.

NUCLEAR MAGNETIC RESONANCE OF SOLIDS

Development of techniques for observing high-resolution nuclear magnetic resonance (NMR) in solids, and application of these techniques to problems in chemistry, are the major research interests of Professor **Alexander Pines.** Under way are experiments on the synthesis, structure, and dynamics of liquid crystals. These systems are of interest because they can be used in studies of phase transformations and critical phenomena and can serve as models for biological membranes. Researchers in this group have observed, for the first time, the effects of liquid-crystal transitions on carbon-13 NMR spectra; the improved understanding of nuclear magnetic shielding that resulted has led them to apply NMR to the investigation of structure and dynamics of liquid-crystal phases. The carbon-13 NMR technique can perhaps be applied in the future to find out how organic material is bound in the oil-shale matrix, an issue that is relevant to oil extraction. Recently, the group has been able to identify the ratio of aliphatic to aromatic carbon in coal, which is crucial in determining the usefulness of the raw material as a fuel source.



Determination of carbon content of coal by ^{13}C nuclear magnetic resonance. (a) First resolution of two gross types of carbon, aromatic and aliphatic, in sample of coal. (b) Spectrum of sample treated to enhance the aliphatic to aromatic ratio.

LOW-TEMPERATURE PROPERTIES OF SOLIDS

Professor Norman E. Phillips and his research associates are investigating low-temperature properties of materials, particularly low-temperature heat capacities, to obtain information that contributes to an understanding of the properties of materials in terms of their atomic structure. Measurements are made in magnetic fields to 80 kOe and at pressures to 20 kbar. The temperature range in which heat-capacity measurements are made is from 0.05 to 25°K, and apparatus is being built that will extend the range to the 10^{-3}°K region.

The materials investigated include superconductors, magnetic materials of various kinds, and superfluids, as well as normal metals and dielectric solids. Some recent accomplishments include heat-capacity measurements on α-uranium that gave information related to its unusual superconducting properties, measurements on dilute magnetic alloys that determined the entropy and energy changes associated with the Kondo condensation of the conduction electrons, and measurements of superfluid ^{4}He that showed the occurrence of anomalous phonon dispersion.

HIGH-PRESSURE CHEMISTRY

The research of Professor George Jura concerns high-pressure chemistry. In this program he is determining the electrical, magnetic, and energetic changes in a solid as a result of changes in the volume produced by high pressure. Heat capacities of metals and alloys are measured as a function of temperature and pressure, as well as a quantity proportional to the heat conductivity of the surrounding medium. Improvements in apparatus design have led to greater convenience and accuracy, and to the need for a more sophisticated theory.

Inorganic Chemistry

HIGH-ENERGY OXIDIZERS AND HEAVY ELEMENT CHEMISTRY

Synthetic and structural studies, largely concerned with fluorides and oxyfluorides of the elements, are being directed by Professor Neil Bartlett. The object of his work is to better evaluate the nature of the chemical bond. The approach is purely experimental and emphasizes the synthesis of new materials, the prime concern being the generation of new oxidation states of the elements or new coordination features. The synthetic work is always coupled with structural studies of the new materials and exploits all applicable structural techniques such as x-ray diffraction, nuclear magnetic resonance, electron spin resonance, and vibrational, Mössbauer, and photoelectron spectroscopy. Among the materials produced in the high-energy oxidizer work are new synthetic metals derived from either graphite or boron nitride. The synthetic metals have particular promise as anode materials for batteries or electrical energy storage systems.

SYNTHETIC AND PHYSICAL CHEMISTRY

Research performed by Professor William L. Jolly and his group uses x-ray photoelectron spectroscopy to study a wide variety of inorganic and organometallic compounds. Shifts in the core-electron binding energies are interpreted to clarify the nature of bonding in the molecules and to deduce structures. Such information aids in the synthesis of compounds and in finding applications, such as catalytic processes. Chemical shifts, when combined with the equivalent-cores approximation, can yield the energies of some chemical reactions; the data are of interest to thermodynamicists and others concerned with energy storage cycles and high-energy chemical processes.

The group also synthesizes and characterizes relatively simple but unusual compounds whose properties are hard to explain using present theoretical concepts. By studying such compounds as ONCN, $NaBH_3OH$, and GeH_3COOH, the scientists determine how ideas regarding chemical reactivity must be modified; and thus they can more accurately predict methods of synthesis and properties of unknown compounds.

DYNAMICS OF CHEMICAL REACTIONS

The nuclear magnetic resonance of oxygen-17 is being used by Professor Robert E. Connick to measure the lifetime of water molecules in the first coordination sphere of metal ions in order to study the dynamics of such exchange reactions. In addition to simple aquated ions, various partially complexed metal ions are under investigation; and in favorable cases, the rates of exchange of geometrically nonequivalent waters on the same metal complex can be resolved. Computer simulation of such replacement reactions in solution is being developed to give details of the exchange process that cannot be obtained from experiments.

The basic chemistry of sulfur dioxide and related compounds is under study. Sulfur dioxide is the worst atmospheric pollutant from power generation plants; but surprisingly, many aspects of its basic chemistry have never been worked out. Raman and ultraviolet spectroscopy, NMR, and other physical methods are being used to identify species, obtain thermodynamic data, and establish rates and mechanisms of reactions.

Electrochemistry

MASS AND CHARGE TRANSPORT

Professor Charles W. Tobias is working toward advancing the scientific foundations of electrochemical engineering and widening the range of useful applications of electrochemical reactions.

Of special interest are the effects of convective mass transport and of migration in the electric field on the surface (charge transfer) reactions in electrosynthesis; in the electrochemical extraction, shaping, and finishing of metals; and in galvanic cells. Transport mechanisms of electrolytic gas evolution and of metal deposition-dissolution processes are studied with the aim of improving energy efficiency, controlling surface morphology, and increasing space-time yield.

