Report on Lawrence Berkeley Laboratory

Program Development Fund

FY 1987

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Prepared by
Office for Planning and Development

Lawrence Berkeley Laboratory
1 Cyclotron Road
Berkeley, California 94720

Prepared for the U.S. Department of Energy under Contract No. DE-AC03-76SF00098

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED
MASTER

Table of Contents

Introduction	1
Background	1
Process	1
Summary of Projects	1
 Project Reports	 7
Accelerator and Fusion Research Division	7
Applied Science Division	13
Biology and Medicine Division	19
Chemical Biodynamics Division	29
Earth Sciences Division	35
Engineering Division	41
Materials and Molecular Research Division	45
Nuclear Science Division	65
Physics Division	71
 Acronyms and Abbreviations	 75

INTRODUCTION

Background

The Program Development Fund (PDF) was established at the Lawrence Berkeley Laboratory (LBL) in August 1984, following the issuance of Department of Energy (DOE) Order 5000.1, Chg. 1, "Guidelines for Use of R&D Exploratory Funds," in December 1983. Funding for this program is allocated from the Laboratory's operating budget and is subject to approval by the Laboratory's Overhead Budget Task Force, the Director, and the DOE.

It is the objective of the Fund to encourage innovative research to maintain the Laboratory's position at the forefront of science. Funds are used to explore new ideas and concepts that may potentially develop into new directions of research for the Laboratory and that are consistent with the major needs, overall goals, and mission of the Laboratory and the DOE.

The types of projects eligible for support from PDF include:

- Work in forefront areas of science and technology for the primary purpose of enriching Laboratory research and development capabilities.
- Advanced study of new hypotheses, new experimental concepts, or innovative approaches to energy problems.
- Experiments directed toward "proof of principle" or early determination of the utility of a new concept.
- Conception, design analyses, and development of experimental devices, instruments, or components.

Beginning in FY 1987, conferences and workshops were no longer eligible for support from the PDF.

Process

Comments from the Panel to Explore New Directions and responses to an informal survey conducted by the Office for Planning and Development led to a review of PDF funding patterns. This review indicated that PDF projects fell into one of two categories: (1) innovative science projects and

(2) institutional projects that could develop significant opportunities or new directions for the Laboratory. However, more than two-thirds of the funding supported projects that fell into the second category. Since a major objective of the Fund is to foster creative science for its own sake, one-third of the FY 1987 Fund was explicitly set aside for innovative science projects.

In May 1986, the call for FY 1987 PDF proposals was distributed to the Associate Directors, sent directly to principal investigators, and announced in *Currents*, LBL's weekly newspaper. In response to this call, investigators submitted proposals to their cognizant Associate Director. Each proposal was categorized as Innovative Science or Institutional Projects based on the following criteria.

Innovative Science projects must be:

- Small scale, require less than \$150 K per year, and have a well-defined lifetime (not more than two to three years);
- Innovative, creative, and at the forefront of science.

Institutional Projects must be:

- Scientifically exciting activities that have the potential to foster new Laboratory directions or new program emphases;
- Likely to have a relatively high potential for future funding by outside agencies.

The Associate Directors then reviewed the proposals and sent them on, with their comments and ranking in each category, to the Director's Office. The proposals were reviewed by the Director's Review Committee, composed of the Director, the Deputy Director, and the Associate Director for Planning and Development. Projects were selected for funding, and the majority of the available funds were allocated. The remaining funds were reserved to fund worthy projects arising later in the fiscal year.

The requirements of DOE Order 5000.1, Chg. 1, were carefully considered during the selection process to identify the extent to which proposals were consistent with the criteria. The ability to

provide funds for exploratory R&D is vital to LBL's future growth and success and, as such, is given significant management attention.

Summary of Projects Funded in FY 1987

In FY 1987, 96 proposals were submitted, divided almost equally between the Institutional Project and Innovative Science categories, requesting a total of \$9.3 M. Of the \$3.1 M available in PDF, \$2.1 M was allocated to Institutional Projects and the remainder was allocated to Innovative Science projects. A total of 38 projects was funded, of which 24 were Institutional Projects and 14 were Innovative Science. Some projects received lower funding than that requested. The projects funded in FY 1987 are listed in Tables 1 and 2.

In the Project Reports section, accomplishments are summarized based on year-end reports submitted by the principal investigators. Several examples serve to indicate the importance and value of these projects to LBL and DOE. Some of the projects fostered the development of advanced instrumentation. As an example, a scanning tunneling microscope designed to operate under liquids, in air, and in vacuum was funded in FY 1986 and 1987. This microscope was originally developed to characterize new surface compounds in the form of very thin films of metals and oxides on a variety of metal and semiconductor substrates. Recently, this microscope was used by a collaborative team of Lawrence Livermore National Laboratory (LLNL) and LBL scientists to obtain the first direct images of individual lengths of native (unaltered) DNA, clearly showing the double helix structure. The resolution achieved was high enough so that the distances between the major and minor grooves in the double helix structure could be measured. This work will have a significant impact on molecular biology and biophysical research in general, and particularly on the effort now under way to map and sequence the human genome.

Other imaging research developed an experimental approach to make holograms of biological objects using soft x-ray radiation. Holograms, including some of zymogen granules, were made with resolution in the 500-angstrom range. A computer-processed electron microscope read-out was used to reconstruct images from the holograms. This technique supplements information provided by scanning x-ray microscopes and complements optical and electron microscopy as tools for study-

ing structures inside cells. Another example of instrumentation development was directed towards detecting dark matter from the halo of the galaxy. Bolometric techniques were studied with the goal of demonstrating the feasibility of energy deposition thresholds as low as 100 eV with detector crystals of at least a few grams. This effort contributed to the establishment of a National Science Foundation science and technology Center for Particle Astrophysics at UC Berkeley in collaboration with LBL.

Other projects supported the development of new research programs that may have long-term national benefits. An example of this was a project which focused on defining the genetic mechanisms responsible for regulation of human plasma lipoproteins and identifying the specific genetic alterations associated with accelerated atherosclerosis. A clinical research unit has been established, in collaboration with a local hospital, which provides a base for referral of potential research subjects with heart disease and lipid disorders. Studies have identified a new human genetic disorder which results in the development of hypercholesterolemia. The cause of this disorder is a mutation in a protein constituent of plasma low-density lipoproteins, which results in its defective binding to its receptor. Research is continuing, supported by the National Institutes of Health and a gift from Merck Chemical, to identify other mutations that may increase risk for heart disease, as well as to define the structure of the low-density lipoprotein receptor binding site.

PDF also supported development of coordinated research programs directed toward critical scientific problems. An Environmental Policy Research effort brought together resources from LBL, LLNL, and UC campuses to study major environmental policy issues. With PDF, planning efforts assessed interest and capabilities of the collaborating institutions, developed direct funding sources, and identified risk assessment, global climatic change, and policy implications of ecological effects as the major areas of emphasis. This effort has been especially timely, and the researchers supported through this project in FY 1987 and FY 1988 are currently working with UC and DOE national laboratory scientists to host a series of workshops on the implications of global warming. DOE is also providing support to undertake an emissions inventory related to global warming.

Table 1. FY 1987 Program Development Fund—Institutional Projects

Division	Investigator	Project	SK
Accelerator and Fusion Research Division			
	M. Cornacchia	Low Emittance Storage Rings	97
	A. Jackson	Lattice Options	92
	H. Nishimura	Three-Dimensional Cavity Field Calculations	92
	M. S. Zisman	ZAP Accelerator Design Code	97
Applied Science Division			
	M. D. Levine	Environmental Policy Research	85
	J. A. Sathaye	World Energy Demand Center	50
Biology and Medicine Division			
	J. C. Bartley	Center for Cancer Biology	100
	P. H. Silverman	Hematozoa and Erythropoiesis	107
Chemical Biodynamics Division			
	H. M. Frei	Singlet Molecular Oxygen	28
	F. Leach	Nuclear DNA Binding Proteins	42
	D. E. Wemmer	Two-Dimensional NMR	25
Earth Sciences Division			
	P. A. Witherspoon	Downhole Shear Wave Source	100
Engineering Division			
	J. M. Jaklevic	Semiconductor X-Ray Detectors	110
	J. E. Rasson	Gas-Driven Absorption Heat Pump	90
Materials and Chemical Sciences Division			
	M. D. Alper	Enzymatically Synthesized Materials	92
	R. M. Cannon	Ceramic/Metal Interfaces	144
	M. L. Cohen	Matter at Megabars of Pressure	150
	T. M. Devine	Film Formation and Degradation	120
	G. M. Rosenblatt	Raman Studies of Surface Processes	180
	P. N. Ross	Metal/Solution Interface	87
	A. Zettl	Novel High Temperature Superconductors	50
Nuclear Science Division			
	D. C. Hoffman	LEAP	77
	H.-G. Ritter	Calorimeter Development	50
Physics Division			
	B. Sadoulet	Low Threshold Bolometers	102
TOTAL			2,167

Table 2. FY 1987 Program Development Fund —Innovative Science Projects

Division	PI	Title	Allocation \$K Budget
Accelerator and Fusion Research Division			
	M.R. Howells	Study of Sickle Blood Cells	33
	M.R. Howells	X-Ray Holographic Microscopy	45
	M.A. Olmstead	Semiconductor Interface Formation	5
Applied Science Division			
	P. Berdahl	Galvanomagnetic Semiconductor Laser	80
	R. Mehlhorn	Ultrasensitive Free Radical Assay	67
Biology and Medicine Division			
	S. Ebbe	Molecular Biology of Hemopoiesis	136
	R.M. Krauss	Human DNA Polymorphisms	150
Chemical Biodynamics Division			
	P.G. Schultz	Synthesis of Catalytic Antibodies	30
Earth Sciences Division			
	I.S. Carmichael	High Temperature Centrifuge	52
Materials and Chemical Sciences Division			
	H. Gould	Electron Electric Dipole Moment	125
	M.B. Salmeron	Tunneling Microscopy of Catalysts	110
Nuclear Science Division			
	J. Cerny	Detectors for Low-Energy Particles	30
	E.B. Norman	Low-Background Counting System	39
Physics Division			
	L. Bosisio	2-D Semiconductor Detectors	75
TOTAL			977

Novel scientific theories were explored by new collaborations of experimentalists and theorists. A study was undertaken of the properties of matter at megabars of pressure. Theorists used the *ab initio* pseudopotential method to calculate ground-state properties of solids as a function of volume. These predictions were then tested by the experimentalists using high-pressure techniques. Part of this project examined the pressure dependence of the new high T_c superconductors, and suggests that there is an optimal bond length at which these materials achieve the high superconducting temperatures. When pressures are increased and the materials are compressed beyond the optimal bond length, superconductivity is destroyed.

Review of Projects Funded in FY 1985 and FY 1986

A survey was distributed to all principal investigators who had projects funded by PDF in FY 1985 and FY 1986. This survey was intended to characterize past projects and follow up on funding and other outgrowths of the research supported by PDF. Although not all investigators responded to the survey, the information provided by those who did respond gives an indication of the success of the exploratory R&D program. Because the survey was incomplete, anecdotal rather than statistical information is provided below. Although it is not possible to quantify the success of LBL's exploratory R&D program based on the available data, the reports provided indicate the value of the program in generating funding for the Laboratory and in furthering the missions of the Laboratory and DOE in regard to transferring technology to the private sector.

Technology Transfer. Four of the projects funded in FY 1985 and 1986 resulted in the filing of patent applications. A patent has been issued for "Method and Apparatus for Measuring Lung Density by Compton Backscattering" which was based on research funded for two years in the Engineering Division. Other patents are pending in the areas of biotechnology, microelectronics, and petroleum science. In addition, a large number of projects initiated industrial interactions, and aided the transfer of technology to the private sector. Most projects resulted in publication of reports and presentation of research results at conferences, universities, and industry. Many students, primarily at the graduate level, participated in the research supported by PDF, and will provide an additional avenue of technology transfer by working in the private sector after completing their degrees.

Funding. A significant number of projects funded by PDF in FY 1985 and 1986 were able to develop direct funding support from DOE and other agencies. Other projects may still attract funding at a future date. Several Earth Sciences projects funded in FY 1985 resulted in support from DOE's Office of Civilian Radioactive Waste Management. Detector development activities in the same year later received funding from DOE's High Energy Physics program. Biological materials synthesis research initially funded by PDF in FY 1986 is now actively supported by the Basic Energy Sciences/Materials Science program in DOE. Research related to molecular composites supported in FY 1986 has continued funding from Dow Chemical. A biotechnology project funded in both FY 1985 and 1986 has received support from DOE's Office of Health and Environmental Research.

Project Reports

Accelerator and Fusion Research Division

Investigation of the Effects of Errors and Misalignments on Low-Emittance Storage Rings

Principal Investigator: Massimo Cornacchia

Funding: \$97,800

Project Description

The effects of magnetic errors and misalignments on the performance of low-emittance storage rings were investigated. Studying these effects will lead to better designs for low-emittance rings as well as better understanding of the critical magnetic field and misalignment errors that should be minimized in the design of magnets and support structures for these rings.

Accomplishments

A thorough analysis, based on tracking simulations and realistic deviations from ideality, of the effects of magnet multipole errors (systematic and random) and of magnet misalignments on the beam dynamics of low-emittance storage rings has been carried out. To separate the effects of different types of "magnet errors," they have been analyzed separately and then summed at the end. The predominant effect of the multipole errors on an otherwise perfect machine is a reduction of the dynamic aperture. There are also small changes in the amplitude-dependent tune shifts and a small amount of coupling introduced between betatron motion in the two transverse planes. Magnet misalignments produce a closed orbit distortion that must be corrected. However, residual distortion remains even after correction, and this residual orbit error gives rise to a random quadrupole component when the orbit passes through sextu-

pole magnets, leading again to a reduction of dynamic aperture. Associated with the residual orbit distortion are the introduction of vertical dispersion and a coupling of betatron motion in the two planes. The result is a vertical equilibrium beam size significantly larger than its "natural" damped value.

Tracking simulations suggest that the main effect of the multipole errors is felt in the radial plane, with reduction of dynamic aperture by 20% at most. The single most harmful component for these low emittances has been identified as the random gradient error in the dipole magnet. Effective closed orbit correction schemes have been found to offset the magnet misalignment effects. The residual dispersion introduced by magnet errors, although very large before correction, can be reduced to very low values, leading to only 2.5% and 10% increases in the horizontal and vertical beam sizes, respectively, compared with their natural values. This study has been significant in understanding the limitations that the construction errors of a real machine impose on the beam dynamics in a low-emittance storage ring.

Study of Sickie Blood Cells by X-Ray Microscopy

Principal Investigators: Malcolm R. Howells and Marcos Maestre

Funding: \$33,300 (second year of funding)

Project Description

Contact x-ray microscopy studies of sickle red blood cells were conducted to reveal the mechanism by which the formation of the harmful polymerized hemoglobin S is initiated.

Accomplishments

In 1986, a soft x-ray contact microscopy station was put into operation. The first images from the apparatus were also generated. These images were of electron microscope grids and normal red blood cells.

This year, improved images of normal red blood cells have been made by trying different readout techniques. The readout of the exposed and etched resist by the scanning electron microscope (SEM) is now done at steeper angles, i.e., 75° instead of head-on. Also, the etched resists are shadowed at angles of 15 and 30°, instead of having an even coat applied by a plasma sputterer. With improved images of normal red blood cells, it was possible to set up a baseline so that protein distribution in abnormal red blood cells, in particular, sickled erythrocytes, can be observed. Earlier, living 9L gliosarcoma cells were imaged, but the resist was spoiled during the readout on the SEM. Nevertheless, the x-ray imaging part of the experiment is working well.

Another accomplishment for 1987 was the absolute calibration for dosimetry of a radiochromic nylon film in the soft x-ray regime. It was found that film was effective in the range of interest, which is roughly 250–1500 eV. The film actually has a much larger effective range and is commonly used in food irradiation in the gamma-ray region. The film has been used during sample exposures to measure the dose to the sample and the resist, and to determine if the apparatus is performing properly.

A final accomplishment was the development of an environmental sample chamber for irradiating living, wet biological samples under atmospheric pressure. The sample chamber was successfully used in an experiment at the National Synchrotron Light Source and can also be used in the soft x-ray contact microscopy station.

This project is an interdisciplinary and thus an interdivisional effort between the Accelerator and Fusion Research Division and the Biology and Medicine Division. The preparation of cells and the SEM readout were done in conjunction with the Biology and Medicine Division. This effort was assisted by contributions from IBM.

High-Resolution X-Ray Holographic Microscopy

Principal Investigator: Malcolm R. Howells

Funding: \$45,300

Project Description

An experimental approach to make three-dimensional images of biological objects was developed. Holograms of the objects were recorded using soft x-ray radiation in the wavelength range 23–44 Å. These recordings were made on a high-resolution x-ray resist and will be converted into the final image by a computer-processed electron microscope readout.

Accomplishments

In the past, it has been demonstrated that the holographic methods used with visible light could also be applied to soft x rays by recording holograms on photographic film. Images with a resolution of about 1 µm have been reconstructed with a visible-light laser. During 1987, two further advances were made, both aimed at achieving significantly better resolution and thereby bringing x-ray holography closer to real scientific applicability. First, a silver halide film detector was used instead of a high-resolution x-ray resist. And second, to compensate for the much lower "speed" of the resist, a much brighter x-ray source, the undulator on the National Synchrotron Light Source's X-17T beamline, was used.

About 100 holograms, including some of zymogen granules, were made, with typical exposure times of approximately 1 hour. The holograms were recorded on copolymer resist layers about 2000 Å thick on a silicon nitride substrate, using 24.7-Å x rays. After exposure, the resist was developed and then shadowed with metal to enhance the relief image, which consisted of an interference pattern formed by coherent superposition of scattered and unscattered x rays. Transmission electron micrographs of the metallized holograms indicated that the minimum fringe period was

about 400 Å. This pointed directly to the possibility of reconstructing images of like resolution.

The holograms themselves served as an important proof that a major obstacle to the use of x-ray holography as a high-resolution method of imaging could be overcome, but it still remained to reconstruct images from the holograms. To take this next step, numerical reconstruction from a digitized hologram was used. The approach was to calculate the wave propagated forward from the hologram that encodes the amplitude and phase of the wave. The reconstructed images show small discrete objects and are similar to the granule images obtained with the scanning x-ray microscope. However, the halos visible in the reconstructions make it difficult to interpret features in the image with complete confidence. Further efforts must be directed toward the study of these halos, along with additional refinement of the model for correcting nonlinearities (an important advantage of reconstruction from digital holograms) and evaluation of the ultimate resolution that can be obtained in reconstructed images from the present holograms.

Study of Lattice Options for Low-Emitance Beams

Principal Investigator: Alan Jackson

Funding: \$87,700

Project Description

Problems associated with low-emittance electron storage rings were investigated, focusing on the dynamic behavior of the electron beam in storage rings, with parameters optimized for damping rings (to be used in the next generation of linear colliders), for free electron laser drivers and for the next generation of synchrotron light sources.

Accomplishments

During this year, a study has been made of the different perturbing mechanisms that can lead to a reduction of the dynamic aperture of low-emittance storage rings. These include the effects of magnetic imperfections, residual closed orbit distortions (after correction), and insertion devices.

The analysis of magnetic imperfections, in particular, benefited from the detailed study of such effects and was funded as a separate Program Development Fund project. The model used most often for this work is the magnet lattice of the LBL Advanced Light Source. However, the techniques developed have been applied to other machines with similar peculiarities, e.g., candidate lattices for damping rings (ICFA Workshop on Low Emittance e⁻e⁺ Beams) and the SRRC storage ring (Taiwan). The results show that all perturbing effects lead to a reduction in the dynamic aperture. Two mechanisms seem to be responsible for the observed behavior: disturbance of the betatron phase between sextupole magnets, and, independently, the effect of higher order fields on the amplitude-dependent tune shift. Further investigation is necessary to unravel the relative importance of these two mechanisms.

Developmental Program for Three-Dimensional Electromagnetic Field Calculation in Structures

Principal Investigator: Hiroshi Nishimura

Funding: \$93,700

Project Description

The computer code COMET was developed for calculating the electric field excited in cavities and other structures by the passage of charged particle beams. Special emphasis was placed on its appropriateness to three-dimensional structures with special boundary conditions and on extending its domain of validity to high frequencies beyond the cutoff of the connecting beam pipe. Other codes (e.g., TBCI, URMEL, MAFFIA) will be installed on LBL computers to complement COMET for useful comparisons and efficient calculation of the impedance of storage ring structures.

Accomplishments

The development of the three-dimensional electromagnetic code put special emphasis on complicated geometries demanding special boundary conditions. It has been possible to verify that the code works well and gives accurate results for the

TM modes of any cross-sectional geometry as long as it has longitudinal translational symmetry. A large fraction of the vacuum chamber of most storage rings belongs to this category, including most of the LBL Advanced Light Source vacuum chamber, which has been used as an example to verify the code (see Figure 1). The cutoff frequency of the coupling between a slot-coupled beam chamber and antechamber in a special vacuum chamber configuration was computed with the code COMET, and the results agreed with an independent laboratory measurement of the same structure. Other codes (TBCI, URMEL, MAFIA) have already been installed on LBL computers and are ready to be used. The most important concern for now is the treatment of the "hybrid mode," which is a mixture of a TM and a TE mode. Attention should be focused on this issue in the near future.

Experimental Investigation of Semiconductor Interface Formation

Principal Investigator: Marjorie A. Olmstead

Funding: \$5,000

Project Description

Atomic and electronic structure of interfaces during epitaxial growth was studied utilizing synchrotron radiation. Core-level photoemission spectroscopy is a powerful tool for the study of heterojunction formation. By probing the chemical environment of atoms at an interface, information can be obtained on the bonding configuration, and in turn the microscopic structure of the interface.

Fig. 1. A three-dimensional electromagnetic field code COMET-3 was applied to a vacuum chamber similar in shape to that of the ALS storage ring. An impulse signal was injected into the beam chamber, and the fields in both the beam and antechamber are traced in time domain and Fourier transformed to frequency domain. The antechamber is isolated below the cutoff frequency of 7.5 GHz (where the vertical gap of the slit is 2 cm and corresponds to half of the cutoff wavelength). [XBL 891-224]

Accomplishments

During FY 1987, a new surface and interface science laboratory was set up and equipped. Among the experimental equipment put in place were components for a molecular beam epitaxy source. The first experiments were performed in November 1987 at the Stanford Synchrotron Radiation Laboratory, in collaboration with the Xerox Corporation. These studies of the growth of crystalline insulators on silicon and the interaction of hydrogen and arsenic with silicon surfaces are expected to yield new insights into the initial stages of semiconductor interface formation.

Extension of the ZAP Accelerator Design Code

Principal Investigator: Michael S. Zisman

Funding: \$96,700

Project Description

The capabilities of the comprehensive computer code ZAP, which is now in use worldwide for the design and performance evaluation of electron, proton, and heavy-ion storage rings, were extended. This work consisted of the inclusion of new effects into the code, the refinement of existing program features, and the comparison of ZAP predictions with both existing storage rings and existing accelerator physics codes.

Accomplishments

An important milestone this year was the completion of the ZAP User's Manual, a comprehensive description of the code and the physics behind it. In addition, during the past year, detailed comparisons have been made with a CERN computer code (BBI) that can produce more or less equivalent results for coupled-bunch instabilities. This work

resulted in modifications to both ZAP and BBI, which now seem to agree well in their area of physics overlap.

Due to widespread interest in ZAP, an invited talk was given at the March 1987 Particle Accelerator Conference. Because of the importance of equilibrium emittance growth from intrabeam scattering—a feature contained only in ZAP—the investigator participated heavily in the ICFA Workshop on Low Emittance Beams, held at Brookhaven National Laboratory in March 1987, serving as Chairman of the Working Group on Storage Ring Collective Effects. ZAP was utilized at the workshop to evaluate the performance of storage rings designed for two different purposes: (i) to serve as a damping ring for a next-generation linear collider and (ii) to serve as a short-wavelength (~ 40 Å) high-gain free-electron laser (FEL) driver. It appears at present that suitable damping ring parameters are achievable, but the severe FEL requirements do not yet have a practical solution.

Calculations were also performed at the request of the Taiwan Synchrotron Radiation Source Project. In addition, the investigator was involved in various aspects of the design and performance evaluation of the Trieste Synchrotron, a storage ring that will be built by a private corporation (in the model of the BESSY storage ring in Berlin, West Germany). As a by-product of this work, some deficiencies were uncovered in the handling of potential-well distortion in ZAP. The problem is not completely understood at present and is now under study.

Another important area of application for ZAP is in the design of compact storage rings for x-ray lithography. One crucial issue here is the viability of low-energy injection, in terms of beam emittance blowup, beam lifetime, and beam instabilities. ZAP is unique in its ability to deal with all of these questions (see Figure 2) in a single integrated computer program. In the recent past, studies have been undertaken of compact storage rings designed by Oxford Instruments (Great Britain), Scanditronix (Sweden), and Ishikawajima-Harima Heavy Industries (Japan).

Fig. 2. (a) Predicted intrabeam scattering (IBS) equilibrium emittance for a typical compact storage ring, assuming a 1% emittance coupling. The dashed curve represents the "natural" emittance of the ring, i.e., that determined solely by the emission of synchrotron radiation. The transverse beam size, which scales as the square root of the emittance, would grow to nearly 8 times its natural size. (b) Predicted Touschek half-life for a typical compact storage ring, including the effects of IBS. The lifetime at low energies is improved (relative to that corresponding to the natural beam size) due to the IBS emittance growth. [XBL 891-225]

Publications

J.P. Delahaye and M. Zisman, "Performance Comparisons of Low Emittance Lattices," LBL-23426 (May 1987); in *Proc. ICFA Workshop on Low Emittance Beams*, Brookhaven National Laboratory, March 20-25, 1987.

M. Zisman, S. Chattopadhyay, and J. Bisognano, "ZAP User's Manual," LBL-21270 (December 1986).

M. Zisman, "ZAP and Its Application to the Optimization of Synchrotron Light Source Parameters," LBL-24089 (October 1987), in *Proc. 1987 Particle Accelerator Conference*, Washington, D.C., March 1987; IEEE Catalog No. 87CH2387-9, p. 991.

M. Zisman, "Influence of Collective Effects on the Performance of BESSY-II," BESSY-II Design Report, Appendix A-1.15 (November 1986).

M. Zisman *et al.*, "Summary of Working Group on Storage Ring Collective Effects," LBL-23484 (June 1987); in *Proc. ICFA Workshop on Low Emittance Beams*, Brookhaven National Laboratory, March 1987.

Applied Science Division

Galvanomagnetic Semiconductor Laser

Principal Investigator: Paul Berdahl

Funding: \$79,500

Project Description

In the course of the Solid State Radiative Heat Pump project (funded by PDF in FY 1984), it was discovered that p-type indium antimonide can emit unexpectedly bright radiation when it is subjected to orthogonal electric and magnetic fields [the general phenomenon is termed galvanomagnetic luminescence (GML)]. As shown in Figure 1, at high current densities (greater than a few hundred amperes per square centimeter), the emission intensity increases greatly for a p-type sample, as compared with an intrinsic (pure) sample. The goal of this project was to investigate whether this luminescence can be used as the basis for a new laser light source.

Fig. 1. Intensity of galvanomagnetic luminescence as a function of current density for intrinsic and p-type indium antimonide samples. The p-type sample contains about 10^{18} impurity atoms (Cd) per cubic centimeter. It does not exhibit stimulated emission in this experiment but shows efficient emission at high current densities. [XBL 858-8950]

Accomplishments

A laser structure was designed that was believed to be relatively straightforward to fabricate. This design is illustrated in Figure 2. It is fabricated by depositing a metalized contact on the p-type indium antimonide crystal and then etching a channel to form two separate electrical contacts. Chemical etching of the channel is required to ensure that the free surface does not catalyze carrier recombination and quench luminescence. Mirrors at the channel ends are formed by cleaving.

Once appropriate devices have been fabricated, experiments with the GML spectrometer can be used to look for stimulated emission. This special type of emission can be identified by a nonlinear light-versus-current characteristic (using short current pulses to avoid heating effects). The other signature of stimulated emission in this context should be a dramatic narrowing of the emitted spectrum. Once stimulated emission has been identified, laser action can be assured by fabrication of sufficiently straight channels and good mirrors.

Fig. 2. Physical configuration chosen for laser devices. The highest electrical current density occurs under the etched channel. Excess electrical carriers are compressed against the channel surface by the Lorentz force due to the imposed magnetic field B . [XBL 881-8001]

In the initial phase of this project, the luminescence data for the p-type samples were subjected to further scrutiny than previously planned for the heat-pump research. It was learned that, for all p-type samples, there is a temperature range over which the galvanomagnetic luminescence increases rapidly with increasing temperature. This is, then, a partial explanation for the behavior shown in Figure 1, since increasing sample current heats the sample. However, this understanding neither ruled out nor proved the laser concept.

Experiences with the cleaving of InSb crystals to form the needed mirrors was developed (with high-refractive-index materials, a flat uncoated surface forms a mirror). The easy cleavage direction is the 110 direction, just as for GaAs crystals. Suitable cleaves turned out to be more difficult to make for the doped samples than for pure crystals, but still possible.

The desired "laser" emission of interest originates from the edge rather than the surface of the semiconductor crystal, as in GML phenomenon studied in the past. Suitable alteration in the GML spectrometer was made, primarily the addition of a mirror, and edge emission was obtained from a cleaved intrinsic InSb sample. This was the first observation of edge emission in this laboratory. The observed signal was weak, but its existence and expected spectral shape, which differs slightly from that of surface emission, were verified.

A number of approaches were considered for fabrication of the desired laser structure. The technique chosen was to metalize the semiconductor chip with a relatively nonreactive metal (gold), using a thin tungsten wire as a mask to cast a shadow where the channel was to be formed. Chemical etching (e.g., with a solution of bromine in methanol) was then used to form the channel. The gold metalization process introduced a number of difficulties that had to be surmounted. First, for the metal to adhere to the substrate, an annealing process was required. This annealing caused oxidation of the samples, so a tube furnace was constructed to permit annealing in flowing nitrogen. Even in the absence of oxygen, a chemical reaction occurred during annealing, presumably forming a gold-indium intermetallic compound. However, the resulting metalization appeared to form an adequate electrical contact.

Efforts to etch the channels, using either the gold or gold-indium layer as a mask, proved unsuccessful.

The etchants used tended to undermine the metalization both at the channel and through the pinholes resulting from the original vacuum evaporation of the gold. However, brief etching times were permissible, so that while etching cannot create the channel, it should be adequate to provide a surface that does not catalyze carrier recombination.

Two alternate techniques have been devised to make the desired physical device structure. The first is quite simple and will be attempted. A metalized sample is scratched with a stylus to form the needed channel. Then a brief chemical-etching step can remove some of the damaged semiconductor material, leaving the required inert surface. The second technique is to use more conventional photolithographic techniques to etch the channel. Suitable optical masks for the lithography were obtained during the course of this work, but additional funding would be required to use this technique to make device structures.

Environmental Policy Research

Principal Investigator: Mark D. Levine

Funding: \$88,100

Project Description

The overall purpose of the project has been to carry out activities that would lead to a new group at LBL devoted to environmental policy research. The project will bring together resources from UC campuses, Lawrence Livermore National Laboratory (LLNL), other California institutions (e.g., Stanford University, NASA Ames Research Center) and LBL staff to perform research on major state, national, and international environmental policy issues.

This year's approach focused on the following steps:

- Assessment of LBL staffing requirements to achieve long-term objectives.
- Discussions with key UC faculty on various campuses to determine the best mechanisms to begin a collaborative research activity.
- Meetings with LLNL staff on the same subject.

- Discussions to establish the content and mechanism for producing a monograph.
- Development of direct funding support for the activity.
- Agreement among key parties within LBL and outside on the major thrusts of the group within the broader area of environmental policy research.

Accomplishments

Assessment of staffing. After several meetings of members of the organizing committee for the project, it was decided to seek a senior researcher to lead the environmental policy group expected to be created as a result of this project. Initial explorations with EPA provided good reasons for optimism about support for a research group at LBL. Two individuals, Paolo Ricci (area of expertise: risk assessment) and Walter Westman (expertise: ecological research), were recruited to play the major role in carrying out this project.

Involvement with UC faculty. The project initiated communications and working relationships with a large number of UC researchers during the year. Virtually all of these individuals expressed support for the idea of forming an environmental policy group and indicated ways in which they or some of their colleagues could participate. Plans are underway to establish one or more environmental research coordinators on each campus to take responsibility for organizing interested faculty and researchers for participation in LBL activities.

Meetings with LLNL staff. Joseph Knox, head of the atmospheric and geophysical sciences division at LLNL, has been active in support of this project. He participated in the extensive interview process to select staff for the emerging environmental policy group at LBL. He also participated in the major planning meetings in the project, was liaison with LLNL researchers, and played a strong role in proposing areas of research interest for the group to pursue. As a result of Dr. Knox's involvement with all aspects of the project and planning for the new group, collaboration between well-established research groups at LLNL (particularly the large atmospheric modeling effort) and LBL activities is expected to be a close one. It is anticipated that this will benefit the LBL effort by linking it closely with an established activity; it should also benefit LLNL by involving a number of interested physical

science researchers in policy-relevant research activities.

Discussions on monograph. Preliminary discussions were held with a number of parties about the content of the monograph and on methods for preparing it. An outline was developed and circulated among UC, LLNL, and LBL participants. The organizing committee decided that active work on the monograph should be delayed so that the new project staff would have an opportunity to shape it according to their interests.

Meetings with EPA and other potential funding agencies. Extensive meetings were held with EPA. Discussions were carried out with both the policy offices (OPPE) and the research offices (ORD). Overall, the meetings were highly successful, with EPA showing significant interest both in the concept of LBL establishing a strong policy group involving collaboration with UC and in specific projects that could be carried out with EPA support. Meetings with other potential funding sources, particularly DOE, also took place.

Major thrusts of group. The discussions among the various participants in the group have resulted in the decision to give emphasis to three areas within environmental policy: (a) risk assessment, (b) global climatic change, and (c) policy implications of ecological effects.

Ultrasensitive Assay for Free Radicals

Principal Investigator: Rolf Mehlhorn

Funding: \$67,000

Project Description

The study of oxidative free-radical damage may well emerge as the next major frontier in biological research, with profound implications for human welfare, including disease prevention and lifespan extension. At the leading edge of this field is the development of noninvasive detection methods that will serve to ascertain the extent of oxidative stress occurring in single cells, animals, or plants under pathological or perhaps normal conditions. This project addresses synthesizing and applying chemical traps, whose products are recoverable as

gases, for the noninvasive detection of free radicals in biological systems. The assay may have sufficiently high sensitivity to detect oxidative damage in animals undergoing chronic rather than acute oxidative stress. It promises to allow researchers to conduct risk assessment of ambient levels of environmental agents like ozone and radon gas without requiring long-term studies on large colonies of rodents or primates and without a requirement for controversial end points such as disease or death. Future extensions of the assay for use in humans are likely. The basic principle is already proven: the production of a volatile gas from the reaction of oxygen-centered free radicals with an appropriately chosen nonvolatile reagent. However, present technology lacks high sensitivity and requires injection of excessive concentrations of the free-radical trap. Radiolabeling is expected to overcome this deficiency. Moreover, ethylene derived from the injected trap will not have to be discerned from a host of other volatile substances associated with microbial metabolism and lipid peroxidation processes, thus greatly facilitating data analysis.

Accomplishments

In collaboration with Professor Rapoport of the National Tritium Labeling Facility at LBL, a novel radiolabeled free-radical trap, tritiated 4-keto thiomethyl butyric acid (KTBA), is being synthesized, which fragments into several products after reaction, liberating a radiolabeled gas that can be collected in the expired breath of an animal.

The reaction of the new trap with hydroxyl radicals is shown below.

Some of the free radicals that are produced in an animal will react with this trap and the ethylene will be volatilized in the lung and expired. Collection of the expired gases in a "cold-finger" or charcoal filter trap will accumulate a variety of volatile metabolic products, but only the products of free-radical reactions will bear the radioactive tracer. Measurement of radioactivity in the collected volatile gases will therefore serve as an

index of oxidative stress. Ultimately it is foreseen that nonradioactive tracers, e.g., ^{13}C and deuterium, will serve to adapt this free-radical trap for human use in clinical settings.

Synthetic efforts. Procedures have been implemented for preparing highly tritiated methionine sulfoxide and KTBA. KTBA, in particular, was a challenging problem and required the conception of a new synthesis by Prof. Rapoport. Conservatively, the synthetic strategy will achieve a labeling density of one tritium atom per KTBA. Only the ethylene decomposition product will be labeled. The pilot-scale synthesis of KTBA, a formidable task, has proceeded to the fifth intermediate in a seven-step reaction sequence and is expected to be completed during the second year of the project. Scale-up will be relatively rapid. Highly tritiated methyl iodide has also been prepared and is ready for condensation with homocysteine to yield labeled methionine. The sulfoxide will be derived from this reagent by oxidation. Efforts are also underway to improve upon available collection schemes for the evolved ethylene. To overcome limitations of physical trapping, chemical methods are being explored to increase the recovery of radiolabeled volatile materials from the expired breath of animals.