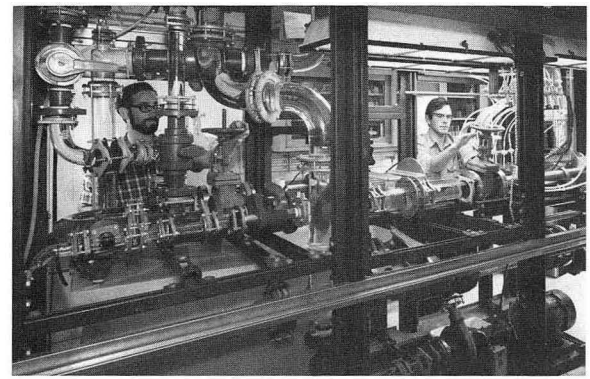
Novel experimental tools developed by Professor Tobias' group include semi-industrial-scale flow cells for the direct observation of mass-transfer boundary layers by double-beam interferometry, and for measurement of the distribution of limiting currents on electrode surfaces in forced and free convection.

To expand the useful applications of electrode reactions, the researchers are exploring nonaqueous ionizing solvents as substitutes for water in ambient temperature electrolysis and galvanic-cell operation. In this work, propylene carbonate has been demonstrated to be suitable for the electrowinning and refining of alkali metals. New solvent-solute systems are being sought to make possible the electroreduction of various transition metals that cannot now be obtained except by high-temperature electrolysis of their molten salts.

ELECTROCHEMICAL PHASE BOUNDARIES

Thin films and boundary layers at electrochemical interfaces are being investigated by Dr. Rolf H. Muller. The purpose is to predict their effect and increase the output and efficiency of electrochemical processes for the storage, conversion, and chemical use of electrical energy. Questions of interest include formation and properties of surface layers in battery reactions, the acceleration of mass transport across boundary layers in electrolysis, and the control of surface forces responsible for the formation of liquid films on metals.

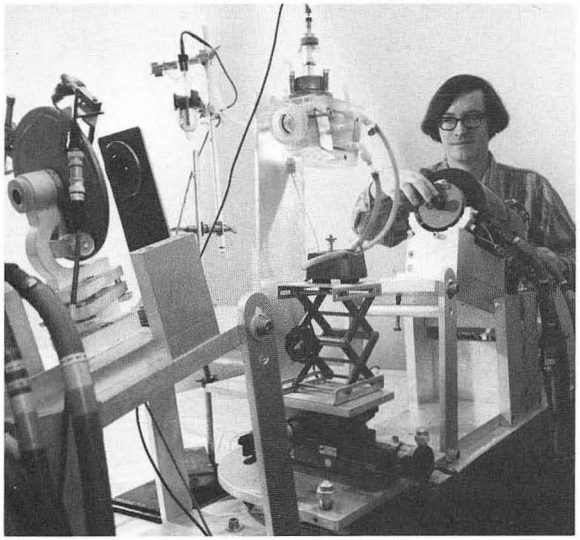
Several unique optical techniques of investigation have been developed for such studies. Among them is an automatic ellipsometer that is capable of observing surface layers ranging from fractional monomolecular coverage to several thousand atoms in thickness, growing at rates up to 2.5 μm/sec, in any transparent medium. Other techniques are optical interferometry, laser Doppler velocimetry, and white-light thin-film interference.



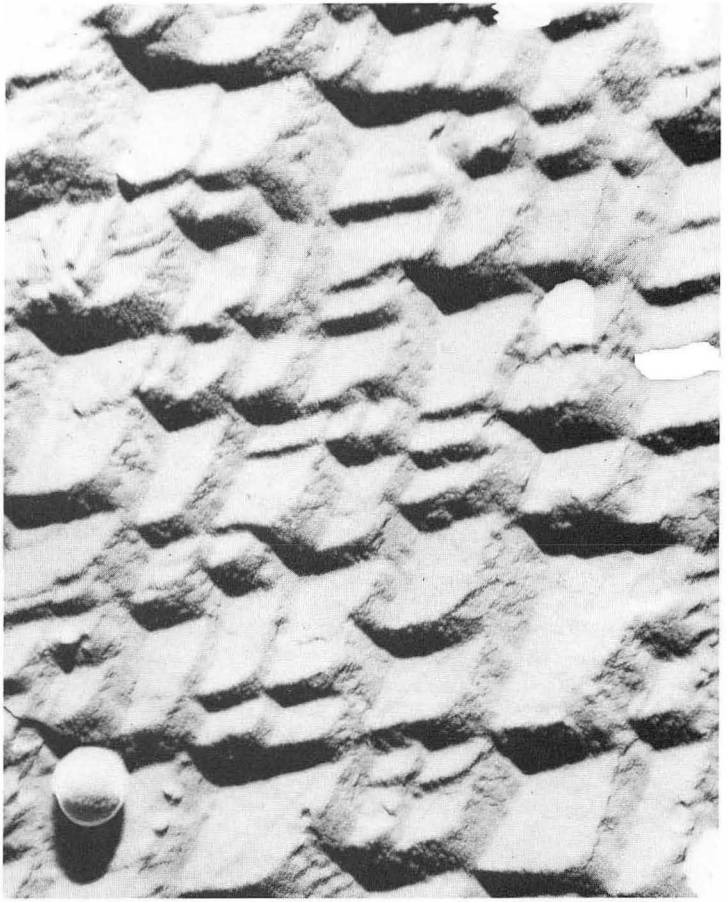
Electrolysis cell and flow circuit developed for studying ionic mass transfer in high-rate electrode processes.

ELECTROCHEMICAL SYSTEMS ANALYSIS

Professor John S. Newman is mathematically simulating electrochemical systems, particularly porous electrodes which are essential components in batteries and which show promise for use in electrochemical reactors for the recovery of metals from dilute solutions. The combination of thermodynamic, mass transport, and kinetic phenomena occurring in these systems defies direct analytical formulation; therefore he is heavily involved with computer work. The objective of this research is to place the design of electrochemical systems, especially batteries, on a more fundamental basis and to optimize energy use and recovery. Other continuing research efforts deal with the physics of fluid flow and mass transport, and with properties of concentrated electrolytic solutions.