Until the radiolabeled radical trap becomes available, preparations are being made for animal studies, and *in vitro* studies are being conducted to assess how KTBA interacts with membranes and with selected oxy-radical species. These studies served to establish a new assay for the presence of this reagent (see photochemical studies, below) and capitalize on this assay to estimate the transmembrane movement of the trap in a model system (see liposome studies, below). They are now being used to establish a quantitative relationship between hydroxyl or alkoxyl radical formation and ethylene production.

Photochemical studies. It is well known that methionine is a photoreductant for flavins. Pursuing this, it has been shown that KTBA, which is an analogue of methionine, can be detected and quantified photochemically. The scheme capitalizes on previous research from this laboratory on flavin-mediated reduction of nitroxides. The concentration of KTBA, inferred from the reduction rate of the nitroxide Tempol, correlates very well with the rate of anaerobic photoreduction of the nitroxide Tempol. This is a new assay for KTBA, which is suitable for studies of the metabolism of this compound by tissue homogenates.

Interaction of the trap with cell membranes. The permeability of KTBA through lipid bilayer membranes (liposomes) has been determined using the ESR methodology pioneered in this laboratory. The data reveal that the kinetics of equilibration are slow, creating opportunities for resolving extra-cellular and intracellular free-radical processes kinetically.

Animal studies. Several small animal chambers have been acquired from colleagues at NASA Ames Research Center that are suitable for collecting radiolabeled gases. These chambers, which were originally used to study effects of prolonged exposures to high oxygen concentrations on rats, have been made available to LBL for an indefinite period. The chambers are being adapted for use with the volatile gas trap.

World Energy Demand Center Initiative

Principal Investigators: Jayant Sathaye, Lee Schipper, and Andrea Ketoff

Funding: \$50,000

Project Description

The long-term objective of this project is to better understand energy demand in industrialized and developing countries in a framework consistent for global scientific understanding of the linkage of energy demand to economic activity in these countries.

During the last two decades, the relative importance of the various countries and institutions on the world oil scene has changed; oil consumption in North America, Europe, and Japan is virtually unchanged from that of 1973, while in the rest of the world it has continued to increase, reaching 43% of world oil in 1985, as compared with only 29% in 1970. Oil and energy production has also seen a restructuring. Finally, increased energy efficiency provided the greatest contribution towards reduced world oil demand; the impact of greater efficiency will continue to be felt even if oil prices remain low. In short, the energy system is significantly different from what it was in the early 1970s, yet many decisions are based on information and mental maps of the older system.

Now it is becoming clear that oil supply and its price, as well as efficiency of use, may be only one part of the story, one whose relative importance is diminishing. There are other concerns that in the long term may be more serious. Most notable is the worsening international or global environmental impacts of energy use. The time scale for global environmental change through man's intervention, spurred by energy use, is rapid in contrast with natural global climatic and environmental changes, although the time scales for responding to problems once identified, ecological as well as political, are not well known. Unfortunately, the resilience of both human societies and the ecosystem to various energy-related "shocks" of varying rapidity, magnitude, and extent is insufficiently understood.

Accomplishments

The project set forth to achieve the long-term objective through a series of meetings among international energy experts who shared this objective. The first such meeting was held at LBL in May 1987. Participants from Europe, Asia, and Latin America attended the meeting. The consensus was that the current comfortable energy supply situation afforded an opportunity to initiate studies of energy use and its link to economic activity, before another crisis overwhelmed the economic scene.

Among those topics that received the most attention in May were the following:

- Global environmental disruption often has consequences not reversible on a short time scale. The growing awareness of its link to energy production and use indicates that limits and critical decisions may be approaching. Are present and future decision makers prepared?
- A similar awareness of the links among energy, food, urbanization, and industrialization makes decision making on the basis of energy alone both difficult and sometimes dangerous. How can present energy models and analysis paradigms be adopted to the wider human and economic context in which energy is but one variable?
- Accelerated restructuring of the demand for energy caused by changing economic growth patterns, rapidly evolving energy-use technologies, and even demographic forces has proven too complex to be handled by the data systems

and models of yesterday. What can be done to improve the understanding of the system today?

- Increased energy efficiency contributed significantly to reduced energy and oil demand, relative to activity, after 1973. Has the scope for improved efficiency narrowed, or will technology drive further improvements?
- Energy matters are now dispersed over a much wider circle of institutions, countries, and cultures than in 1973. What is the appropriate language today for understanding the problems and communicating the concerns in this diverse environment?
- The transformation of the world oil market into a commodities market with round-the-clock operation places a new actor, namely the oil trader, between oil in the ground and the final consumer. How does this affect the stability and long-term development of the world oil and energy market? What are the new roles of the actors, and the new rules under which they act?
- Availability and price stability of oil has been a major concern internationally. Does the current price of oil and increased availability mask impending shortages?
- The role of local biomass fuels (such as wood, charcoal, or dung, often termed "non-commercial energy") has been largely overlooked by national and international authorities, although this is the predominant energy form in many countries or regions. How would local, regional, and world energy decisions be affected if biomass and its associated problems are included in the picture?

These issues all point to the most important difference in the energy system of today *vis-a-vis* that of fifteen years ago: the linkages between energy and other inputs and outputs in the economy, including those involving human capital and information, have changed and will continue to evolve with rapidly transforming dynamics of the world economy. The changing linkages could lead to future energy-related crises that would require adoption of new options important to both private and public institutions.

The consensus of the group that met at LBL was that a new approach is needed that will quickly sense global and regional changes in economies, geopolitical factors, and shifting demands for energy and its forms and sources. A new learning process could greatly improve the understanding of the linkages among energy, economic security, environment, and food. This process should be a new, international effort, far beyond that of a single study. Participation in such an effort would be open to experts from any country, and an effort would be made to avoid groupings around familiar regional lines, i.e., North vs. South, industrialized vs. developing, etc. This effort could provide a forum to voice unencumbered views on controversial issues of international concern. As many of these links are too complex and are changing too rapidly for any single institution to follow, as well as becoming more international and interdependent, only a decentralized effort could provide the forum for such an activity.

This forum will have as its primary responsibility the identification of issues and options, and the subsequent improvement of the learning and analytical tools needed to deal with them, in meeting the new kinds of energy-related problems expected in the 1990s and beyond. Policy and economic analysis and synthesis from this effort will have an international perspective, which is essential to identify emerging global energy issues. An international perspective will provide a much more accurate determination of emerging perceptions and values regarding important energy issues. Policy development explorations will reflect interaction between experts from research institutions and policy officials from government and professionals from industry.

Publication

P. Berdahl, "Galvanomagnetic Luminescence and the Quantum Efficiency of Radiative Recombination of InSb," *J. Appl. Phys.* 63, 5846 (1988); LBL-23234.

Biology and Medicine Division

Center for Cancer Biology

Principal Investigator: Jack C. Bartley

Funding: \$100,200 (second year of funding)

This project developed a coordinated, innovative approach to research in carcinogenesis and mutagenesis, focusing on three areas: (1) Basis for Resistance to Alkylating Carcinogens, (2) Oxidative Damage in DNA of Human Mammary Epithelial Cells following Low-Level Irradiation, and (3) Analysis of Cell Surface Antigens to Distinguish between Normal and Transformed Human Mammary Epithelial Cells. Each program is described separately.

1. BASIS FOR RESISTANCE TO ALKYLATING CARCINOGENS

Project Description

Agents capable of alkylating intracellular DNA also induce mutations and are therefore carcinogenic. Most cells have specific enzymatic mechanisms for repair of such damage. In cell lines that lack these mechanisms, resistant populations can nonetheless be isolated. The goal of this portion of the project is to identify the molecular basis for this increased resistance. The hypothesis that the resistant cells are better able to repair damage in critical regions of the genome will be tested in two ways. The possibility that actively transcribing genes are preferentially repaired will be tested by a method using monoclonal antibodies to select repaired DNA followed by hybridization using probes for specific DNA sequences. The possibility that DNA undergoing replication is preferentially repaired will be tested by adapting a technique with *E. coli* for separation of replicating from nonreplicating regions of the genome.

Accomplishments

The first possibility was tested by separating DNA regions containing bromodeoxyuridine (BrdUrd)

substitution in repair patches from all other DNA by using a monoclonal antibody against BrdUrd. Currently, parallel experiments are being conducted with alkylating agents in the resistant and sensitive population of Chinese hamster ovary cells. The results of these investigations will provide a direct answer to the suggestion that repair in actively transcribed genes endows the cells with resistance to alkylating damage.

With respect to the second approach, recent bacterial studies have shown that DNA damage introduced in the vicinity of DNA replication forks requires a specific inducible process for their repair. Structural constraints at the growing fork make repair at this site refractory to the constitutive repair process (Figure 1). Preliminary studies indicate that this technique and approach for analyzing repair in replication forks can be adapted to DNA from mammalian cells, even though this DNA is in a more complex configuration. This technique is currently being applied to the resistant and sensitive mammalian cell lines exposed to various alkylating agents. This approach will provide, for the first time, a direct test of the concept that repair in the vicinity of replication forks has special importance in the increased resistance to DNA damage in mammalian cells. In this respect, because this repair capability appears to be inheritable, this study could provide unique insights into the basis for familial susceptibility to cancer.

A final possibility considered as being responsible for the increased resistance to alkylating agents is

Fig. 1. Schematic representation of the DNA replication fork with the likely sites that are refractory to DNA repair due to structural constraints. [XBL 892-451]

the "alarmone" response. Cells subjected to various types of environmental stress (e.g., heat, massive DNA damage, increased oxygen tension) respond with a complex set of metabolic adaptations that appear to increase cell survival. One indicator of this response is an increase in the intracellular level of diadenosine tetraphosphate. This possibility has been studied by measuring the concentration of diadenosine tetraphosphate in resistant and non-resistant cell populations after exposure to various alkylating agents. The indications are that the "alarmone" response may be greater in the resistant cells. Much work remains to be done in verifying this promising finding and, if true, in establishing the molecular mechanisms providing for increased cell survival.

2. OXIDATIVE DAMAGE IN DNA OF HUMAN MAMMARY EPITHELIAL CELLS FOLLOWING LOW LEVEL IRRADIATION

Project Description

Benzo(a)pyrene (B(a)P) is a potent mutagen and carcinogen. Its metabolism and subsequent binding to DNA has been extensively studied in cell culture. It has previously been shown that human mammary epithelial cells (HMEC) in culture are capable of metabolizing B(a)P. A major pathway of B(a)P metabolism also leads to the formation of free radicals. There is increasing evidence implicating such free radicals, particularly those derived from molecular oxygen, in many stages of chemical carcinogenesis. To understand the role of damage induced by chemical carcinogens in carcinogenesis, it is important to identify the primary DNA lesions produced directly by adduct formation and indirectly by free radicals. The purpose of this second subproject is to investigate these questions in the context of B(a)P metabolism.

Accomplishments

One product that is formed in DNA as a consequence of chemical oxidation or ionizing radiation is thymine glycol. A sensitive immunoassay for thymine glycols has been developed using a monoclonal antibody to this product in DNA. This method has been used to determine whether reactive oxygen species are being produced during

the metabolism of B(a)P by HMEC and what role these reactive oxygen species play in cellular toxicity.

The results show that (a) thymine glycols are produced in DNA in a dose-dependent manner at levels comparable to direct B(a)P-DNA adducts following exposure of HMEC to B(a)P; (b) the production of thymine glycols, but not that of B(a)P adducts, is reduced if superoxide dismutase (SOD) is present at the time of treatments; (c) survival is increased if SOD is present during treatment with B(a)P; and (d) at equitoxic doses, ten-fold more thymine glycols are produced following B(a)P than ionizing radiation.

3. ANALYSIS OF CELL SURFACE ANTIGENS TO DISTINGUISH BETWEEN NORMAL AND TRANSFORMED HUMAN MAMMARY EPITHELIAL CELLS

Project Description

Mammary systems are particularly valuable for the study of human cellular carcinogenesis because: (a) large quantities of normal, atypical, and malignant tissues are readily available from individuals of all ages as discard material from commonly performed surgical procedures; (b) functionally differentiated cells are available from lactation fluids; (c) the mammary epithelial cell is a major site of malignant transformation *in vivo*; and (d) the breast glandular epithelial cells perform a variety of specialized functions in response to hormonal stimuli. However, the human mammary systems are limited by the lack of available tissue from a variety of differentiated states, and by the lack of recourse to *in vivo*, whole-animal experiments. Consequently, well-defined culture systems are especially important. Correlating experimentally induced aberrancies with the properties found in cells derived from human breast tumors can help determine if similar transformation pathways are being utilized *in vivo* and *in vitro*.

This investigation will concentrate on the development of antibodies to components of the cell surface as one means of studying the nature of the transformed cells produced. Since the cell surface determines many aspects of tumor cell behavior, this study may elucidate crucial determinants related to malignancy.

Accomplishments

A major difficulty in establishing *in vitro* transformation systems for human epithelial cells lies in defining markers to identify the transformed cell, if and when it appears. Markers that permit easy selection or detection of small numbers of transformed cells within a large cell population are most useful. A marker largely specific to human mammary cells is human milk fat globule antigens. Expression of specific mammary cell antigens has been correlated with both the state of differentiation and with transformation. Six monoclonal antibodies were employed to screen the cell lines. Although both normal and transformed cells were recognized by some of the antibodies, differences in expression were observed. The antibodies designated P₂B₁ and P₂C react with antigens on the cell surface of two lines of transformed cells, even though these cells have quite different phenotypes. The applicability of these antibodies as the basis for a transformation assay is currently being tested; however, the reactivity of antibodies P₂B₁ and P₂C correlates with metabolic activity in transformed mammary epithelial cells, which, in turn, is associated with the metabolic pattern of cells isolated from mammary carcinomas.

Molecular Biology of Hemopoiesis

Principal Investigator: Shirley Ebbe

Funding: \$135,800

Project Description

The goal of this project was to further the understanding of cellular and molecular mechanisms that regulate hemopoiesis *in vivo*. The approach was to establish collaborative research between hematologists and molecular biologists with the aim of applying some of the methods of molecular biology to hemopoiesis. The method of particular interest was *in situ* hybridization. Specific hemopoietic areas of interest were originally megakaryocytopoiesis and repopulation of the marrow by transplanted stem cells. Quantitative *in situ* hybridization has initially been applied to erythropoiesis with the ultimate aim of identifying erythroid stem cells and determining the spatial organization of erythropoiesis in relationship to other hemopoietic cells and stromal elements.

Accomplishments

Erythropoiesis. The methods used for *in situ* hybridization on mouse bone marrow cells have been adapted from those used on a different project involving collagen (type I) expression in avian tendon cells. In this case, it could be shown that the *in situ* technique had a high signal-to-noise ratio (>30), first order kinetics with excess probe, and quantitative accuracy. Using approximately the same protocol on bone marrow smears but with a tritium-labeled beta-major hemoglobin probe, all the expected erythroid progenitor cells were labeled (by autoradiography), while the cells from other lineages were not. Most importantly, immature erythroid cells that would otherwise have been difficult to distinguish on staining properties could be resolved on the basis that they contained hemoglobin mRNA.

To determine how far back in the erythroid lineage one can detect hemoglobin mRNA, bone marrow cells from hypertransfused mice were used. Due to the presence of excess erythrocytes (hematocrit >70% for 5 days), erythropoietin (epo) production is repressed and the production of reticulocytes approaches zero. In three experiments, colony assays in culture showed only BFU-E and no CFU-E (two successive stages of erythroid progenitor cells; time 0 in Table 1).

Table 1. Colony Assays in Culture

Hours after epo	BFU-E/10 ⁵ cells	CFU-E/10 ⁵ cells
0	6	0
2	6	46
8	6	78
24	7	95
normal	12	106

In situ hybridization with the hemoglobin probe showed no cells with an accumulation of grains above background after a one-week exposure. Since background counts were extremely low, exposure time of the autoradiographic emulsion was increased to three months. At this point, sufficient grains had accumulated to clearly mark specific cells as containing hemoglobin mRNA. The large nuclei and small cytoplasmic nature of the positive cells were consistent with their being

BFU-E or earlier precursor cells. By comparison with results obtained with tendon cells and a glucose metabolism enzyme (glyceraldehyde phosphate dehydrogenase) that was present at 200 copies/cell and just discernible after a one-week exposure, these early erythroid cells probably contained hemoglobin mRNA at the levels of about 10 molecules/cell.

Marrow from hypertransfused mice induced with erythropoietin showed a rapid induction in the concentration of CFU-E (two hours, above) and no change in BFU-E. This rapid change in CFU-E numbers raises questions about how epo affects the stem cell pool. Is this a maturation or a cell division event? Additionally, the strong action of epo *in vivo* contrasts strongly with the fact that epo is present in the CFU-E assay yet shows no effect on hypertransfused marrow cells. New information gained from the *in situ* hybridization assay should help resolve these apparent inconsistencies by being able to more clearly identify the stem cell population.

Another advantage of an *in situ* hybridization assay is that it retains spatial information and can aid in an analysis of the hemopoietic microenvironment (HME). This assay will be especially important in determining how the HME affects the committed stem cell. In bone marrow smears, the well-cited erythroblastic islet was observed, which shows a hybridization pattern as expected (Figure 2). To retain more spatial information, frozen sections of marrow were used for *in situ* hybridiza-

tion, and it was found that erythroid development occurs in localized areas. In addition, studies were begun to localize extracellular matrix (ECM) molecules that make up the HME. Combining this with an *in situ* hybridization assay will allow the identification of the ECM around the committed stem cells.

Stem cells. The initial intention of using retrovirus markers for hematologic stem cells to trace their proliferation and differentiation had to be abandoned. The available technology requires a number of cells that could not be obtained by bleeding a mouse. Hence the plan of serial measurements in the same animal proved impractical. To kill animals sequentially at different time periods would not solve the problem, because different DNA fragments are tagged by the virus in different cells. The methodology was not suited to follow the progeny of a given stem cell, because it could not be done in the same animal.

A different approach to follow stem cell proliferation and maturation is being actively pursued. Two isoenzymes of glucose-phospho-isomerase occur in different strains of mice, some of which are congenic so that they can be used for marrow transplantation without risk of graft versus host disease and also for marrow transplantation into normal, nonirradiated hosts. Although the production of a monoclonal antibody will be time consuming, the payoff should be well worth the effort. It should be possible, for the first time, to identify small numbers, at most a few hundred, of transplanted stem cells and their location, multiplication, and differentiation by antibody-labeled histologic techniques. This is in contrast to the best methods presently available, which require 15,000+ cells to distinguish donor and host cells and hence cannot be used to identify the earliest stem cells.