Graduate student aligns automatic ellipsometer in a boundary layer measurement.



Electron micrograph of a copper single-crystal surface after electrochemical dissolution.

Nuclear Engineering

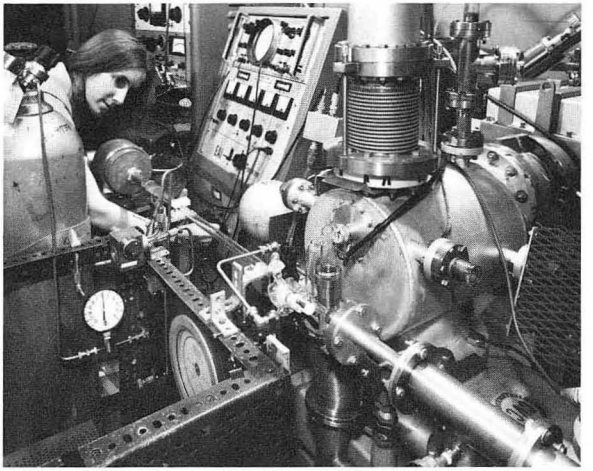
NUCLEAR TECHNOLOGY PROBLEMS

Chemical and materials problems in the high-temperature and intense radiation fields encountered in fission and fusion reactors are the special interests of Professor **Donald R. Olander.** The modulated molecular beam method of studying gas-solid chemical reactions is applied to systems of practical interest such as atomic hydrogen attack on graphite and alumina structural components in fusion reactors.

In other work, a Van de Graaff accelerator is utilized to provide a proton beam for the study of the radiation chemistry of impurity gases in the helium coolant of the gas-cooled reactor. The enhanced chemical reactivity of the irradiated gas leads to accelerated corrosion of the graphite core of the reactor.

Vaporization processes at very high temperature are studied using high-intensity laser pulses as a heat source. This method permits the measurement of vapor pressures of very refractory solids (such as uranium dioxide), which cannot be accomplished by any other technique.

Detailed analysis of the methods of constructing cascades of gas centrifuges has led to novel arrangements which promise to greatly improve the efficiency of uranium enrichment.



Experimental setup for studying the radiation chemistry of impurity gases in reactor coolants.

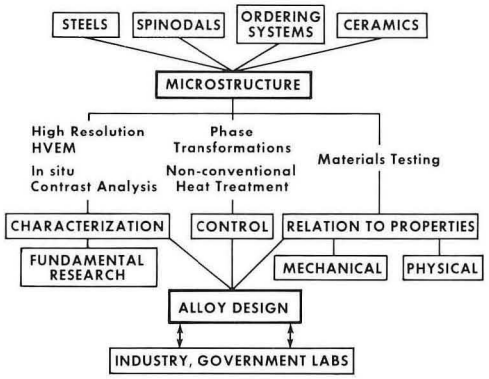
Physical Metallurgy

MICROSTRUCTURE; ELECTRON DIFFRACTION AND MICROSCOPY

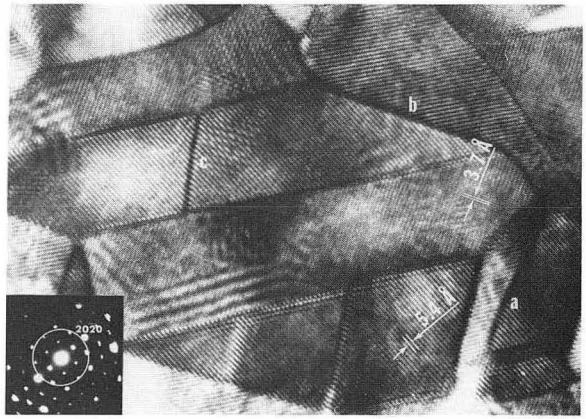
Professor Gareth Thomas is investigating the factors that control the strength and toughness of technologically important structural alloys (steels and spinodal systems). His group has designed experimental martensitic steels having high strength and toughness without tempering after quenching; they have eliminated quench-cracking in high-carbon steels, and have developed new heat treatments for improving the strength of low-alloy steels for use in mining and transportation. Structural investigations of these alloys are carried out mainly by electron microscopy, but x-ray analysis and other techniques also are used.

Experiments using high-resolution transmission electron microscopy will establish at the atomic level the mechanisms of phase transformations and the nature of lattice defects in metals and ceramic materials. High-resolution electron microscopy and lattice imaging are being applied to studies of electron radiation damage and swelling in ordered alloys, and of early stages in ordering.

Research on ceramic materials has developed with the help of high-voltage electron microscopy and work on microstructures and phase transformations in ceramic ferrites; of particular interest is the correlation of microstructure with magnetic properties, especially coercive force. In the high-temperature materials program, studies are being made of the microstructure and mechanical properties of refractory ceramics, notably silicon carbide and silicon nitride, with a view toward their eventual use in high-temperature gas turbines.



Summary of experimental program.



Electron micrograph of ordered Mg_3Cd showing simultaneous lattice resolution of the $10\bar{1}0$ and $11\bar{2}0$ planes and the microdomain substructure. Unit-cell-high steps are resolved at several domain boundaries. Inset shows imaging conditions for this resolution (aperture is circled).

THEORETICAL PROBLEMS IN ALLOY DESIGN

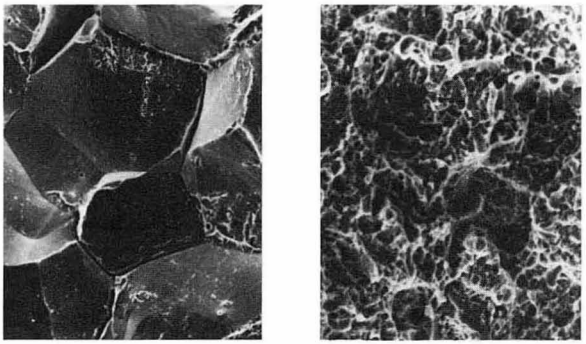
The research interests of Professor J. William Morris, Jr., are two-fold: to develop theoretical understanding needed for the design of new materials and to design new classes of alloys to meet important current engineering needs.