Megakaryocytopoiesis. The first questions asked were about the presence of platelet-derived growth factor (PDGF) in megakaryocytes and if it was produced by megakaryocytes. By immunohistochemistry, it was found that an antibody to human PDGF reacts with cytoplasmic granules in mouse megakaryocytes. Methods are being revised to permit convincing photographic demonstration of the reaction.

Portions of the gene for the B chain (c-sis) and the A chain of PDGF have been cloned, and riboprobes have been prepared. Thus far, the results of repeated hybridization of probes for genomic DNA with bone marrow cells and leukemic cell lines

Fig. 2. Bone marrow smear *in situ* hybridized with a hemoglobin probe and exposed for 7 days. The macrophage-like cell in the middle of the field is surrounded by normoblasts, characteristic of an erythroblastic islet. [CBB 891-251]

have been inconclusive. Experiments are in progress with the viral counterpart, *v-sis*. Genes for more abundant megakaryocyte proteins may be more appropriate for the goal of establishing the use of quantitative *in situ* hybridization for megakaryocytes as well as for erythroid cells.

Human DNA Polymorphisms and Genetic Regulation of Plasma Lipoproteins

Principal Investigator: Ronald M. Krauss

Funding: \$ 140,300

Project Description

Definition of genetic mechanisms responsible for regulation of human plasma lipoproteins and identification of specific genetic alterations may give rise to disease states associated with accelerated atherosclerosis.

Accomplishments

Analysis of DNA polymorphisms in patients with a new lipoprotein phenotype associated with increased cardiovascular disease risk. Methods were successfully established for isolation of DNA from white blood cells and for Southern blot analysis of several DNA restriction fragment length polymorphisms (RFLPs) involving the gene for human apoprotein B on chromosome 19 and the gene complex including apoA-I, apoC-III, and apoA-IV on chromosome 11. RFLP analyses were carried out on DNA samples from kindreds of probands with the dense LDL subclass phenotype that was recently discovered in this laboratory, and which recently has been shown to be associated with increased risk of coronary artery disease. Linkage analysis has not as yet shown significant positive or negative linkages of the candidate genes to the new phenotype. However, RFLP haplotypes from these kindreds revealed few informative matings, and it is anticipated that more informative kindreds will be identified as more samples are examined. Very recently, with the assistance of Dr. Edward Rubin of the Howard Hughes Medical Institute at UC San Francisco (UCSF), new methodology for RFLP analysis employing the polymerase chain reaction (developed by investigators at Cetus Corporation) has been implemented. This method-

ology promises to be far more efficient and rapid than the Southern blot approach and should allow for sufficient analyses in the coming year to assess possible linkages to an array of candidate genes involved in lipoprotein structure and metabolism.

Discovery and characterization of familial defective ApoB-100. In the past year, in collaboration with investigators at the University of Texas and UCSF, a new human genetic disorder was discovered that results in the development of hypercholesterolemia. The cause of this disorder is a mutation in apoB-100, the major protein constituent of plasma low-density lipoproteins (LDL), which results in defective binding of LDL to its receptor. This is the first description of a functionally significant mutation affecting LDL structure and the first single gene disorder to be associated with hypercholesterolemia since the discovery of LDL receptor deficiency by Brown and Goldstein in 1973. This laboratory has been involved in separating and characterizing the LDL products of the mutant and normal alleles in heterozygote patients with this disorder and in studying the effects of the mutation on levels of potentially atherogenic lipoprotein subfractions. In addition, as described below, hypercholesterolemic patients are being screened for additional affected probands, with the hope of identifying a cluster of mutations in apoB-100 that may help to define the structure of the LDL receptor binding site.

Establishment of a clinical research unit for the study of genetic disorders leading to accelerated atherosclerosis. A major aim of this project has been to establish a clinical research unit in order to screen patients and their families for genetic variants affecting lipoprotein metabolism and to carry out studies linking these variants to specific DNA polymorphisms. Development of this unit has been made possible by an institutional collaboration of LBL with Alta Bates Hospital. This unit will provide a strong base for referral of potential research subjects with heart disease and lipid disorders and will also provide resources for nutritional counseling and other forms of treatment for patients who have been found to be at increased heart disease risk as a result of these research studies. The unit is now beginning to screen potential subjects and their families for the several genetic disorders that have been studied, and it is anticipated that new variants will be discovered by application of the analytic techniques developed in this laboratory. DNA is being isolated from all probands and their families, with

a census to date of over 200 samples. Over the next few years, it is planned to assemble a library of at least 1,000 samples from 200 or more kindreds. This resource should be of great value not only for linkage studies, but also for identifying other DNA RFLPs using probes developed by the Human Genome Center. Full implementation of the range of research activities made possible by this clinical unit will require additional sources of funding, and proposals are now being prepared for this purpose.

Hematozoa and Erythropoiesis

Principal Investigators: Paul H. Silverman and Kathleen L. Miller

Funding: \$111,000 (third year of funding)

Project Description

The purpose of this project is to elucidate the cellular mechanisms involved in the anemia and the immunosuppression associated with malaria infection. In addition to understanding the pathophysiology of malaria, these studies will increase the understanding of the hemopoietic system and how its response to disease and environmental stress can be manipulated. By studying how malaria infection alters the proliferation and differentiation of hemopoietic stem cells, the development of therapeutic strategies can begin.

Accomplishments

The initial focus of this project has been to examine the effects of malaria infection upon early pluripotent hemopoietic stem cells, the cells from which all red and white blood cells are derived, and committed erythroid progenitor cells. It has been shown that infection of mice with three strains of *Plasmodium* led to a depletion of bone marrow pluripotent stem cells (CFUs). A concomitant rise in the spleen stem cells failed to compensate for the loss in the bone marrow. Studies are now under way to determine whether these mobilized stem cells are functionally altered and therefore contribute to the anemia and immunosuppression observed in malaria infection.

Studies of erythropoiesis in malaria-infected mice, using ^{59}Fe uptake, colony assays for erythroid progenitor cells, and an *in vitro* assay to measure

the proliferative response of erythroid progenitor cells to the hormone erythropoietin (epo) required for mature red blood cell development, demonstrated that erythropoiesis is inhibited during the course of malaria infection. Thus it appears that cells committed to the erythroid lineage as well as pluripotent stem cells may be altered by malaria infection. Experiments investigating the relative number of erythroid progenitor cells in the spleen and bone marrow of *Plasmodium berghei* infected mice, using an *in vitro* colony assay, showed that both the early progenitors, burst forming unit-erythroid (BFU-E) and the later progenitors, colony forming unit-erythroid (CFU-E), declined in both the spleen and bone marrow of infected mice over the course of infection (Figure 3). There was a transient rise in CFU-E, no doubt in response to the increased levels of erythropoietin observed in infected mice, but this increase was not sustained. Infected mice appear to be unable to sustain erythropoiesis despite increased pressure for red

Fig. 3. The number of colony forming units-erythroid (CFU-E) and burst forming units-erythroid (BFU-E) in the spleen and bone marrow of BALB/c mice infected with 1×10^5 parasitized red blood cells at various times after infection with *P. berghei* CFU-E and BFU-E were determined by *in vitro* colony assays. Results are expressed as the percentage of control values for normal BALB/c mice. [XBL 8711-4911]

blood cell development and the presence of significant levels of erythropoietin.

Experiments employing an *in vitro* proliferative assay to measure the response of erythroid progenitor cells to epo have provided further evidence that erythropoiesis is inhibited during malaria infection. Spleen cells from mice made anemic by injections of the drug phenylhydrazine (PHZ) were greatly enriched for erythroid progenitors and showed significant levels of cell proliferation in the presence of epo, while spleen cells from malaria-infected mice with a similar degree of anemia showed low levels of cell proliferation in the presence of epo (Figure 4). It was also found that spleen or bone marrow cells from malaria-infected mice, when added to cultures of uninfected spleen cells, could inhibit the response of these erythroid progenitor cells to epo. When spleen cells from infected mice were separated into nonadherent and adherent (macrophage-rich) populations, it took far fewer adherent cells to inhibit the response. In addition, the ability of spleen cells from infected mice to inhibit the response could be abrogated if the spleen cells were treated with antibody and complement to deplete the cells of macrophages (Figure 5). Further experiments demonstrated that inhibition could be mediated by soluble factors, as

Fig. 4. The *in vitro* proliferative response of various spleen cell populations to epo as measured by the incorporation of ^3H -thymidine into DNA. Normal Sp = spleen cells from normal BALB/c mice; P. berghei and P. vinckei Sp = spleen cells from BALB/c mice infected with 1×10^5 parasitized red blood cells seven and five days previously, respectively; PHZ Sp = spleen cells from BALB/c mice treated with the drug phenylhydrazine. Results are expressed as the mean counts per minute (cpm) of six replicate cultures and represent the total amount of ^3H -thymidine (^3H -TdR) incorporated into DNA. [XBL 8711-4913]

EFFECT OF DEPLETION OF Mac-1 CELLS

Fig. 5. The effect of the addition of various spleen cell populations on the proliferative response to epo of spleen cells, enriched for erythroid progenitor cells, from phenylhydrazine (PHZ) treated mice. NSp = spleen cells from normal BALB/c mice; PbSp = spleen cells from P. berghei infected mice; NSp-Mac 1 = normal spleen cells treated with anti-macrophage antisera and complement (C'); PbSp-Mac 1 = spleen cells from P. berghei infected mice treated with anti-macrophage antisera and C'. Results are expressed as the percentage of control values for PHZ treated spleen cells. [XBL 8711-4910]

conditioned medium produced from malaria-infected spleen cells could also inhibit the proliferation of erythroid progenitor cells in the presence of epo (Figure 6). This inhibition could be somewhat overcome with higher doses of epo, suggesting a cytostatic rather than a cytotoxic effect. In addition, conditioned medium produced from normal spleen cells preincubated with parasitized red blood cells could also inhibit this response. Together these results demonstrate that soluble mediators released by macrophages may mediate the anemia that is associated with malaria.

In parallel studies in collaboration with Chiron Corporation and Pfizer, the ability of purified recombinant macrophage factors, such as interleukin-1 (IL-1) and tumor necrosis factor (TNF), to inhibit erythropoiesis both in the *in vitro* colony assay and in the proliferative assay has been examined. TNF was found to inhibit erythroid colony development in a dose-dependent fashion (Figure 7). It has previously been shown that mice infused with TNF via osmotic pump implants show alterations in pluripotent stem cell kinetics very similar to those described earlier in malaria-infected mice. Currently, erythropoiesis in mice infused with TNF is being investigated, and preliminary evidence has been obtained that erythropoiesis is indeed inhibited in these mice. IL-1 was also shown to inhibit the response of

Fig. 6. The effects of conditioned medium from *P. berghei* infected spleen cells (PbCM) and from *P. vinckei* infected spleen cells (PvCM) on the proliferative response to epo of spleen cells, enriched for erythroid progenitor cells, from phenylhydrazine (PHZ) treated mice. Results are expressed as the mean counts per minute (cpm) of six replicate cultures and represent the total amount of ³H-thymidine (³H-TdR) incorporated into DNA. [XBL 8711-4906]

Fig. 7. The effects of recombinant murine tumor necrosis factor rMuTNF on in vitro bone marrow colony forming units-erythroid (CFU-E) and burst forming units-erythroid (BFU-E). Results are expressed as the percentage of control values obtained for normal BALB/c bone marrow cells in the absence of added rMuTNF. [XBL 8711-4909]

erythroid progenitor cells to epo. Future work will determine whether the factor in the conditioned medium from the spleens of malaria-infected mice that is responsible for the inhibition of erythropoiesis is IL-1 or TNF.

The project is currently being expanded to include an examination of the immunosuppression that is also associated with malaria. Studies examining the ability of lymphocytes from infected mice to respond to the mitogens lipopolysaccharide (LPS), phytohemagglutinin (PHA), and concanavalin A (ConA), which are used to monitor lymphocyte functional capacity, showed that lymphocyte responsiveness is also inhibited during the course of malaria infection (Figure 8). In addition, spleen cells from infected mice were able to suppress the

Fig. 8. The proliferative response of spleen cells from mice infected with 1×10^5 parasitized red blood cells to the mitogens lipopolysaccharide (LPS), phytohemagglutinin (PHA), and concanavalin A (Con A) at various times after infection with *P. berghei*. The results are expressed as the percentage of control values obtained for spleen cells from normal BALB/c mice. [XBL 8711-4908]

response of normal spleen cells to these mitogens when added to the cultures. The relationship of the inhibition of erythropoiesis to inhibition of the immune response is under investigation. It is not yet clear whether similar mechanisms are involved.

In summary, it has been shown that alterations in the kinetics of pluripotent hemopoietic stem cells (CFUs) and alterations in the functional capacity of committed erythroid progenitor cells and lymphocytes occur during the course of malaria infection. These results suggest that soluble mediators, such as IL-1 and TNF released by macrophages activated by malarial parasites, may mediate some of the pathology that is associated with malaria infection. This no doubt reflects a more general phenomenon that is not unique to malaria infection. Determination of the factors that are involved and their mechanisms of action will aide in the understanding of the anemia and immunosuppression that are often associated with infectious agents such as malarial parasites.

Publications

- R. Goth-Goldstein, "MNNG-Induced Partial Phenotypic Reversion of Mer⁺ Cells," *Carcinogenesis* 8, 1449 (1987).
- R. Goth-Goldstein and R.M. Hughes, "Increased Resistance of CHO Cells to Methylating Agents after Previous Exposure to Them" (in press).
- S.A. Leadon, M.R. Stampfer, and J.C. Bartley, "Production of Thymine Glycols during the Metabolism of Benzo(a)pyrene by Human Mammary Epithelial Cells," *Proc. Natl. Acad. Sci. USA*, in press.
- L. Moss, D. Greenwalt, B. Cullen, N. Dinh, R. Ranken, and G. Ojakian, "Cell to Cell Heterogeneity in the Expression of Carbohydrate Based Epitopes of Mucin-type Glycoprotein on the Surface of Human Mammary Carcinoma Cells," submitted to *J. Cell Physiol.*
- G. Parry, J. Beck, L. Moss, J.C. Bartley, and G. Ojakian, "Determinants of Apical Membrane Polarity in Mammary Epithelial Cell Cultures: The Roles of Cell-Substratum, Cell-Cell, and Membrane-Cytoskeleton Interactions," submitted to *Proc. Natl. Acad. Sci. USA*.
- J.C. Schooley, B. Kullgren, and A.C. Allison, "Inhibition by Interleukin-1 of the Action of Erythropoietin on Erythroid Precursors and Its Possible Role in the Pathogenesis of Hypoplastic Anemia," *Brit. J. Haematology* 67, 11 (1987).
- P.H. Silverman, J.C. Schooley, and L.J. Mahlmann, "Murine Malaria Decreases Hemopoietic Stem Cells," *Blood* 69, 408 (1987).
- P.H. Silverman, J.C. Schooley, L.J. Mahlmann, B. Kullgren, K.L. Smith, and K.L. Miller, "Effects of Malaria upon Hemopoiesis," Annual Meeting of the Northern California Parasitologists, Fresno, CA, May 30-31, 1987.
- P.H. Silverman, J.C. Schooley, L.J. Mahlmann, B. Kullgren, K.L. Smith, and K.L. Miller, "Mechanisms of Hemopoietic Suppression by Murine Malaria," 36th Annual Meeting of the American Society for Tropical Medicine and Hygiene, Los Angeles, CA, Nov. 29-Dec. 4, 1987.
- M.R. Stampfer and J.C. Bartley, "Growth and Transformation of Human Mammary Epithelial Cells in Culture," in *Cellular and Molecular Biology of Experimental Mammary Cancer*, D. Medina, W. Kidwell, G. Hepner, and E. Anderson, eds., Plenum Publishing Corp., New York, in press.
- M.R. Stampfer and J.C. Bartley, "Human Mammary Epithelial Cells in Culture: Differentiation and Transformation," in *Breast Cancer: Cellular and Molecular Biology*, R. Dickson and M. Lippman, eds., Martinus Nijhoff Publishing Co., Norwell, MA, in press.

Chemical Biodynamics Division

Conversion of Singlet Molecular Oxygen Electronic Excitation into Electrical Energy

Principal Investigator: Heinz Frei

Funding: \$27,100 (second year of funding)

Project Description

The purpose of this project is to explore ways to accomplish chemical storage and efficient conversion into electrical energy of near-infrared solar quanta. This is a currently untackled problem in solar photochemistry whose importance derives from the fact that more than half of the solar irradiance at ground level lies in the near-infrared spectral range. The goal is to demonstrate the feasibility of chemical storage of near-infrared photon energy and its quantitative conversion into electrical energy.

The proposed concept is based on the chemical storage of metastable $^1\Delta$ (singlet delta) molecular oxygen (Figure 1), parts of which have been shown to be feasible in the previous year of funding. Near-infrared photons are captured by a dye that very efficiently sensitizes singlet delta O_2 (O_2 in its first excited electronic state). Temporary chemical storage of the near-infrared quantum is accomplished by insertion of $O_2(^1\Delta)$ into an acceptor molecule like an aromatic hydrocarbon to form an endoperoxide. Thermal back reaction of the endoperoxide regenerates O_2 in the $^1\Delta$ excited state in very high yield, which in turn opens a way to directly convert the stored chemical energy into electrical energy without involving a Carnot cycle with its inherent losses. The idea is to initiate an excited state redox reaction with the thermally retrieved $O_2(^1\Delta)$ whose products would spontaneously regenerate the ground state reactants (See Figure 1, where the conversion cycle is shown for a halide-halogen reaction). Such a redox cycle, conducted in an electrochemical cell, would permit quantitative conversion of stored chemical energy into electricity.

Fig. 1. Concept for chemical storage and conversion into electrical energy of near-infrared solar quanta by singlet oxygen chemistry. X^- = halide, X_2 = halogen. [XBL 891-336]

In the first year of this two-year project, a water-soluble endoperoxide storage system, that of 3,3-(1,4-naphthylidene) dipropionate endoperoxide, was explored. Retrieval of $O_2(^1\Delta)$ from this storage molecule was directly demonstrated by observation of $^1\Delta \rightarrow ^3\Sigma$ near-infrared chemiluminescence. In this second year, a $O_2(^1\Delta)$ excited state redox reaction in aqueous solution was explored that would allow conversion of $O_2(^1\Delta)$ electronic energy into electricity. The chemical reaction was studied in real time by laser flash emission and transient absorption spectroscopy in order to elucidate mechanistic details.