Theoretical research projects in the group address the thermodynamics, phase transformations, and mechanical properties of metals through both analytic studies and direct computer simulation of materials phenomena. Current work includes research on the mechanical equation of state of solids, the computer simulation of dislocation glide, nucleation and growth transformations in simple solids, and the computer simulation and analysis of microstructures.

In alloy design, the group employs modern metallurgical techniques to create new materials having unique properties to meet needs projected for modern systems. Current projects include the design of cryogenic ferritic steels which remain tough in liquid helium; the design of strong, tough nickel-free steels for cryogenic containers; and the design of ultrahigh-strength austenitic steels for use in electrical machinery. Basic experimental research in support of this alloy design effort includes projects on the effect of austenite on the toughness of ferritic steels, on relevant ordering reactions in Fe-Ni alloys, and on the sources of grain boundary embrittlement in Fe-Mn alloys.

DISLOCATIONS, POINT DEFECTS, AND THE PROPERTIES OF MATERIALS

The investigations of Professor Jack Washburn are aimed at more accurate characterization of crystal defects, and at a more complete understanding of their mutual interactions and their effects on materials properties. The following are some recent examples.



Intergranular fracture at -196°C is suppressed in Fe-12Mn-0.2Ti steel by addition of 1% Mo.

The underlying cause of radiation-induced swelling of metals is being studied using a hot-stage in the 650-kV electron microscope to directly and continuously observe the climb of dislocations as they preferentially capture interstitial atoms. Also, the swelling produced in stainless steel and special "low-swelling" alloys by very high fluence (several hundred displacements per atom) is being studied using proton irradiation.

The mechanism of the shape-memory effect in NiTi (Nitinol) is under investigation. It has been shown to be associated with the migration of the accommodation-twin boundaries within the martensite plates and the preferential growth of those martensite plates that are favorably oriented. Below about 6% strain low-temperature deformation is entirely due to these processes and is completely reversed on transformation back to the high-temperature phase.

Ion implantation in silicon results in amorphous zones and high concentrations of point defects. The nature of this damage and the changes that occur

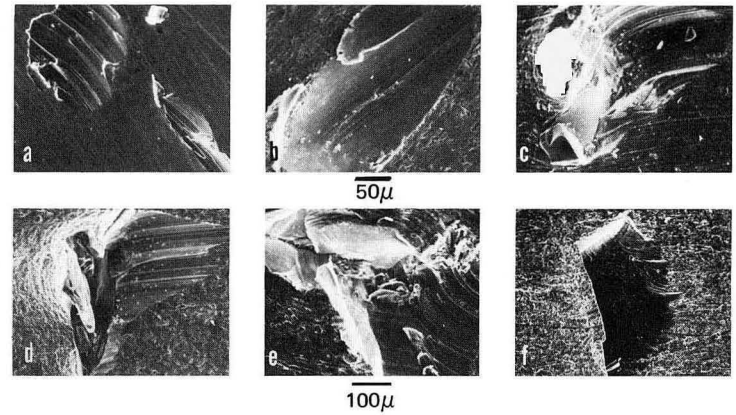
during subsequent annealing are being studied and correlated with changes in electrical properties.

FUNDAMENTALS OF ALLOY DESIGN

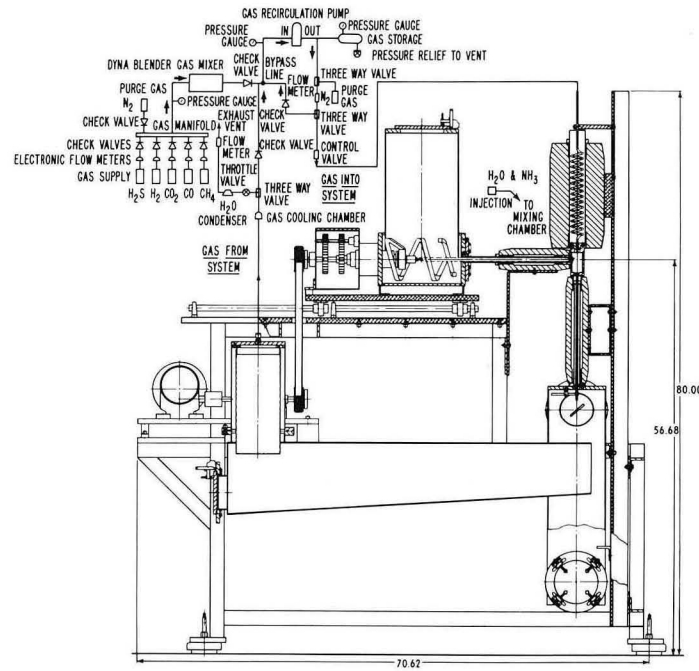
Insight into the relationship between the microstructure of an alloy and its mechanical properties, gained through years of research, has enabled Professors **Earl R. Parker** and **Victor F. Zackay** to design complex, multiphase alloys with superior properties. In this work, microstructure has been controlled through chemical composition and processing treatments to produce materials with unusual mechanical properties, such as alloys having both high toughness and high strength at room or cryogenic temperatures, and alloys having good creep resistance at elevated temperatures. The research groups also have designed model low-alloy steels that have combinations of toughness, strength, and ductility now possessed only by the best of the high-alloy steels. Structural alloys have been designed that contain no carbon; strengthening is obtained by use of stable intermetallic compounds rather than by thermally unstable carbides.

Recently, the research interests have expanded toward understanding the erosion and corrosion of metals and ceramics exposed to liquids and gases at high temperatures, with expectations of eventually providing criteria for materials selection and for synthesis of improved materials.

Also under way are efforts to derive the physical properties of metals by fundamental quantum mechanical methods.



Scanning electron micrographs of various active mechanisms of erosion in a commercially pure aluminum alloy impacted at room temperature by angular silicon carbide particles.