Accomplishments

The search for regeneration $O_2(^1\Delta)$ excited state redox reactions in aqueous solution was begun by exploring the reaction with iodide. Thermodynamically, the $O_2(^1\Delta) + I^-$ reaction is spontaneous at pH < 11 if reduction stops at H_2O_2 , and under acidic as well as basic conditions if reduction proceeds all the way to H_2O . Regeneration of ground state O_2 and I^- from H_2O_2 and I^- is spontaneous at pH > 3, and from H_2O and I_2 at pH > 12. Since the driving force for the $O_2(^1\Delta) + I^-$ reaction increases with decreasing pH while the opposite holds for the regeneration of $O_2(^3\Sigma)$ and I_2 , the forward reaction would be best run in neutral or acidic solution, while the back reaction would require changing to basic conditions.

Study of $O_2(^1\Delta)$ quenching by I^- in H_2O and D_2O using the time-resolved near-infrared emission technique revealed a (total) bimolecular quenching rate constant of $8.7 \times 10^5 \text{ l/mole} \cdot \text{sec}^{-1}$. After developing a very sensitive visible/near-infrared dual-beam transient absorption spectrometer based on an Ar-ion laser-pumped CW dye laser (detection limit: 10^{-5} absorbance units; time resolution: nanosecond to millisecond), a search was made for oxidation products. Absorption was found in the spectral range from 458 nm (the shortest probe wavelength available) to 520 nm, which exhibited a pronounced H_2O/D_2O isotope effect both on product rise and asymptotic yield, as shown in Figure 2. This solvent isotope effect on the product absorption constitutes a direct proof for $O_2(^1\Delta)$ initiated chemistry. The wavelength dependence of the blue-green product absorption identified I_3^- as the absorber.

Since the I_3^- product rise precisely mirrored the $O_2(^1\Delta)$ reactant decay, as shown in Figure 2, all elementary reaction steps following the initial

Fig. 2. Solvent isotope effect on I_3^- product absorbance rise at 458 nm (top curves) and $O_2(^1\Delta)$ reactant emission decay at 1.27 micron (bottom curves) in O_2 -saturated 0.1 M iodide solution. [XBL 883-699]

encounter of $O_2(^1\Delta)$ and I^- must occur in a microsecond or less, which implies that the reaction follows a multielectron transfer path. The most probable mechanism consistent with the temporal behavior of I_3^- and its pH-dependence is transient formation of iodoperoxy anion by what can formally be described as a two-electron oxidation of I^- : $O_2(^1\Delta) + I^- \rightarrow IO_2^-$. Iodoperoxy anion so produced would react in aqueous solution with I^- to give I_3^- in less than a microsecond at the iodide concentrations used in these experiments. Hence, aside from having produced the first direct evidence for $O_2(^1\Delta) + I^-$ excited state redox chemistry, these time-resolved experiments allowed the elucidation of the mechanism of this important reaction of $O_2(^1\Delta)$.

The $O_2(^1\Delta) + I^-$ excited state redox reaction, combined with the previously demonstrated temporary storage of $O_2(^1\Delta)$ in aqueous solution in the form of an ionic endoperoxide, establishes the feasibility of two key steps of the new concept for storage and conversion of near-infrared photon energy outlined in Figure 1. Crucial for the practical implication of the conversion of $O_2(^1\Delta)$ electronic energy into electricity is development of an electrochemical cell that could be driven by the $O_2(^1\Delta) + I^-$ reaction studied here, or other $O_2(^1\Delta)$ excited state redox reactions in aqueous solution yet to be explored, like reaction with Br^- . The main task is

identification of p-type semiconductor electrode materials that would permit reduction of O_2 in its $^1\Delta$ excited state by dark-hole injection into the valence band. Examples of materials with appropriate valence band edge potentials [more negative than $E^\circ(O_2(^1\Delta)/O_2^-)$] are GaAs, GaP, and Si. Time-resolved laser flash kinetic spectroscopy could again be used to test the efficiency of these materials in terms of $O_2(^1\Delta)$ reduction if colloids can be obtained. This technique for evaluation of electrode materials would have the unique advantage of giving direct mechanistic insight into the heterogeneous reaction.

Aside from its significance with respect to identification of semiconductor electrodes for generation of electricity from $O_2(^1\Delta)$ excited state redox reactions, reduction of $O_2(^1\Delta)$ by spontaneous hole injection into the valence band of a p-type material would constitute a prototype example for semiconductor catalysis of a near-infrared induced reaction. Semiconductor catalysis of chemical reactions initiated by long wavelength quanta in a room-temperature environment is a very important future research area in solar photochemistry since it has the potential of providing access to low-energy pathways of many reactions with the very abundant low-energy solar photons.

Identification of Target Sites for Nuclear DNA Binding Proteins from Root and Leaf Tissue of Nicotiana tabacum

Principal Investigator: Francesca Leach

Funding: \$41,900 (second year of funding)

Project Description

The long-term goal of this project is to understand how tissue-specific expression of a root-specific and a leaf-specific gene occurs in tobacco. Originally, it was planned to study the two promoters by fusing them to a reporter gene, CAT, and monitoring the activity of the chimaeric constructs by transient protoplast transformation. In the past funding period, all biological and genetic tools

were built, and the techniques crucial to carry out the main experiments were mastered.

Accomplishments

Sterile cultures of plantlets, isolated roots, and tobacco leaf calli suspensions have been established, and have been propagated a sufficient number of times to obtain enough experimental material.

The 5' upstream regions of the two ORF of the *pRiA4 T-DNA* (ORF 12-leaf specific and ORF 15-root specific) and transcriptional fusions to the CAT gene have been cloned. Each of the 5' regions has been further subcloned to yield overlapping subsets of fragments ending at the same 3' nucleotide (just before the ATG codon), but with several combinations of 5' end deletions. These subfragments have been fused to the newly available GUS gene in preparation for promoter analysis by deletion mutagenesis and S1 mapping experiments.

Techniques for the genetic transformation of plant cells by using a binary vector system derived from pBIN to obtain transgenic plants or by direct protoplast transformation with naked DNA in view of testing for transient expression of the constructs have been mastered.

The capacity to prepare clean and intact tobacco root and leaf nuclei has been tested. A good isolation procedure has been developed by modifying a published technique. Filter-binding assays of nuclear proteins to the isolated root and leaf promoters have been undertaken. Although preliminary, none of the conditions tested have brought to light a repeatable difference in the DNA-binding qualities of the two promoter regions.

As a consequence of the above experimental considerations, this work is being modified in two ways:

- GUS is now being used as a reporter gene because it is more sensitive and the product is easier to assay.
- The possibility that the differing amounts of mRNAs from ORF12 and ORF15 in leaf and root tissues is due to post-transcriptional rather than transcriptional events will be tested.

Synthesis of Catalytic Antibodies

Principal Investigator: Peter G. Schultz

Funding: \$27,500

Project Description

The objectives of the project were to structurally characterize a catalytic antibody that hydrolyzes methyl-p-nitrophenyl carbonate 1 and to generate antibodies to N-methylporphyrin (2) transition state analogues for the metalation of porphyrins.

Accomplishments

NMR studies of catalytic antibodies were carried out. A series of nitroxyl-nitrophenyl phosphate transition state analogues have been synthesized in the laboratory. These spin labels bind tightly to the antibodies that hydrolyze carbonate 1. Difference NMR in the presence of reduced and oxidized spin label has provided information on the amino acids side chains in the antibody combining site. ^1H or ^{15}N -labeled Phe, Tyr, Arg, and Trp amino acids have been incorporated into the antibodies to specifically identify residues involved in binding and catalysis.

ESR studies were also carried out with spin labels of differing lengths. These studies have demonstrated a high degree of steric complementarity between the antibody and transition state analogue and have provided a cavity depth of 9–12 Å. Chemical modification experiments suggest the presence of Tyr and Arg in the combining site.

Conjugates of N-methylporphyrin to BSA and KLH have been isolated and prepared. High titer monoclonal antibodies to these antibodies have been generated. Ascites should be available by February 1, 1988. These antibodies will then be assayed for their ability to strain the porphyrin to a conformation favorable for metalation.

NMR Studies of the Structure and Dynamics of Biopolymers

Principal Investigator: David E. Wemmer

Funding: \$25,300 (second year of funding)

Project Description

The intent of this project was to develop a new program in the use of nuclear magnetic resonance (NMR) spectroscopy for the determination of biomolecular structures in solution, particularly molecules involved in storage, expression, and regulation of genetic expression. This requires development of models for such systems that are amenable to NMR study, the production of the appropriate molecules (or their isolation from natural sources), obtaining the necessary NMR data to determine the structures and dynamics of these molecules, and as necessary, to develop new methods for obtaining and analyzing the data.

Accomplishments

During this second year of PDF funding, the DSPACE distance geometry program from Hare Research has been implemented (basically as a β -test site). This has allowed the calculation of coordinates for a number of different molecules.

Using previously determined assignments in the bee venom peptide apamin, extensive NOE intensity measurements have been carried out to get interproton distances, and the distance geometry algorithm was used to calculate structures consistent with the NMR data (see Figure 3). The structures which result are quite close to one another, indicating that the structure is well defined from the data. The analysis will now be extended to other related peptides.

Fig. 3. Distance geometry derived structures of apamin. (A) all side chains shown; (B) only cystine and proline side chains shown with backbone atoms. [XBL 891-226]

The complete assignments of the proteins RP_{II} and RP_{III} isolated from the sea anemone *Radianthus pumotensis* have been determined, as have preliminary structures for RP_{II} . These are now being used to extend the NMR assignments, which, when incorporated into the structure analysis, will result in higher resolution.

The structure of a DNA that has the strands covalently cross-linked by psoralen has been determined. Initial calculations were based on an energy refined model, which was described previously. The NMR data were used to modify this model and are now being used for distance geometry calculations as well. These data have shown that there is significant unwinding of the DNA and bending at the site of psoralen addition.

A DNA model that contains a gap in the sugar phosphate backbone has been developed using loop-containing synthetic DNA oligomers. The structure of this DNA, particularly near the site of the gap, is being compared with a normal linear DNA of the same sequence. There are small but significant differences seen in the structures. Refinement of B-DNA models using the NMR constraints are presently underway.

Characterization of residues near the active site of catalytically active antibodies has begun. It has been found that hapten binding is in the slow exchange limit on the NMR timescale, and an approach has been developed for obtaining clean difference spectra between paramagnetically (spin) labeled haptens and their reduced counterparts. The line broadening observed will allow the distance to the nitroxide radical to be estimated, and hence the binding site to be modeled. Several residues that are likely candidates for participation in catalysis have been identified. The studies are now being extended by deuteration of specific amino acids in the protein.

The binding of maltose to the maltose binding protein from *E. coli* has been examined. This is an excellent system (which has intrinsic interest as part of the maltose transport system) which will allow the further development of saturation transfer and exchange-transferred NOE methods for large proteins. Studies have also begun using 3H NMR of specifically tritiated maltose (from the

National Tritium Labeling Facility) to characterize the binding site on the protein. Studies have also been carried out of NMR methods to determine the positions and distribution of 3H incorporation into small molecules.

Analysis has begun of the structure of a new enzyme cofactor. Initial studies have shown that it does not have the anticipated structure, and hence represents a new type of cofactor. The studies have identified several structural units within the cofactor, but these cannot yet be unambiguously connected. NMR and mass spectrometer studies are continuing to complete the determination of the structure.

^{13}C NMR of histidines in the catalytic subunit of aspartate transcarbamylase has been used to show that this group does not function as a general acid in catalysis, as thought previously. The pK value and chemical shift indicate that it functions instead as a hydrogen bonding source, which can position the substrate in the active sites.

Publications

G. Braathen, P.T. Chou, and H. Frei, "Time-Resolved Reaction of $O_2(^1\Delta)$ with I^- in Aqueous Solution," *J. Phys. Chem.* 92, 6610 (1988).

P.T. Chou, S. Khan, and H. Frei, "Time-Resolved $O_2(^1\Delta) \rightarrow ^3\Sigma^-$ Chemiluminescence upon UV Laser Photolysis of an Aromatic Endoperoxide in Aqueous Solution," *Chem. Phys. Lett.* 129, 463 (1986).

C. Kleanthous, D.E. Wemmer, and H.K. Schachman, "The Role of an Active Site Histidine in the Catalytic Mechanism of Aspartate Transcarbamylase," *J. Biol. Chem.* 263, 13062 (1988).

N.V. Kumar, D.E. Wemmer, and N.R. Kallenbach, "Structure of P401 (Mast Cell Degranulating Peptide) in Solution," *Biophys. Chem.* 31, 113 (1988).

M.T. Tomic, D.E. Wemmer, and S.-H. Kim, "Structure of a Psoralen Cross-Linked DNA in Solution by Nuclear Magnetic Resonance," *Science* 238, 1722 (1987).

Earth Sciences Division

Development of a High-Temperature Centrifuge

Principal Investigators: Ian S. Carmichael and
Leif J. Hansen

Funding: \$55,500

Project Description

A feasibility study was conducted for an advanced ultracentrifuge capable of operating at an acceleration of 10^5 g in the temperature range 1300–1600°C. Such an apparatus would make it possible to spin liquid silicate samples consisting of nine or more components, quench in the compositional gradients induced by the acceleration field, and analyze the gradients to obtain thermodynamic data on the liquids. In other experiments, partially solidified silicate samples could be run and the compacting induced in such samples could be measured to provide data on the rheology and permeability of partially molten rock.

Accomplishments

Considerable effort has resulted in definition of the scientific and operational requirements for which the engineering design was subsequently tailored. Points 1–7 relate to the mandatory scientific needs that must be fulfilled. Points 8–10 were added to ensure high productivity.

1. Operational temperature range: 1300°C–1600°C.
2. Sample acceleration: 10^6 ms⁻² or higher.
3. Duration of run: Up to two weeks.
4. Sample shape and size: Cylindrical, typically 3–4 mm in diameter by 6–8 mm long.
5. Sample temperature gradient: The maximum temperature difference across any sample dimension must not exceed 2°C during steady state operation.
6. Sample quench: The sample must be quenched at the end of a run as rapidly as feasible to

ensure formation of a glass (10 seconds or less) while maintaining full speed.

7. Sample contamination: The sample container must not contaminate the sample.
8. The number of samples that can be processed per run of the centrifuge must be reasonably large.
9. It must be reasonably easy to change samples and to achieve, verify and, if necessary, correct rotor balance.
10. The centrifuge must be designed such that required disassembly/assembly for part change or maintenance is minimized and reasonably simple, yet allows machine alignment to be maintained.

The engineering design effort focused on critical apparatus parameters and resulted in six conclusions.

1. **Centrifuge rotor/furnace atmosphere.** The two simplest choices for the atmosphere are vacuum and inert gas. The requirement for very fast sample quench, however, makes the use of a gas for sample capsule cooling mandatory. The best inert gas for quench purposes is helium, due to its excellent transport and thermodynamic properties.
2. **Centrifuge rotor and sample arrangements.** The centrifuge rotor must have sufficient strength at 1300–1600°C to accommodate the “payload” deadweight stresses from the samples and their containment/installation arrangement in addition to the stresses from the weight of the rotors own (load carrying) structure at the required 10^6 ms⁻² sample acceleration. The only material that will meet all of the required operational conditions is a carbon fiber–carbon matrix (C–C) composite.

The rotor must incorporate arrangements that allow reasonably simple and convenient insertion, retention, and removal of samples. It is proposed that an externally tapered cylindrical sample capsule with lid be designed for immediate containment of the sample. This capsule will now be inserted in a matched

taper bore normal to and intersecting the axis at its midpoint of a straight or tapered cylindrical C-C sample capsule plug.

The sample must not be contaminated by the capsule material with which it is in direct contact. A suitable material is vitreous carbon (cellulose carbon, glass-like carbon). A grade of this material that is compatible with the required operating temperature has moderate room temperature compressive strength ($150\text{--}200 \times 10^6 \text{ Pa}$) and, being fragile, low and unpredictable tensile strength. It has low density ($1500\text{--}1550 \text{ kg m}^{-3}$) and medium high thermal conductivity (about $25 \text{ W m}^{-1}\text{K}^{-1}$ at room temperature), thus high thermal shock resistance.

3. **General configuration.** The centrifuge axis will be vertical. The furnace is mounted on top of the centrifuge drive system for sample access and thermal reasons. The C-C centrifuge rotor top surface is accessible from above for sample insertion and removal by upward removal of the self-contained upper part of the furnace. The centrifuge rotor is overhung upward into the furnace from the drive unit. In dynamic terms, it is basically a two-bearing machine with overhung weight, even though axis loads are carried by a separate third bearing, leaving the two radial bearings free to carry radial loads only.
4. **Critical frequencies.** Critical frequencies—or speeds—are mechanical resonances in the rotor system that occur when a natural frequency of the rotor system coincides with the shaft's rotational frequency. If the speed is kept at or near the critical speed, the amplitude, and thus stresses, of the resonance mode will build up until available damping power equals available shaft power.

Three basic approaches can be used to deal with this serious problem.

- The problem can be avoided altogether by designing for operation below the first critical frequency of any natural frequency in the system (which may or may not be possible).
- Amplitude limiters can be installed, when feasible.
- Provisions can be made for the ability to accelerate through critical speeds fast enough to ensure that the amplitude

buildup does not reach excessive values. This is a matter of a high range of torque being available and controllable at all speeds of the system.

The first two can suitably be used in combination. Damping is always desirable.

All three approaches were used in a combination, of sorts, for the conceptual layout. The outer shaft, with bearing and turbine rotor, is designed to—by itself—always operate well below its first critical speed. The inner cantilever shaft, attached to the outer shaft at its fixed end and carrying the C-C centrifuge rotor at its free end, will need to go through a number of critical speeds. The cantilever shaft amplitudes are limited by co-rotating “bumpers”; the magnetic bearings provide system damping, and provisions are made to ensure high acceleration capability.

5. **Bearings.** The problem with all conventional bearings stems from the fact that they do not allow the shaft to spin about its inertia axis due to unavoidable failure in achieving perfect coincidence of the geometrical axis of the shaft, as determined by its machined bearing surfaces, with the shaft's inertia axis. The conventional “fix” consists of attempting to move the inertia axis to coincidence with the geometrical axis by balancing of the shaft. Another fix entails attempting to make the geometrical axis approach coincidence with the inertia axis by the use of compliant suspension of low mass stationary bearing surfaces.

Both schemes will with care result in acceptable vibration levels at ordinary shaft speeds. However, as the unbalance forces for a given separation between geometrical axis and inertia axis increase with the square of the shaft speed, problems quickly tend to become severe with increase in shaft speed. The rotor unbalance problem becomes particularly acute if radially asymmetric temperature differentials or shifts in rotor masses occur during operation, as this may shift locations of geometric and inertia axes.