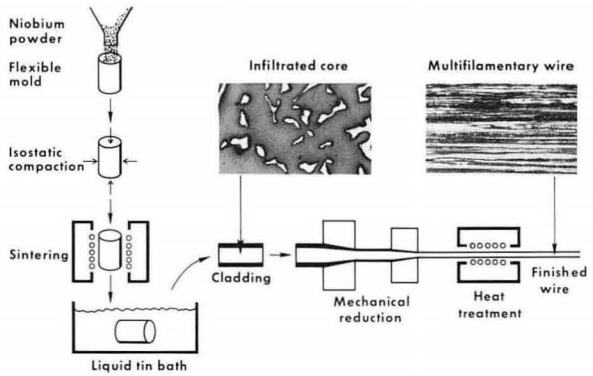
In the erosion-corrosion test device target materials are bombarded with high temperature solid particles entrained in gas mixtures which simulate exactly the compositions and flow rates that occur in coal gasifiers and coal-fired turbine power plants.

POWDER METALLURGY AND HIGH-FIELD SUPERCONDUCTIVITY

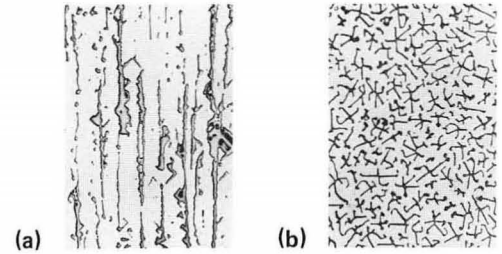
The research of Dr. Milton R. Pickus has focused on alloy and process design, with emphasis on the unique capabilities of powder metallurgy to provide materials essential to new energy systems and advanced technologies. For example, practical high-field superconductors are required in the form of wire or tape; but the best materials (A-15 compounds such as Nb_3Sn) are extremely brittle, making fabrication in the desired form extremely difficult.

A recent accomplishment is high-field superconducting tape and wire containing filaments of Nb_3Sn in a ductile matrix of niobium. The group is now trying to scale up the process to produce wire in kilometer lengths, and to use other A-15 compounds with good superconducting properties.

Use of powder metallurgy as a substitute for machining conserves both energy and materials. The group hopes to make improvements in the powder-metallurgy process so that its advantages are not offset by poor mechanical properties due to porosity, as is now usually the case.



Schematic of the infiltration process for producing multifilamentary superconducting wire.



Microstructure of Al-Si eutectic alloy after unidirectional solidification with growth direction vertical. (a) Longitudinal cross section. (b) Transverse cross section.

STRUCTURE AND PROPERTIES OF CARBON AND COMPOSITE MATERIALS

Glassy carbon, an impervious, vitreous-appearing substance with unique physical properties, is being investigated by Professor Robert H. Bragg. Although glassy carbon is chemically identical with other forms of carbon, wide-range diffraction data indicate it has a quasi-amorphous structure typical of non-graphitizing carbons. Its electrical properties, the most unusual of which is a negative magnetoresistance, are similar to those of small band gap amorphous semiconductors. The aim of this work is to determine the mechanism by which structural changes in this class of materials are induced by heat treatments at high temperatures.

Also under way is an investigation of the structure and electrical properties of eutectic alloys that have been frozen directionally under a steep temperature gradient. Under appropriate conditions, aligned two-phase (in-situ) composites of the Al-$CuAl_2$ and Al-Si eutectics are obtained. The work thus far suggests that the properties of the composite can be predicted if the properties of the individual components, the microstructure, and the prior heat-treatment history are known.

Ceramic Science

HIGH-TEMPERATURE REACTIONS OF CERAMICS

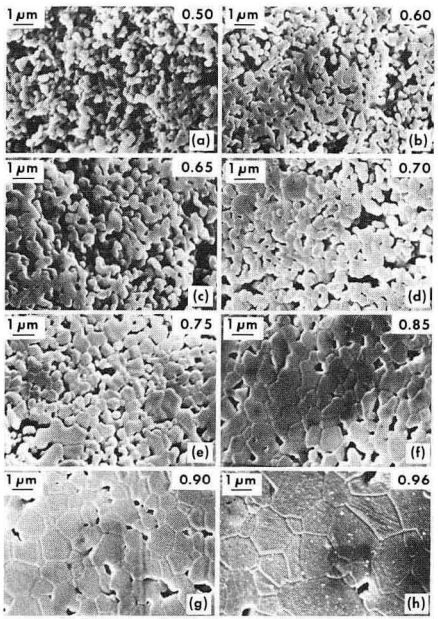
Professor Alan W. Searcy's research includes theoretical and experimental work on the kinetics of decomposition reactions and the transport of gases and vapor through porous solids. Studies of vapors passing through porous alumina disks have furnished the information that some vapors are screened out more than others; applying this principle of selective surface diffusion may provide a practical means for ridding gas mixtures of undesired components – such as SO_2 and H_2S in coal gasification.

He also has found that the slow chemical step of a decomposition reaction is not always a surface step of the gaseous product, as supposed; instead, diffusion or an interfacial step of the solid component may be rate-limiting. Thus in industrial processing, decomposition reactions can perhaps be made to go faster by catalyzing the formation of the stable reaction product. It also seems that rates of some reactions can be greatly increased by reducing the pressure of the product at the reaction surface, while other reactions are much less sensitive to such maneuvers.

RELATION OF MICROSTRUCTURE TO PROPERTIES IN CERAMICS

The importance of microstructure in determining the physical properties of ceramics is emphasized in the work of Professor Richard M. Fulrath. The densification of powder compacts, particularly the rate of densification and its relation to microstructure, is basic to the production of ceramic materials and important in powder metallurgy. This subject is under investigation using the MMRD-developed hot-stage scanning electron microscope which can operate at temperatures up to 1800°C at a magnification of over 4000X. The potential of hot-stage electron microscopy for studying sintering through all stages of heat treatment surpasses any other technique developed to date.

Another area of research is the relation between processing and the properties of piezoelectric and ferromagnetic ceramics, which are widely used in the electronic industry. Under development are new methods of producing thick-film electrically conducting systems; a first goal is to reduce the precious-metal content of thick-film conductors through the control of microstructure.



Microstructure development during densification of Al_2O_3 (numbers in upper right indicate relative density).

MICROSTRUCTURE AND MECHANICAL BEHAVIOR OF CERAMIC MATERIALS: GLASS AND CERAMIC-METAL SYSTEMS

The research program of Professor Joseph A. Pask is concerned with developing a fundamental understanding of solid-state chemistry factors that can be used to control microstructures in ceramic materials. Work has been in progress for a number of years on the equilibria and phase transformations of the refractory system SiO_2 - Al_2O_3 – a system which is of interest because of the large volumes of such refractories needed for energy-conversion equipment. Detailed knowledge is necessary to design and realize microstructures that will perform satisfactorily. Of particular interest is the development of a dense, glass-free, alumina-free mullite-type of ceramic ($3Al_2O_3 \cdot SiO_2$) with superior mechanical properties.

Another major program deals with MgO materials which have potential high-temperature applications, and is concerned with the nature of grain boundaries and their interaction with dislocations in the presence of impurities and additives. The goal is to evaluate the mechanical behavior of polycrystalline MgO and provide information for the design of microstructures with specific capabilities.

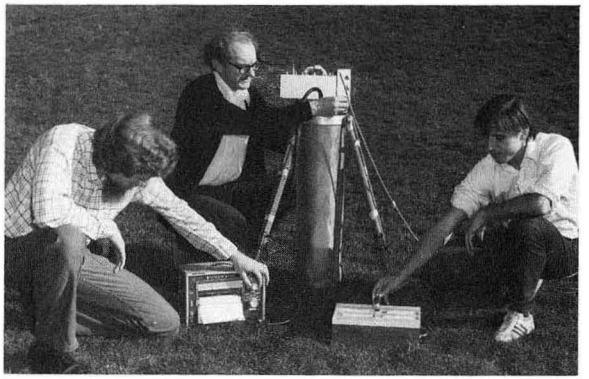
Fundamental studies of reactions and bonding at glass-metal and ceramic-metal interfaces are under way. Such interfaces are relevant to the production of temperature- and corrosion-resistant protective coatings, electronic and electrical components, and composites.

Solid State Physics

SUPERCONDUCTORS AND SUPERCONDUCTING DEVICES

Research conducted by Professor John Clarke is concerned with superconductors and superconducting devices. He has recently developed a superconducting magnetometer that measures changes in magnetic fields as low as 10^{-10}G/Hz$^{1/2}$. One version of this device has been used in remote areas to take geophysical data: by simultaneously measuring the fluctuations in the magnetic and electric fields of electromagnetic waves incident on the Earth's surface from the magnetosphere, the researchers are able to estimate the variation of the electrical conductivity of the Earth's crust with depth. This technique, useful down to perhaps 50 km, has great potential in locating geothermal sources and mineral deposits. Incorporated into a gradiometer, the device also will measure the spatial derivatives of magnetic fields and thus should find application in medicine and seismology.

At frequencies of a few Hz, most electrical measurements are limited by flicker or 1/f noise. Professor Clarke's research has shown that 1/f noise in metals arises from temperature fluctuations that modulate the resistance of the metal. His theory of noise quantitatively accounts for 1/f noise observed in metals at room temperature, in superconductors at their transition temperature, and in Josephson junctions. The result is a new ability to design superconducting bolometers and Josephson junction magnetometers with significantly reduced 1/f noise.



Geophysical field measurements were made with this 3-axis magnetometer. Three SQUIDS are mounted orthogonally in a lightweight, portable fiberglass cryostat, with the electronics mounted on the top.

The theory will be extended to other materials, especially semiconductors.

INFRARED SPECTROSCOPY

The techniques of infrared spectroscopy, especially those of Fourier transform spectroscopy, are being applied by Professor **Paul L. Richards** and associates in a wide variety of scientific investigations including low-temperature physics, infrared astronomy, and pollution and energy problems.

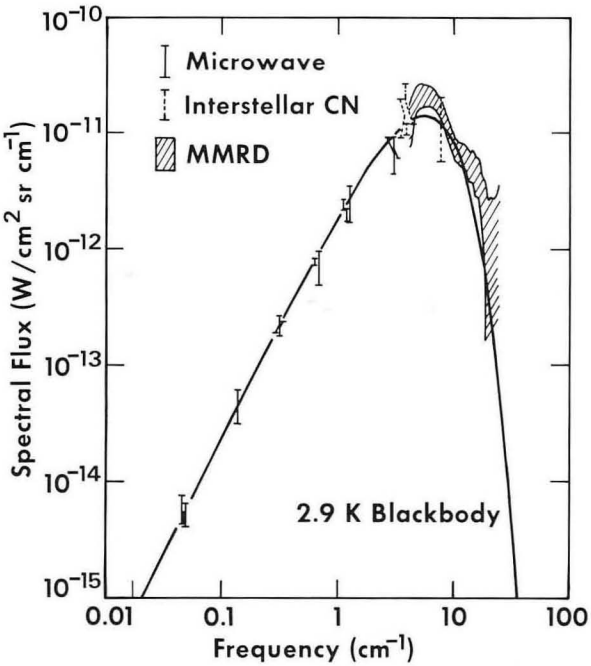
Measurement of the far-infrared cosmic background radiation has recently been shown to fit a blackbody curve with a temperature of 3°K. This is the first measurement of the spectrum of ~70% of the radiant energy in the Universe. It provides strong support for "big bang" cosmology and limits to a few per cent any drift in the value of Planck's constant during 99.9% of the life of the Universe. Extensions of these measurements will provide very sensitive far-infrared spectra of the stratosphere, which will yield information about a number of

atmospheric pollutants as well as precise values of line strengths for common atmospheric gases.

Work in semiconductor physics includes an exploration of electron-hole drops in optically-pumped Ge, as well as the far-infrared photothermal ionization spectroscopy and the high-resolution near-infrared spectroscopy of ultrapure Ge.