The best choice of conventional bearings here is the use of gas-lubricated compliant-support foil bearings. As the entire centrifuge internal assembly must be operated in a helium atmosphere, the lubricating gas will also need to be helium. This is a good choice from the point of view of generated friction heat and ease of its

removal, but there is concern about whether square-cube law considerations will allow the bearings to develop adequate load capability with helium lubricant. The bearings would need to be custom designed and made, and thus expensive.

A very capable unconventional bearing type now becoming commercially available is an active magnetic bearing. These bearings have a number of desirable features that make them uniquely suited for application in the centrifuge.

6. **Centrifuge drive.** The centrifuge is best driven by a direct drive. There are two apparent choices: electric motor drive or helium turbine drive. A helium turbine drive is recommended for three reasons.
 - The turbine can be run as a cold gas turbine. Even though its exhaust's isentropic temperature drop (large for helium) is reduced appreciably due to the small power and thus inefficient size, it can be designed to be an active part of the overall drive heat removal solution—rather than being a contributor to the problem.
 - By appropriate design, it is possible to achieve a large and controllable torque range at all speeds, though of course maximum torque will be available at stand-still.
 - As the axial bearing rotor is required, it offers a tempting starting point for the turbine design by keeping necessary added inertia down, and thus acceleration ability up.

These two coupled efforts have yielded conceptual design criteria that should make construction of the centrifuge feasible if the specified materials and components are available.

Design and Development of a Downhole Shear and Compressional Wave Source

Principal Investigator: Paul A. Witherspoon

Funding: \$93,300 (second year of funding)

Project Description

Beginning in FY 1986, a project was funded to design and develop an innovative downhole shear and compressional seismic wave source. The device will have wide application in petroleum and geothermal reservoir studies, toxic and nuclear waste disposal site investigations, and many other studies requiring subsurface imaging or acoustic tomographic reconstruction of rock mass characteristics. The device will generate shear (*S*) waves of two polarizations and compressional (*P*) waves over the frequency range of 0.1 kHz to 1 kHz, and will rely on the swept frequency signal principles for analysis by correlation techniques commonly used in seismic exploration. The goal is a working prototype borehole tool demonstrating proof of concept and potential for realization of a unit with an effective signal range of 1 km and operating depth to 5 km.

Conceptual studies led to the conclusion that the proposed device can readily be divided into four component parts for purposes of design and preliminary testing. These four parts are: (1) *S*-wave source with axial vibratory motion, (2) *S*-wave source with torsional/rotational vibratory motion, (3) *P*-wave source with radially directed vibratory motion, and (4) borehole clamp.

Accomplishments

In FY 1986, a complete set of engineering drawings were produced and principal components were fabricated for the *S*-wave source with vibratory motion (*SV*) parallel to the axis of the borehole. In addition, conceptual studies were completed for a torsional (*SH*-wave) source, *P*-wave source and the borehole clamp. In FY 1987, primary emphasis was placed on completion of the *SV*-wave and preliminary engineering design calculation for the *SH* source.

Linear axial (*SV*) shear wave source. The design concept for this device is illustrated in Figure 1, which is a schematic cross section of the central portion of the unit. The vibratory motion is produced by interaction of the coil with the magnetic field produced by samarium cobalt magnets mounted on the core. The magnets are radially magnetized so the magnetic flux lines are perpendicular to the direction of the current flowing in the coil. The magnetic circuit is completed through the housing and the central core. By applying an alternating current to the coil, vibratory motion of

Fig. 1. Schematic cross section illustrating design concepts for vertical shear wave source. [XBL 8612-5972]

the same frequency results. A symmetric component configuration was chosen as shown in Figure 1, with each magnet-core assembly holding five ring magnets. With an input power of 700 W, the total static force output of the magnet coil system was calculated to be about 130 lb.

In order to increase the force transmitted to the borehole wall, a design was adapted that enabled the device to operate in a resonant condition at all frequencies. This is achieved by a pneumatic spring of variable stiffness. The spring action is provided by compression of the gas volume as shown in Figure 1. As the coil-piston assembly moves, the gas is compressed. The resistance of the gas to compression translates into a force that acts on the core magnet assembly and is ultimately transmitted to the borehole wall. Varying either the volume of gas or its pressure results in a change in the stiffness of the pneumatic spring. The stiffness is adjusted to achieve resonant motion of the coil-piston assembly as the driving frequency is swept over the desired bandwidth. Assuming a reasonable damping factor, a peak force output of 1300 lb was calculated for the configuration described above.

Figure 2 shows the source components, including the coil-piston assembly, magnet-core assemblies, core-insert assemblies, housing, and housing extension. The coil-piston assembly is the vibratory element, as described above. One of the magnet-core assemblies bolts to the housing. The other assembly slides inside the housing and is used to control the volume of gas in the pneumatic spring. Its motion is sensed by an LVDT located in the housing extension. The core-insert assemblies contain tubes for supply of gas to the pneumatic springs and the electrical leads for the coil. Current flows from the core-insert to the flexible spring, shown on the end of the magnet assembly.

Fig. 2. Photograph of principal components of the vertical shear wave source. [CBB 870-10700A]

blies, into the piston to the coil. Each core-insert assembly also houses a pressure transducer which monitors the gas pressure in the pneumatic spring.

Performance testing was carried out by securely fastening the source to the floor of the laboratory and monitoring the cyclic pressure response of the pneumatic spring at resonant conditions. From this, the maximum force amplitude transmitted by the source was calculated to be about 127 lb for an input current of 0.7 A rms. At the maximum design input power of 700 W, a maximum force amplitude of about 700 lb would be expected. This performance will be further enhanced by minor design modifications of seals in the pneumatic spring.

In addition to assembly and testing, analysis was also carried out for a control system for the source. This design is based on using the drive current as the resonance indicator in a phase-locked loop system. When the coil is vibrating in a resonant mode, the drive current is at a minimum and the phase is also zero, increasing or decreasing monotonically on either side of resonance. Hence, the control system would change the pneumatic spring pressure or volume to keep the phase locked at zero as the frequency of the vibrating motion changed.

Torsional shear wave source. Design and preliminary engineering studies were completed for the torsional shear (SH) wave source. Figure 3 is a schematic cross section illustrating the principal components of the device. Torsional forces are produced by rotating eccentric masses. The masses are attached to two shafts as illustrated in Figure 3. The shafts rotate in the same angular direction so that a force couple is produced when the masses are located 180° apart in the plane of rotation. The resulting torque is transmitted through the source housing to the rock as shear motion in the horizontal plane. Variable frequency response is achieved by controlling the speed of the motor driving the shafts. Vibratory motion in the range of 50 Hz to 400 Hz is provided by a high speed motor capable of speeds of 24,000 rpm. Use of a rotating body of constant mass would generate inadequate torque at low frequencies and excessive torque at high frequencies, so it was necessary to design a system permitting variation of the mass of the rotating bodies. The mass of these bodies will be varied by injection or withdrawal of mercury. Preliminary engineering specifications were completed for the

principal components, including motors, gearing, bearings, and configuration of the rotating masses. The calculated torque output of the device is a minimum of about 1000 ft lb at 50 Hz. At higher frequencies, higher torques can be achieved depending on the volume of mercury in the rotating masses.

Fig. 3. Schematic cross section illustrating design concept for torsional shear wave source. [XCG 891-4619]

Engineering Division

Semiconductor X-Ray Detectors for Synchrotron Applications

Principal Investigators: Joseph M. Jaklevic and John T. Walton

Funding: \$111,500

Project Description

This project investigates the extension of existing LBL semiconductor detector fabrication and evaluation capabilities to the design of detectors optimized for synchrotron radiation applications. Immediate research objectives include the development of improved methods for the detection of low-energy x rays, the evaluation of high resolution array detectors for fluorescence detection, and the design of position-sensitive devices for diffraction applications.

Accomplishments

A major effort in FY 1987 has been devoted to the study of low-energy x-ray detection. Although semiconductor detector spectrometers are capable of measuring x rays with energies from 0.2 to 50 keV or more, little emphasis has been placed on the low-energy region below 2 keV. These studies have been directed toward understanding the mechanisms that influence detection efficiencies and background artifacts for this energy range in order to devise fabrication techniques that minimize undesirable effects.

A tunable x-ray source capable of providing monoenergetic photons in this energy region has been constructed and used to evaluate a number of alternative entry window contact structures in terms of x-ray absorption and background levels. These contacts include evaporated Schottky barrier and ion-implanted layers on both LBL fabricated Si(Li) and HPGe devices. The studies show significant variability among the device structures in terms of the parameters measured. A theoretical model describing the detector response in terms of the fundamental parameters involved in x-ray

absorption and electron-hole transport in semiconductors has been developed and applied to the interpretation of the data. In addition to providing considerable insight into the fundamental processes which affect detector performance, the studies have recommended specific contact structures to reduce the effective window thickness and minimize unwanted spectral background.

Table 1 is a partial list of contact structures that have been evaluated in terms of effective window thickness. In addition, measurements of the continuum background generated by high-energy x rays has also been determined for most of the cases shown. On the basis of these measurements, the evaporated Al n⁺ contact has been shown to be superior for Si(Li) detectors, whereas the low-energy boron-implanted contact exhibits optimal window and background performance for the HPGe case.

A second area of interest involves the study of optimum detector configurations for the measurement of synchrotron-induced x-ray fluorescence. It is known that in the measurement of fluorescence EXAFS that, although semiconductor detectors exhibit superior energy resolution, they suffer serious limitations due to inherent count rate limitations imposed by pulse processing requirements. The factors that determine these limits have been explored in detail and measurements have been performed at SSRL using state-of-the-art processing electronics in order to evaluate the effect of these limitations under realistic operating conditions. Based on this experience, the development of a multi-element monolithic Si(Li) x-ray detector using multiple pulse processing channels is being explored to overcome the count rate limitations and to extend the range of applicability of semiconductor detectors in synchrotron x-ray fluorescence measurements.

A study has also been initiated on the design and use of position-sensitive semiconductor detectors for synchrotron x-ray applications. Preliminary studies will involve the use of one-dimensional strip detectors with 100-micron strip pitch. A collimated x-ray source employing asymmetric diffraction elements is being used to generate a narrow beam laboratory source of 8-keV photons.

Table 1. Contact structures evaluation.

Detector Material (Contact)	Process	Measured Window Thickness at 1.8 keV	
		Si(Li)	HPGe
Au (p*)	evaporated	0.09 μm	—
Ni (p*)	evaporated	0.08 μm	0.57 μm
Al (n*)	evaporated	0.02 μm	—
Pd (p*)	evaporated	0.07 μm	>0.60 μm
B (p*)	implanted at 25 keV	>0.1 μm	0.37 μm
	implanted at 50 keV	—	0.45 μm
	implanted at 100 keV	—	0.47 μm
BF ₂ (p*)	implanted at 25 keV	>0.1 μm	0.28 μm
BF ₄ (p*)	implanted at 25 keV	—	0.44 μm

The response of the strip detectors in terms of noise, cross-talk, and quantum efficiency will be evaluated.

Recent developments in high resolution, parallel strip readout involving the use of hybrid integrated circuits will be adapted to the problem in order to facilitate the simultaneous readout of several hundred strips. The hardware and methods developed in this phase of the study can then be adapted to the future design and fabrication of more elaborate one- and two-dimensional detection schemes.

High-Efficiency Gas-Driven Absorption Heat Pump

Principal Investigators: Joseph Rasson and Michael Wahlig

Funding: \$90,600

Project Description

In the course of LBL research on absorption-cycle cooling, a new thermodynamic cycle was discovered capable of higher efficiency than any other

absorption cycle known to date at gas-driven temperatures of 400°F and higher. The basic underlying concept of this new approach was proven experimentally during previous work at LBL on lower-temperature absorption cycles for solar-driven operation. As shown in Figure 1, the gas-driven cycle (the absorber-coupled double-effect regenerative, or ADR, cycle) would have substantially higher efficiency than the lower-temperature cycles (designated as the 2R and 1R cycles in Figure 1).

From an energy conservation viewpoint, high-efficiency heat pumps based on these regenerative absorption cycles would represent a very energy-efficient method of heating and cooling buildings. For utility companies, these gas-driven heat pumps offer a means of avoiding electricity peak loads (for driving electric air conditioners) in the summer, while providing a year-round demand for gas. Consumers would benefit from lower heating and cooling costs, and avoiding peak-demand electricity charges.

The planned project tasks included preparation of a preliminary heat pump design suitable for an initial costing estimate, and a study of design alternatives to evaluate trade-offs between performance and design simplicity. In addition, it was expected that extensive interactions would take

Fig. 1. Cooling-mode COP values as a function of the inlet boiler temperature for various advanced regenerative absorption cycles. The 2R and 1R cycles were designed earlier, to be driven by variable temperature solar-heated hot water. The higher-efficiency ADR cycle is designed to be driven by a constant temperature gas source at about 400°F. [XBL 891-227]

place between the LBL researchers and potential outside supporters of the subsequent development effort.

Accomplishments

All of the essential project objectives were accomplished. The analytical models necessary to perform initial design trade-offs and to prepare a *heat pump design suitable for costing* were developed by adapting the chemical engineering process simulator ASPEN to model ammonia-water

absorption heat pumps. The results of the analytical study led to a new, simpler cycle configuration that would reduce the manufacturing cost at the expense of a slight reduction in cycle efficiency. Interactions with an experienced outside costing firm were initiated, establishing the requirements for LBL-generated information necessary to conduct the costing study. A set of conceptual design drawings suitable for costing purposes were then generated. The assistance of expert consultants was used for parts of this work.

The PDF project also allowed the investigators to interact with and respond to the concerns of outside organizations that constitute potential sources of support for the subsequent development phase. As a result, support for the first part of this development effort has been obtained from three funding sources: PG&E, DOE/Conservation, and the Gas Research Institute (GRI). In addition, PG&E has submitted a proposal to the California Energy Commission (CEC) to secure additional funds for partial support of the heat pump development effort. It is expected that LBL will perform the bulk of the development work if PG&E receives a CEC award.

Publications

J.M. Jaklevic, J.T. Walton, R.E. McMurray, Jr., N.W. Madden, and F.S. Goulding, "Semiconductor Detector Performance for Low-Energy X-Rays," presented at the 5th National Conference on Synchrotron Radiation Instrumentation, Madison, WI, June 21–25, 1987. To be published in *Nucl. Instrum. Meth.*

R.E. McMurray, Jr., P.N. Luke, J.M. Jaklevic, and J.T. Walton, "Effects of Germanium Detector Contacts on Dead Layer Performance for Soft X-Rays," presented at the SSRL User's Conference, October 22–23, 1987.

J.E. Rasson and M.A. Wahlig, "High Efficiency Absorption Heat Pump," LBL-25241 Draft (1988).

Materials and Chemical Sciences Division

Enzymatic Synthesis of Materials

Principal Investigators: Mark D. Alper, Peter G. S. nultz, Jack F. Kirsch, Harvey W. Blanch, David S. Soane, Douglas S. Clark, and Mark D. Bednarski

Funding: \$87,500 (second year of funding)

Project Description

The goal of this project is to exploit the recent breakthroughs in molecular biology, biochemistry, chemistry, and chemical engineering (commonly referred to as biotechnology) to produce novel materials for nonbiological applications. The uniqueness and applicability of these new materials lies in their synthesis through the use of enzymes, either as they are found in nature (wild type) or after their specific and rational redesign for this purpose. Enzymes can control the stereochemistry of both the monomers they bind and the linkages they form between those monomers as they make polymers. As a result, a wide variety of materials with enhanced properties not attainable by other, more conventional synthetic routes can be produced in this manner. The overall research plan includes correlation of monomer and polymer structure with desired materials properties, identification of enzymes that are appropriate for synthesis of these polymers, purification of the genes for these enzymes, specific modification of those genes so that nonnatural monomers can be used in synthesis, large-scale production of the modified enzymes, use of these enzymes in polymer synthesis, and characterization and processing of the polymer products.

Early efforts have been focused on three goals:

- Identification of target materials with potentially interesting properties that can be synthesized enzymatically, and the determination of the chemical structures of polymers that would have these properties.
- Development of techniques to synthesize these polymers.

- Characterization and processing of the newly synthesized polymers.

Specific research projects involve studies of two model systems (AATase and phosphorylase) designed to demonstrate and define the major aspects of the technology of the program, and two long-term systems, one using lysozyme and the other using papain, that are expected to result in production of novel materials of interest.

Accomplishments

I. Model Systems

AATase. The "wild-type" enzyme, aspartate amino transferase (AATase), converts the negatively charged amino acid aspartate to the corresponding 2-oxo-acid. The isolated gene for AATase was manipulated: the codon specifying one of the ten amino acid residues that line the active site and make contact with the substrate was specifically replaced with a codon specifying a different amino acid. The mutant enzyme was then synthesized under the direction of the altered gene. This new enzyme was found to have a five-orders of magnitude reduced activity on aspartate and also a nine- to sixteen-fold increase in activity on another amino acid, the positively charged arginine for which this alteration was designed. The new enzyme has been characterized completely, both biochemically at Berkeley and structurally through the use of x-ray crystallography by a collaborator, Dr. Dagmar Ringe at MIT.

Phosphorylase. Fluorinated glucose monomers have recently been successfully synthesized as substrates for this enzyme in the synthesis of the group's first nonnatural polymer. The scheme developed for this synthesis will also be applicable to the synthesis of fluorinated sugars to be polymerized using the enzyme lysozyme.

II. Materials Synthesis Systems

Materials synthesis using lysozyme. Chicken egg-white lysozyme is one of the enzymes designated to produce the first carbohydrate-like polymer candidates suitable for investigation as new materials. The gene for lysozyme was

successfully cloned into a strain of the bacterium *E. coli* in which genetic engineering of the amino acid sequence can be readily accomplished. The mutant genes were next moved from bacteria to a yeast host for production of the protein. Neighboring genes were engineered so that the wild type (or mutant) lysozyme is excreted by the yeast cells into the medium in its correctly folded state. As a result it can be easily purified in quantities of several mg/liter. Such supplies should be more than sufficient to prepare experimentally useful quantities of novel polymers.

A major experimental problem that has to be overcome in bringing this new technology to the point where it can be used routinely is that of the precise definition of the modes of interaction of this and other enzymes with their natural substrates. This is a required prelude to the rational and directed alteration of the active site to allow it to accept other substrates. To this end, it was reasoned that it would be useful to design a mutant that would retain its binding site intact but would be incapable of catalyzing any chemical reaction so that the binding process could be experimentally segregated and studied. Aspartic acid 52 and glutamic acid 35 are the two residues that are primarily responsible for the hydrolysis of the glycosidic bond. Each of these was converted to its corresponding inactive amide form by site-directed mutagenesis. Both changes reduce the catalytic activity by 20- to 100-fold. The double mutant having both changes in a single enzyme molecule has also been constructed and is expected to have virtually zero activity. The affinity constants for small oligosaccharide ligands were, as predicted, changed by less than a factor of two, indicating that the strategic objectives have been met, and that binding can now be studied isolated from catalysis.