Far-infrared techniques for plasma diagnostics are being developed: of special interest is a far-infrared heterodyne mixer for measuring the ion temperature in Tokamak plasmas.

The group's new high-resolution, near-infrared Fourier spectrometer will be used for studies of pollution-deposited films, the infrared absorption of the surfaces of solids, and the spectra of molecules of interest to high-temperature chemistry and to astrophysics.



LASER OPTICS OF SOLIDS

Professor Yuan-Ron Shen's group works in the field of laser interactions with matter. They have made a thorough quantitative study of the self-focusing of laser beams as they propagate in a medium. The results give a much better understanding of self-focusing dynamics. Self-focusing is a strong detrimental effect which must be avoided in the design of high-power lasers and in high-power beam transmission. Research on laser-matter interaction also finds applications to nonlinear optical devices, to effective heating of a plasma in laser fusion, and to devising an efficient laser-induced isotope separation method.

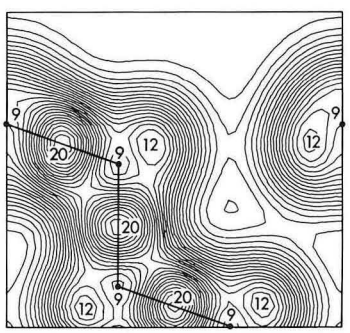
A new class of nonlinear optical materials – liquid crystals – is being studied; they are excellent Kerr-cell materials and possibly can be used to construct fast optical shutters with variable speed. In making their own lasers, the researchers have also added to laser technology: for example, they have invented a method of generating a dye laser beam with two separately-tunable, discrete frequencies. The group also does pioneering work in the field of resonant Raman scattering; they have demonstrated that this new spectroscopy can yield detailed information about electronic structure, phonon (or magnon, etc.) structure, and the electron-photon interactions of a material – all at the same time.

Present status of measurements of the cosmic background radiation. The frequency range of the MMRD measurements (shaded region) includes about 80% of the energy of the background radiation, and thus about 70% of the radiant energy in the Universe.

THEORETICAL SOLID STATE STUDIES

Working in theoretical solid state physics, Professor **Marvin L. Cohen** is studying a variety of problems related to the electronic structure of solids. His research treats both bulk and surface properties of solids such as optical properties, superconductivity, phonons, dielectric functions, vacancies, surfaces, interfaces, and molecules of interest for solid state physics. Much of the research has concentrated on the properties of semiconductors with emphasis on the more common diamond and zincblende materials. Narrow-gap and amorphous semiconductors, and chain, layer, and polymer materials are also studied. The calculations produced are among the most accurate available for the electronic structure of these materials.

Recently, theoretical methods designed to calculate the bulk properties of solids were extended to calculate the properties of localized configurations. This work gave detailed information about the surfaces of semiconductors and metals. In addition, interfaces between semiconductors and metals were studied, revealing some important aspects of the system. Since the electronic structure is basic to understanding the behavior of semiconductors and metals, these results and methods developed have had wide application.



Total valence charge distribution for an unrelaxed Si (111) surface. The plotting area starts in the vacuum and extends 4 atomic layers into the crystal. Positions of atoms are indicated by dots and bond directions by heavy lines. Clearly displayed are the smoothing-out of the charge around the cut and dangling bond, and the valley that extends from the surface into the bulk (along which impurities probably migrate).

QUANTUM FLUIDS IN SOLIDS

The electron-hole pairs (excitons) that are created when semiconductors such as Ge are irradiated with visible light are the subject of multidisciplinary studies by Professor **Carson D. Jeffries** and his research group. At low temperatures, and at sufficient density, these excitons condense into a degenerate electron-hole Fermi liquid which undergoes a phase separation from an exciton gas into small liquid droplets a few microns in diameter. This electrically conducting liquid is an anisotropic compensated plasma of finite lifetime having many new properties.

It has been discovered that an appreciable volume of the liquid can be confined into a simple large "drop" by suitably inhomogeneously stressing a Ge crystal. Such a drop has been photographed. Studies of the Alfven wave resonance exhibited by the drops, using microwave frequencies and fields of a few kilogauss, give information on drop size, pair density, and collision time. The method also is used to study the flow of pairs into the potential well inside the stressed crystal, and the kinetics of formation and decay of droplets in unstressed Ge.

Magnetoacoustic measurements have given precise values for the Fermi level and density; these data will be used to test theoretical predictions.

Atomic and Molecular Physics

ATOMIC PHYSICS

The Atomic Physics Group led by Professor Howard A. Shugart is involved in many projects in experimental and theoretical atomic physics:

- Professor Eugene Commins directs a project which is searching for a possible weak neutral current interaction between the nucleus and atomic electrons. Detection of the effect involves laser light scattered from atoms and would be of fundamental importance in physics.
- Professor Richard Marrus studies the spectra and lifetimes of ions with only one or two electrons surrounding a highly charged nucleus. This work utilizes the SuperHILAC (heavy-ion linear accelerator) and has possible application in controlled thermonuclear reactor diagnostics.
- Professor Howard Shugart measures with high precision the lifetimes and the electromagnetic and mechanical properties of certain states in atoms and molecules in neutral atomic beams.
- Dr. Michael Prior uses electromagnetic ion traps to hold ions for times long enough to study many inherent properties of the ions and of the interaction of these ions with other colliding atoms.
- Dr. Tetsuo Hadeishi investigates and develops atomic and molecular absorption detectors which allow assaying of mercury, lead, cadmium, and other materials more accurately and in less time than by previous methods. This work has practical application in medical and environmental monitoring.

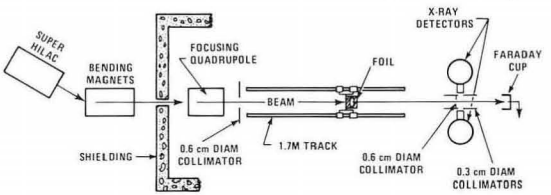
Most of the experimental work described here uses combinations of the related methods of atomic beams, optical spectroscopy, lasers, radiofrequency spectroscopy, ion traps, and beam-foil excitation. All are noted for their sensitivity, accuracy, and unambiguous interpretation. These projects have as goals the experimental testing of theoretical predictions, exploring new areas of physics, and developing new techniques and ideas.

HIGHLY-STRIPPED HEAVY IONS

The program of Professor Richard Marrus' group is concerned with studying the spectra of highly-stripped ions produced by beam-foil excitation of beams from the SuperHILAC. Their goals are two-fold: to provide spectroscopic information on those ions important in plasma research, and to study those systems which are particularly useful as tests for theories of atomic structure.

Examples of recent work are:

- Successful observation of the $2^3P \rightarrow 2^3S$ ultraviolet transitions in heliumlike argon. These transitions are important in plasma diagnostics, so accurate knowledge of their wavelengths and lifetimes is important.
- Observation of the x-ray transition $2^3S \rightarrow 1^1S$ in helium like krypton. This is the highest-Z two-electron system so far observed in nature. The lifetime is important for electron density determinations in low-density plasma; it also serves as a test of theories of relativistic and radiative corrections to electromagnetic decay.



Schematic of experimental equipment for studies of highly-stripped ions.

Advanced Isotope Separation Technology

Isotope separation with a high separation factor and a low energy consumption appears possible by the combination of molecular beam and laser technologies. Goals are the development of practical new isotope-separation schemes, and the advancement of the basic science that is urgently required for isotope-separation technology.

In this program, Professors **Yuan T. Lee** and **C. Bradley Moore** and their associates will investigate several laser isotope separation methods:

Photopredissociation. Molecules with excited state lifetimes longer than 10^{-10} seconds have sharp absorption spectra which may be excited isotopically selectively. When such a state decays by dissociation, the fragments are isotopically enriched. At Berkeley this process yielded the first successful laser separation of isotopes.

Selective Decomposition of Van der Waals' Molecules. In the isentropic expansion of gas molecules forming a beam of molecules, a large fraction of molecules will associate through a termolecular process and form Van der Waals' molecules. If an infrared laser is used to excite vibrational motion in the Van der Waals' molecules containing the desired isotope, the excited molecules will decompose; the recoil velocity associated with dissociation will then send molecules containing desired isotopes away from the beam.

Chemical Reactions of Selectively Excited Molecules. The change of chemical reactivity by selective excitation is still one of the most promising approaches for isotope separation. Hg is separated commercially by photochemistry. We are studying chemical reactions of electronically excited Br_2 and ICl for practical separation schemes.

Multiphoton Excitation Processes. Recently, it has been demonstrated by Letohkov's group in Moscow, the Los Alamos group, and others that selective multiphoton dissociation of molecules is an effective means to achieve isotope separation. However, most of the physical processes involved are yet to be fully investigated.

We propose to study first the multiphoton absorption process which leads to photodissociation and then the dynamics of a dissociation process. Both molecular beams and low-pressure gases will be used.

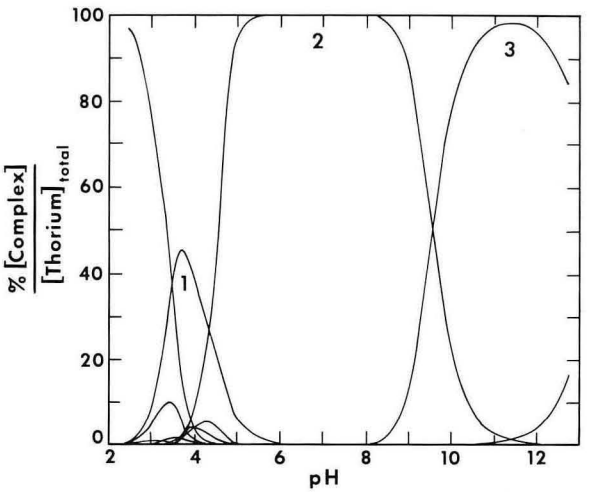
Selective Condensation of Molecules. In the process of condensation of gas molecules on a cold surface, the sticking coefficient might depend significantly on the internal excitation of molecules. If the sticking coefficient could be reduced drastically under suitable conditions through the laser excitation of molecules, a very efficient isotope separation method could be developed with a molecular beam condensation arrangement.

Actinide Chemistry

Studies of the chemistry of the actinide elements provide the basic knowledge necessary for the safe and economical use of actinides in present and future technologies. This program extends earlier work on heavy actinides and is coordinated with the Laboratory's biomedical efforts. Participants are: Dr. Norman Edelstein, Professor Neil Bartlett, Mr. John G. Conway, Professor Kenneth N. Raymond, Professor Glenn T. Seaborg, Professor Andrew Streitwieser, Jr., Professor David H. Templeton, and Dr. Allan Zalkin.

A major aspect is the design of sequestering agents for actinide ions that can engulf the ion and generate neutral or charged complexes. The sequestering agents will have a very high specificity for individual actinide ions, as well as large absolute formation constants with these ions. Such compounds are expected to be of use in the treatment of actinide poisoning by allowing the removal of Pu from body tissues, and in new processing schemes for nuclear waste where Am, Pu, and Cm need to be selectively separated. The researchers will systematically apply various macrocyclic polydentate chelating agents containing such functional groups as hydroxamate and catecholate anions to the lower-oxidation-state actinide ions. Reagents will be developed that can be used to extract the actinides from aqueous media.

The program also will include studies of the preparation and physical and chemical properties of a variety of new gaseous, liquid, and solid phases of the actinides. Synthesized compounds will be identified and characterized by x-ray diffraction, optical and vibrational spectroscopy, and magnetic resonance and magnetic susceptibility techniques. New organoactinide compounds may serve as a source of gas-phase actinide atoms for use in laser isotope separation processes.



Distribution curve of thorium-catechol complexes in aqueous solution: Peaks 1, 2, and 3 correspond to the formation of a thorium complex with one catechol ligand, two catechol ligands, and three catechol ligands, respectively, as a function of pH.

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