There are six subsites in lysozyme, designated A, B, C, D, E, and F. Each binds one monosaccharide subunit (NAG or NAM) of a polysaccharide substrate. Aspartic acid 101 lines the A subsite where it interacts specifically with the monosaccharide subunit bound to that position. As part of the effort to understand and then manipulate the substrate binding site of the enzyme, this position was systematically substituted with a variety of other amino acids bearing both neutral and positively charged side chains. The attempt was to engineer a protein that would have altered substrate-recognition characteristics. Activity was examined at three different values of pH to assess the effect of charge on binding and the effect of

local environment on charge. A cationic side chain at position 101 is mildly detrimental to binding. Binding of (NAG)₃ to the lysine variant becomes tighter between pH 7.5 and 8, suggesting that the pK_a of the Lys 101 ϵ -NH₂ group is within this range. This ionization of Asp 101, for example, was shown to contribute between 1-1.3 kcal/mol to the free energy of association with the substrate.

Substrates for use by the enzyme lysozyme in synthesizing polymers have been produced. Since oligomers of NAG are not commercially available, a procedure to prepare them was developed. Acid hydrolysis of chitin, the natural water-insoluble polymer of NAG, was selected as an appropriate route. Hydrochloric acid hydrolysis of large quantities of chitin was followed by neutralization with sodium hydroxide and a series of gel filtration steps. In this manner, sufficient quantities of oligomers of a variety of sizes were obtained.

The required analytical system for assaying levels of oligomers of specific length has been devised. Previous researchers have employed thin-layer chromatography, liquid chromatography, radio-labeling, and derivatization for detection and analyses. A more rapid, simple analytical procedure for both substrates and products is required for work described here. This has been accomplished by the use of gel high-pressure liquid chromatography with microbore tubing, and detection of sugars at 200 nm with an ultraviolet detector. NAG has an extinction coefficient at 200 nm, sufficiently high to permit detection to 1 ppm and sufficiently accurate for the proposed research.

Two solvents that are suitable for substrate solubilization have been shown to allow maintenance of lysozyme hydrolytic activity. The substrates for lysozyme (NAG, NAM, and related sugars) are polar and thus insoluble in apolar organics. The NAG polymer chitin is insoluble in water and soluble in a limited range of organics. Solvents have been examined in terms of their ability to solubilize chitin and oligomers of NAG, while at the same time not fully denaturing the native enzyme.

Solvents found suitable for both substrate solubilization and enzyme stability are DMA (N,N dimethyl acetamide) and MP (1-methyl-2-pyrrolidinone). Lysozyme activity was examined in both solvents at various volume percent organics. It was found that 5-20% DMS did not reduce lysozyme activity below 60%, yet significantly enhanced substrate solubility. A temperature

optimum for the enzyme was found at 50–55°C. Continuing work will examine enzyme-condensation activity in these solvents.

Materials synthesis using papain. The proteolytic enzyme papain shows specificity for amino acids with nonpolar side chains. Thus, it might be expected that aqueous environments would limit the length of the growing polymer chain and also promote the back, or hydrolytic, reaction. Work on papain has just begun, and early experiments in water have been successful in producing, for the first time, polymers of the amino acid phenylalanine. Use of nonpolar environments will be required, however, not only to prevent cleavage of the growing chains but also to solubilize them. The polypeptide produced reached a maximum length of about ten amino acids before coming out of solution, curtailing further polymerization.

III. Techniques Developed for General Applicability

Considerable success has been achieved in developing a system to incorporate synthetic amino acids at specific points in an enzyme. A universal amino acid carrier has been synthesized that will identify a unique position locator codon inserted at specific points in the gene for the protein. Success to date allows insertion of a natural amino acid using this carrier at the locator codon, setting the stage for attempts to use it to insert unnatural amino acids.

Failure of Ceramic/Metal Interfaces for Coatings

Principal Investigator: Rowland M. Cannon

Funding: \$144,000

Project Description

Industrially important problems of degradation of reactively formed coatings are being studied to incorporate basic treatments of several key elements, including oxide-formation mechanisms, damage evolution during sintering of oxides, interfacial failure, and thin-film decohesion. Such coatings often have high residual stresses from growth and can fail by buckling or splitting, delamination, and spalling.

The treatment being developed for the interrelated mechanisms of oxide growth, stress development, and pore or crack formation has broader applicability. Expected benefits include methods to improve the integrity of coatings such as oxide, boride, silicide, or nitride layers.

The stress state, morphology, microstructure, and defect population of scales and the internal mass transport are highly interdependent. Thus, the approach has been to develop coating-formation theories that address these issues and to combine these with theories for film degradation by splitting and delamination or by buckling and delamination. Experimental evaluation of kinetics, growth stresses, and degradation mechanisms in specific cases are being correlated with film microstructures and utilized to refine the theories. Comprehensive models for the formation, degradation, and susceptibility to mechanical damage for corrosion-resistant coatings should emerge.

Currently the program emphasizes fundamentals of scale formation, interface decohesion, and oxide fracture. Application to technological problems will derive from dissemination of methodologies, both conceptual and experimental, and of advanced characterization procedures. As the effort evolves under other sponsorship and with industrial cooperation, representative industrial problems will be attacked with the goal of improving adherence and protective qualities of coatings by control of composition, structure, and morphology of coatings and substrates.

Accomplishments

Oxidation theory. Models are being developed that treat the stresses generated during the growth of oxide layers. Several different growth regimes have been identified in terms of the key parameters controlling stress development; the degree of coherence of the metal/oxide interface is a primary determinant. Diffusion-controlled models have been developed and refined during this year for the limiting situation of an incoherent interface. A high degree of interfacial coherence causes appreciable modification of the stresses, which then depend explicitly on the transformation strain tensor for oxide of a specific orientation, and on internal faults.

For an incoherent interface, a quasi-steady-state model developed for formation of oxide by boundary diffusion, in combination with prior

theory developed here for oxidation by volume diffusion, permits the prediction of oxidation stresses and specific microstructures that ameliorate them, as well as the oxidation rates. It is found that generation of large stresses (e.g., enough to induce buckling) is expected often; they depend upon the relative diffusion rates of metal ions out and oxygen in through the oxide, the dominant diffusion paths, the relative oxide and metal molar volumes, and the morphologies of the oxide scale and base material.

For columnar grains within the oxide, if lattice diffusion controls scale formation (e.g., at high temperatures), large in-plane tensile stresses usually develop. In contrast, where enhanced grain-boundary transport is controlling, compressive in-plane stresses are predicted. When oxygen diffusion dominates along the boundary, the average stresses are larger than when metal diffusion is predominant; however, the bending moments (stress gradients) may be larger and of opposite sign for rapid metal diffusion. Curling of delaminated films induced by these gradients should permit affirmation of the rapidly diffusing species and may assist in initiating buckling. In addition to in-plane stresses, a periodic stress normal to the oxide-metal interface develops, which averages to zero. At high enough pO_2 ratios, which raise the stresses, the predicted stresses are sufficient to induce pore nucleation within the oxide or at the metal-oxide interface in response to the normal stresses. Sliding of the scale along the interface or the presence of grain boundaries parallel to the scale in an equiaxed microstructure can appreciably reduce the stresses.

For curved substrates, the added geometrical constraints inevitably modify the stresses, as explicitly expressed within the diffusion-control theories. High stresses normal to the scale-metal interface arise to maintain continuity; these induce appreciable in-plane stress components of opposite sign. Rapid metal diffusion would lead to normal tension, whereas if oxygen diffusion were predominant, the stresses would be opposite only if the molar volume of oxide exceeds that of the metal.

Stress-induced rupture within porous oxides. The flaws controlling interfacial failures may result from mechanical or chemical damage exacerbated by geometrical stress concentrations but can also be generated internally. Treatments have been

undertaken that reveal the extent to which induced stresses in polycrystalline oxides can cause growth or shrinkage of pores. The theoretical results to date provide bounds for the stresses that can be maintained in porous oxides without rupture of the grain boundaries. These results pertain to the problem of flaw generation in oxide layers. In addition, they explicitly address the issues of stress generation and maximum attainable stresses that would occur during the formation of a coating by the sintering of an oxide powder layer applied to a rigid substrate.

Coating and interface characterization. As research progress requires employing state-of-the-art microstructural characterization methods, the exceptional LBL capabilities have been utilized and extended as a subsidiary but crucial aspect of coating degradation and delamination studies. While earlier work was being completed, the high-voltage electron-diffraction (HVED) facilities of LBL's National Center for Electron Microscopy were used to obtain more accurate atomic structure factors, which are essential to interpret high-resolution electron micrographs via simulation. A direct extension of this work also provided insights into the bonding and high stiffness of Al-Li alloys. This effort makes LBL the only U.S. Laboratory with capabilities to acquire and interpret HVED critical voltage information.

An effort was also undertaken to determine internal stress gradients in surface layers and films using x-ray techniques. The large gradients indicated in some vapor-deposited metallic films are being assessed for verification. More precise analytical methods are needed to quantitatively determine the stress gradients predicted to exist in oxide films and also to result from the fracture involved with rapid delamination of oxide films. The method would be more precise with the use of synchrotron radiation, and appropriate experiments are being planned.

Novel Properties of Matter at Megabars of Pressure

Principal Investigators: Marvin L. Cohen, Raymond Jeanloz, and Peter Y. Yu

Funding: \$144,900

Project Description

The purpose of this research project is to experimentally and theoretically investigate the properties of matter at megabars of pressure. The objective is to combine the expertise of experimentalists and theorists in the area of high-pressure technology, materials characterization techniques, inorganic synthesis, and theoretical computation of properties of matter to synthesize and investigate new materials with unusual properties or with potential applications to energy technology. Examples of these new materials are ultrahard solids with strengths comparable to or exceeding that of diamond, and solids with unusual electrical, superconducting, optical, and magnetic properties.

The approach of this project that distinguishes it from other high-pressure projects is the close interaction between the Cohen theoretical group and the Jeanloz and Yu experimental groups. The theoretical group uses the *ab initio* pseudopotential method to calculate the ground-state properties of solids as a function of volume. These properties include total energy of the solid, bulk modulus of the different phases, transition pressure and volume from one phase to another, electronic and vibrational spectra of the high-pressure phases, electron-phonon interactions, and superconducting transition temperatures. The theoretical predictions are tested by experiments performed by the two experimental groups, using high-pressure techniques such as high-temperature synthesis of inorganic materials, x-ray crystallography, Raman and emission spectroscopies, Fourier-transform infrared spectroscopy, and low-temperature electrical-transport measurements.

Accomplishments

Synthesis of new alloys of C-B-N with diamond structure. A new model in which the bulk moduli of solids with diamond and zincblende structure scale with only the nearest-neighbor bond length has been proposed. Results obtained from this empirical approach were found to compare favorably with values calculated by a full *ab initio* pseudopotential method. Based on this method, it was predicted that a compound with the formula of CBN and the structure of diamond will be more densely packed and therefore harder than diamond. A new material with the composition $C_x(BN)_{1-x}$ has been synthesized under pressures of 10–30 GPa and temperatures of 1000–2000 K inside a laser-heated diamond anvil cell using graphite

and boron nitride as the starting materials. X-ray diffraction has shown that these new alloys have the diamond structure. The lattice parameters and bulk moduli of these alloys have been measured as a function of x . Contrary to Vegard's law, the lattice parameter for values of x between 0 and 1 was found to be larger than the value obtained by a linear interpolation between the end-point values. This was contrary to expectations based on theoretical calculations, which suggested a normal behavior according to Vegard's law where the lattice parameters should be smaller than a linear interpolation. The bulk moduli also varied nonlinearly with x and suggested that the alloys have bulk moduli lower than that of diamond. Although these binary alloys probably will not be harder than diamond, they may still have important applications in electronics and machine-tool manufacturing.

Pressure dependence of the new high- T_c superconductors. Using diamond anvil cells, the pressure dependence of both the room-temperature resistance and T_c has been studied in $LaBaCuO$, $LaSrCuO$, and $YBaCuO$ compounds up to 20 GPa. Typically it was found that the room-temperature resistance of these ceramic superconductors decreased by several orders of magnitude at pressures ranging from 8 GPa in $LaSrCuO$ to 5 GPa in $YBaCuO$. The transition temperature in the $LaBaCuO$ and $LaSrCuO$ compounds showed strongly nonlinear pressure dependence. At pressures below 3–5 GPa, T_c increased rapidly with pressure. At pressures above 5 GPa, T_c tended to saturate and then decrease with pressure. In $YBaCuO$, T_c was at first almost independent of pressure and then decreased with pressure. In both $YBaCuO$ and $LaSrCuO$ above a well-defined pressure, the sample became a better metal at room temperature but also lost its superconducting properties. These results suggest that the high superconducting temperatures in these materials are very sensitive to bond lengths. There is an optimal bond length for the highest superconducting temperature. In $YBaCuO$, this optimal bond length is achieved at atmospheric pressure. When the materials are compressed beyond this optimal bond length, superconductivity is quickly destroyed.

For the first time, a theoretical study of the bulk modulus of solids based on first-principles calculations has been performed and used to guide experimental work in the search for new materials with unusual mechanical properties. Based on a

systematic investigation of the electronic structure, bulk moduli, lattice constants, and lattice vibrational spectra of hard materials such as diamond, BN, SiC, and BP, the theoretical group has concluded that materials synthesized from carbon and BN under high temperature and pressure can have a bulk modulus higher or comparable to diamond. The resulting experimental investigation has shown that alloys of the composition $C_x(BN)_{1-x}$ can be formed with new interesting properties. The mechanical properties and lattice constant of these new alloys are still being investigated.

Film Formation and Dislocation Substructures in Corrosion-Induced Cracking: Application of Advanced Characterization Techniques

Principal Investigators: Thomas M. Devine, Ronald Gronsky, and Robert O. Ritchie

Funding: \$94,800

Project Description

The structural integrity of engineering materials in chemically aggressive media hinges on their ability to form thin (approximately 1-nm thick) passive films that effectively isolate them from their environment. Such films inhibit general corrosion, yet they have paradoxically been implicated as an essential contributory factor in environmentally assisted cracking (e.g., stress-corrosion cracking and corrosion fatigue). Mechanistically, the rupture of such films in a corrosive environment due to localized plastic flow at the crack tip causes local changes in the identities and/or rates of electrochemical oxidation and reduction processes that, in turn, lead to further localization of plastic flow and accelerated crack growth. Typically, *information on such films is obtained by extracting data from globally averaged electrochemical techniques, or by using conventional microscopy with its inherent limitation in spatial resolution (approximately 20 nm).*

The two possible fracture morphologies, intergranular and transgranular, represent an appropriate basis for the subdivision of the extensive topic of environmentally assisted cracking. The

present investigation seeks to examine the properties of the films responsible for each failure mode.

Perhaps the most technologically significant example of environmentally assisted cracking is the SCC of Fe-Ni-Cr stainless steel. Since stainless steels are susceptible to both intergranular stress corrosion cracking (IGSCC) and transgranular stress corrosion cracking (TGSCC), the single Fe-Ni-Cr alloy system can serve to study the passive films responsible for both. While TGSCC occurs through compositionally uniform microstructures, the intergranular fracture mode during IGSCC of stainless steel occurs most often in sensitized microstructures. These are characterized by grain boundaries with low chromium contents caused by the intergranular precipitation of chromium-rich carbides.

The initial question addressed is what are the compositions of the grain boundaries that stress-corrosion crack? Once identified, macroscopic size samples with these compositions will be prepared and subjected to the analytical techniques that will (i) probe the surface electronic structure, (ii) characterize the surface films formed, and (iii) characterize the subsurface dislocation substructure developed during deformation in aqueous solutions.

The approach followed in this program will take advantage of the tunability and high-intensity radiation provided by a synchrotron source to characterize the surface electronic structure of Fe-Ni-Cr compositions along grain boundaries susceptible to IGSCC and of alloys susceptible to TGSCC. The intent is to understand the role of electronic structure in electrochemical film formation as it affects environmentally assisted intergranular and transgranular cracking. Complementary morphological information will be provided by the high-resolution techniques of electron microscopy and microanalysis to probe the role of substructural defects and associated compositional changes. *This approach will ultimately yield a better understanding of crack-tip phenomena specific to stress-corrosion cracking and corrosion fatigue.*

Accomplishments

Having subdivided the extensive subject of environmentally assisted cracking into fractures occurring either intergranularly or transgranularly,

effort has been devoted to the understanding of the former. The first task was to determine the composition of the grain boundaries of alloys susceptible to IGSCC. Microchemical analyses by analytical electron microscopy (AEM) indicated that there was a substantial boundary-to-boundary variation in the chromium concentration in any sensitized sample. In fact, there can be a significant variation in chromium concentration with distance along a single grain boundary. Hence, the chromium concentrations of a very large number of grain boundaries would have to be measured in each sample to assure the statistical significance of the measurements. This amount of testing would be prohibitively time consuming and expensive for an AEM. What is required, therefore, is a technique that is capable of measuring the chromium composition of a large number of grain boundaries. During the past year, work in this program has developed a novel electrochemical technique that is capable of measuring the chromium content in zones as narrow as 5 nm with an uncertainty of less than ~1%. The technique is capable of readily measuring the chromium contents of a large number of grain boundaries and of detecting the variation in chromium composition along grain boundaries.

The procedure involves measuring the passivation potentials of Fe-Ni-Cr alloys as a function of their chromium contents in 0.5 M H_2SO_4 + 0.01 M KSCN. This solution was selected because the transition from active to passive behavior with increasing potential was found to be reproducible and to occur over a very narrow range of potentials. This is illustrated by the results presented in Figure 1. At potentials lying below the lower curve, the alloys dissolved actively; gross, easily measurable changes were produced in the dimensions of samples following 24 hours of immersion. On the other hand, at potentials lying above the upper curve, the alloys behaved in a passive manner; corrosion rates were five to six orders of magnitude lower than those measured for samples that actively dissolved. The surfaces of passive samples remained bright and shiny following the 24 hours of immersion. The region in between the two curves in Figure 1 represents the uncertainty in the passivation potential. Samples tested within this range of potentials exhibited mixed active-passive behavior during 24-hour tests. A passive film would form, but after a period of minutes to hours it would break down and the alloy would actively dissolve for a period of minutes to hours, and then the cycle would repeat.

The results shown in Figure 1 can be used to identify the chromium contents in stainless steels of unknown chromium compositions. For example, if the passivation potential of an alloy of unknown chromium composition were known to be +130 mV vs. standard calomel electrode, then the results in Figure 1 indicate that its chromium content would be $6.0 \pm 0.5\%$. Similarly, consider the case in which a sensitized sample was immersed in 0.5 M H_2SO_4 for 24 hours and its grain boundaries were found to actively corrode at an applied potential of -75 mV but were passive at an applied potential of -25 mV. Combining these results with those in Figure 1 would indicate that the grain-boundary chromium composition of the alloy was less than $13.3 \pm 0.1\%$ and greater than $12.8 \pm 0.3\%$.

In addition to the rather accurate estimate of the grain-boundary chromium content possible with this new electrochemical technique, there is another advantage. Namely, the electrochemical procedure examines the chromium content of a vast number of grain boundaries. This is precisely what is required to characterize the sensitization behavior of an alloy. Because of the variation from boundary to boundary in the amount of carbide precipitation, it is to be expected that the grain-boundary chromium content will vary from boundary to boundary. Hence, to characterize the

Fig. 1. Influence of chromium on the passivation potential of Fe-10Ni-Cr ternary alloys in 0.5 M H_2SO_4 + 0.01 M KSCN. At potentials greater than the upper curve, the alloy is passive; at potentials less than the lower curve, the alloy is active. [XBL 892-448]

grain-boundary chromium content by AEM, for example, would require that a large number of measurements be made on a large number of boundaries. The process would be prohibitively costly and time-consuming.

Figures 2 and 3 plot the variation in chromium concentration along boundaries in samples of austenitic and duplex stainless steels, respectively, as a function of the time of heat treatment at 600°C. Such information was previously unattainable. Chief among the facts uniquely revealed in these figures are: (1) the greater amount of chromium depletion along austenite-ferrite boundaries as compared to austenitic grain boundaries; (2) the rapid replenishment of the chromium content along austenite-ferrite boundaries with time of heat treatment at 600°C; (3) the extremely slow replenishment of the chromium content along the austenitic grain boundaries during heat treatment at 600°C; and (4) the distinct stages in the sensitization and desensitization processes of austenitic and duplex stainless steels. These observations and a wealth of others have markedly advanced the understanding of the sensitization of stainless steels.

The electrochemical technique for measuring chromium was used to identify the most probable composition of chromium along grain boundaries of 308 stainless steel following each of seven

Fig. 2. Influence of applied potential and time of heat treatment at 600°C on the intergranular corrosion susceptibility of austenitic 308 stainless steel in 0.5 M $H_2SO_4 + 0.01$ M KSCN. x: no intergranular cracking (IGC); □: IGC visible at 500X; +: IGC visible at 200X; ▲: IGC visible at 100X; ■: IGC visible at 1X. [XBL 892-449]

Fig. 3. Influence of time of heat treatment on the chromium depletion of boundaries in two-phase stainless steel. Solid line plots chromium content along austenite-ferrite boundaries; dashed curve plots chromium content along austenitic grain boundaries. [XBL 892-450]

different isothermal heat treatments. Four of the latter induced varying degrees of susceptibility to IGSCC; three heat treatments did not result in susceptibility to IGSCC. Alloys of each of the seven grain boundary compositions were melted, cast, and thermomechanically processed into plates and wires.

In addition, the technique was utilized to determine the chromium contents along the grain boundaries of stainless steel samples that were tested for susceptibility to IGSCC in pressurized, high-purity water at 288°C. The latter mimics the environment inside commercial nuclear power plants. The results lead to a new understanding of the role of environmental variables such as the dissolved oxygen content of the water on the SCC process. This finding has considerable consequences concerning the experimental procedures used for studying and evaluating the SCC behavior of nuclear reactor components.

Electron Electric Dipole Moment

Principal Investigators: Harvey Gould and Eugene Commins

Funding: \$128,100

Project Description

This project is an experiment to search for an electric dipole moment (EDM) of the electron. An

electron EDM can exist only if the product of charge conjugation (C) and parity (P) symmetries are not conserved. CP nonconservation has been observed in neutral K decay and in no other system; it is not explained by the conventional models and is one of the most important unsolved problems in physics.

A large number of models based upon new physics predict an electron EDM at values up to about 10^{-24} cm $\times$ e. Among these are calculations based on left-right-symmetric models, lepton family mixing, supersymmetry, and superstring-inspired models. This experiment is designed to ultimately be sensitive to an electron EDM of 10^{-28} cm $\times$ e, a factor of 10,000 below the current upper limit.

The experiment will search for a shift, linear in an applied electric field, between the $m_F = 0$ and $m_F = +1$ and -1 magnetic sublevels of the $F = 1$ hyperfine level of the $6^2P_{1/2}$ ground state of atomic thallium. If the electron has an EDM, it will result in an atomic EDM that gives rise to a linear Stark effect. An atomic EDM in the $6^2P_{1/2}$ state of atomic thallium would be roughly 700 times larger than an electron EDM.

A beam of thallium atoms in the $F = 1$, $m_F = 0$ hyperfine level of the $6^2P_{1/2}$ ground state will be prepared by optical pumping of the 378-nm $6^2P_{1/2} - 7^2S_{1/2}$ transition. A linear Stark shift will be looked for in the radio frequency (rf) resonance transition between the hyperfine levels $F = 1$, $m_F = 0 \rightarrow F = 1$, $m_F = +1/-1$ of the ground state. The transition is detected by repolarizing the atom with 378-nm linearly polarized light. The linear Stark-effect measurement is made by applying a dc electric field of about 250 kV/cm and periodically reversing its polarity relative to a static magnetic field. A shift in the resonance transition phase, linear in the electric field, is the signature for an EDM.

The most important systematic effect in EDM experiments is a linear shift in the resonance phase produced by a motional magnetic field, $B = v \times E/c$, seen by the atom moving in the electric field. If E and the static external magnetic field are not exactly parallel, a component of the motional magnetic field lies along the static magnetic field and reverses when the electric field is reversed. This mimics a linear Stark effect.

This problem can be overcome in two ways. First, different velocities in the beam are compared. The orientation of the static magnetic field is adjusted

until the same resonance shift is observed for all velocities when the electric field is reversed. A nonzero shift indicates an EDM or a very unusual systematic effect. A second cancellation will be achieved by mounting ovens at either end of the apparatus and running the complete experiment in both directions, canceling the motional magnetic field effect. If a signal is still observed, the entire experiment will then be run on the $2^2S_{1/2}$ state of lithium. This atom has very small EDM enhancement factors, and hence the measurement can check if any observed signal in the $6^2P_{1/2}$ state of thallium is due to an EDM or an unexplained systematic effect.

The large improvement in sensitivity will come from new methods to reduce noise and cancel systematic effects. The improvement in experimental sensitivity over previous atomic-beam EDM experiments comes from beam-intensity normalization and reduced detector noise made possible by the use of laser optical pumping, the rapid switching of frequencies, and fields and polarizations made possible by computer control and laser optical pumping. The more complete cancellation of systematic effects comes from the near elimination of beam-trajectory differences. This is accomplished by using vertical beams, more homogeneous electric and magnetic fields, and especially by using laser optical pumping in place of inhomogeneous magnetic fields as the polarizer and analyzer. (Inhomogeneous magnetic fields deflect the atoms according to their velocity, mass, and magnetic moment.)

Accomplishments

In the first year of this project, extensive calculations of systematic effects and of noise sources at the most sensitive level of the experiment have been completed. Sources considered included $v \times E/c$ effects from electric- and magnetic-field misalignments in three directions; misalignments and $v \times E/c$ effects due to gravitational deflection; misalignments of the laser, atomic beam, and rf fields; electric- and magnetic-field inhomogeneity effects; electric-field switching effects; effects caused by possible inclusions of magnetic material; and others. The most important finding is that gravitational deflection of a horizontal beam, especially in the presence of electric- or magnetic-field inhomogeneities, would lead to incomplete cancellation of $v \times E/c$ effects. To eliminate problems caused by gravitational deflection, a vertical apparatus has been built (see Figure 4).

Fig. 4. Experimental apparatus used to search for electron EDM. [XBL 8612-9300]

As an aid to detecting subtle systematic effects, a computer model has been written and operated to calculate the effect of arbitrary alignments of static electric, magnetic, and rf fields, and motional magnetic fields on the $6^2P_{1/2}$ and $6^2P_{3/2}$ states of thallium and the $2^2S_{1/2}$ state of lithium.

A detailed analysis of noise sources, signal strength, and beam-velocity distributions has been made. The optical-pumping requirements, rf requirements, and signal intensity for different beam velocities have been studied. A design for the entire apparatus has been completed. The vacuum system, consisting of five chambers spanning 10 feet from floor to ceiling, has been completed, installed, and pumped down to a few microtorr of pressure. The laser optical pumping system has been set up and has achieved design power in single-mode 378 nm. The fluorescence detectors have been constructed and installed. A thallium beam has been produced and fluorescence radiation detected. Simple laser spectroscopy was performed on the thallium atoms to verify proper operation of the laser and the beam. Intensities appear to be very large.

Raman Studies of Surface Processes

Principal Investigator: Gerd M. Rosenblatt

Funding: \$184,100 (third year of funding)

Project Description

New instrumentation for Raman studies of surfaces was developed. Unenhanced spontaneous Raman spectroscopy was used to gain a new understanding of surface composition and of vibrational and rotational energy levels, dynamics, and reactivity of molecules on surfaces.

Accomplishments

A unique apparatus has been completed that uses an imaging photomultiplier tube to obtain Raman spectra that have unprecedented sensitivity and yield a one-dimensional Raman image of sample composition along a few millimeters of an illuminating, focused laser beam (Figures 5 and 6). The Raman spectroscopy system was used in the studies described below.

ILLUMINATION AND COLLECTION OPTICS

Fig. 5. (top) Schematic diagram of the Raman spectroscopy experimental apparatus. (bottom) Configuration of beam-shaping and collection optics for gas (or liquid) and surface samples. The laser is focused to about 20- μ m beam waist at the sample. The angle ϕ is 45° to the surface normal in the plane orthogonal to the plane containing the surface normal and the incident laser beam. [(Top) XBL 8612-5600; (Bottom) XBL 8612-5999A]

Raman spectroscopy applications of an imaging photomultiplier tube. A Raman spectroscopy system having an unparalleled combination of high sensitivity and low noise has been built incorporating an imaging (two-dimensional) photomultiplier tube. The number of photons detected for a vibrational band approaches the theoretical limit set by the Raman cross section and experimental configuration. A detector dark count of 10^{-4} counts/s/pixel is the major electronic source of noise. The spectrum of air revealed low concentration gas components, specifically ^{16}O , ^{18}O , and CO_2 . Vibrational Raman spectra were obtained from solid samples as thin as 20 nm with low laser powers, e.g., 6.5 mW. The imaging photomultiplier yielded

Fig. 6. Gray-scale image of the data array from a water-cyclohexane mixture. The gray scale represents the number of counts in a pixel. The X axis is wavelength dispersion, and the Y axis is along the laser-beam waist. [CBB 875-3689]

one-dimensional (along the focused laser beam) Raman images of interfaces or concentration gradients.

Ultrahigh vacuum apparatus for unenhanced Raman spectroscopy at cryogenic temperatures. An ultrahigh-vacuum (UHV) apparatus for studying submonolayer molecular coverages on well-defined single crystals by means of unenhanced surface Raman spectroscopy (SRS) has been built (Figure 7). Surface studies at controlled temperatures from 13 K to 900 K are possible. Sample cooling is achieved with a flexible thermal braid and closed-cycle helium refrigerator. Sample manipulation includes translation in the XYZ directions, tilt, and two degrees of rotation. This wide range of sample movement allows surface Raman spectroscopy, low-energy electron diffraction, and Auger spectroscopy to be carried out while maintaining a controlled temperature. Optical ports at two incident angles permit the study of a variety of substrates with differing optical properties. Unenhanced Raman spectra of nitrogen physisorbed on silver have been obtained (Figure 8).

Structure and properties of sputtered carbon overcoats on rigid magnetic media disks. In collaboration with Professor D. B. Bogy of the UC Berkeley Department of Mechanical Engineering, diamond-like sputtered carbon overcoats on commercial rigid disks with thin-film magnetic media were studied using transmission electron

Fig. 7. Schematic diagram of the ultrahigh-vacuum chamber used for Raman studies of samples between 15 K and 800 K. [XBL 8612-9300]

analysis (microscopy, microdiffraction, and energy-loss spectroscopy), Raman spectroscopy, Auger spectroscopy, ellipsometry, x-ray diffraction, and microhardness testing. Data from transmission electron analysis, Raman spectroscopy, and ellipsometry suggest that the carbon overcoats are composed of small graphite crystallites (≥ 2 nm), randomly oriented, with a small percentage (0–5%)

Fig. 8. Raman spectra of physisorbed N_2 on the (111) face of clean, single-crystal Ag at 15 K with increasing exposure: (a) 1 Langmuir, (b) 4 Langmuirs, (c) 13 Langmuirs, and (d) 23 Langmuirs. The data for (b), (c), and (d) have an increasing offset for clarity. The observed 2329 cm^{-1} is shifted from liquid N_2 at 2326.5 cm^{-1} [S.A. Akhmanov et al., JETP Lett. 27, 243–246 (1978)] and coincides with the α -phase of solid N_2 at 2329 cm^{-1} [A. Anderson, et al., Can. J. Phys. 48, 2265–2271 (1971)]. [XBL 881-301]

of fourfold coordinated carbon bonds. Auger spectroscopy and transmission electron-energy-loss spectroscopy indicate the presence of a small amount of oxygen. Auger spectroscopy also shows some surface nitrogen. The optical constants $n = 2.1$ and $k = 0.78$ exhibit a small wavelength dependence. In addition, the extinction coefficient k shows a dependence on film thickness. X-ray diffraction and microhardness testing did not yield any information concerning the carbon overcoats. There was no indication of diamond from any of the techniques that distinguish between diamond and other forms of carbon. Differences in structure and bonding are seen with Raman spectroscopy in samples from different manufacturers and in annealed samples.

Application of spatially resolved Raman spectroscopy in the study of transformed zones in partially stabilized ZrO_2 (PSZ). Raman vibrational spectroscopy provides an effective phase-characterization technique in materials systems containing particle dispersions of the three polymorphs of ZrO_2 , each of which yields a unique Raman spectrum. The capabilities of spatially resolved Raman spectroscopy in the study of phase-transformation zones around crack tips in PSZ were assessed. The experimental arrangement makes use of an imaging (two-dimensional) photomultiplier tube to produce a one-dimensional map of chemical composition along a laser beam without translating either the sample or the laser beam and without scanning the spectrometer. Results were obtained from phase-characterization studies of size, frontal morphology, extent of transformation, and degree of reversibility of the transformation zone surrounding cracks produced under monotonic and cyclic loading conditions.

Structure Determination at the Metal/Solution Interface

Principal Investigators: Philip N. Ross, Jeff Kortright, and Michel Van Hove

Funding: \$88,900 (second year of funding)

Project Description

The continuation of proof-of-principle experiments for the determination of structure at the metal/solution interfaces, specifically addressed to the understanding of epitaxial growth during the

electrolytic deposition of metals and semiconductors. New methods are being developed for the determination of the solid surface structure *in situ*. The methods that have produced promising initial results are scanning tunneling microscopy (STM) and grazing-incidence x-ray scattering (GIXS). The latter method encompasses a number of techniques, including surface diffraction (grazing-incidence diffraction, or GID), in-plane wide-angle scattering (WAXS), and surface extended x-ray absorption fine structure (SEXAFS) analysis.

Accomplishments

The potential-dependent structure of underpotentially deposited lead on silver (111) and the initial stages of bulk lead deposition on the adlayer have been studied using GIXS. Measurements were made *in situ* and under potential control. The close-packed hexagonal lattice formed by the underpotential deposition of lead (at full monolayer coverage) is compressed 1.4% relative to bulk lead. This strain increases linearly with applied potential until the onset of bulk deposition, where the adlayer is compressed 2.8%. Bulk lead is not deposited epitaxially on this template because of the large strain. Instead, it grows as islands with (111) texture that are randomly oriented in the plane of the substrate. After the deposition of approximately five equivalent monolayers of bulk lead, the initial adlayer reconstructs, apparently becoming disordered in the plane of the silver substrate.

The potential-dependent reconstruction of the Au(111) surface was observed by *ex situ* GID analysis of a single crystal emersed (removed from solution, leaving a thin miniscus of liquid covering the surface) from electrolyte under potential control. Independent analysis of this surface in vacuum by low-energy electron diffraction (LEED) and photoemission spectroscopy (PES) indicated that, at cathodic potential, the surface is probably reconstructed into a structure resembling the ($\sqrt{3} \times \sqrt{3}$) structure observed for the clean annealed surface. The emersed surface, however, has a disordered adlayer of Cs ions representing the surface excess charge produced by the cathodic potential at emersion. The resolution of the superlattice features (representing the reconstruction) in the GID scans were far superior to the resolution in the corresponding LEED patterns. The superior resolution was obtained in spite of the fact that in the GID experiments the surface was covered by a 1- μm film of liquid, whereas in the LEED experi-

ments all the water (but not the charge-compensating ions) was removed by evacuation prior to LEED analysis.

Tunneling Microscopy of Catalysts and Surface Compounds

Principal Investigator: Miquel B. Salmeron

Funding: \$104,800 (second year of funding)

Project Description

The objective of this project is to produce a scanning tunneling microscope (STM) to operate under liquids, in air, and in vacuum environments. The STM will be applied in its first stage of development to characterize new surface compounds in the form of very thin films of metals and oxides on a variety of metal and semiconductor substrates. These include FeO on Pt(111), TiO_2 , and Al_2O_3 on rhodium, S monolayer films on Re(0001) and Mo(001), and hard carbon films. New electronic, chemical, and mechanical properties appeared that resulted from their unique structure and two-dimensional nature. Some of the films were prepared by molecular and atomic-beam epitaxy in ultrahigh-vacuum (UHV) environments. Focus is on the atomic-scale characterization of electronic structure, growth, morphology, and composition. Other techniques used include photoelectron spectroscopies (core level, valence band), electron diffraction, ion scattering, and Auger spectroscopy.

Accomplishments

The development effort in the construction of the STM has culminated in its successful application to

Fig. 9. Three-dimensional view of a stepped region of the Re(0001) basal plane. [XBL 882-364]

some of the problems in the area of surface-structure determination in real space and in atmospheric environments. The faceting of Au(334) single crystals as a result of segregation of iron oxide when heated in air was imaged before and after the faceting. The structure of S-passivated Re(0001) surfaces was studied in air in detail. The presence of steps of various heights and orientation separated by large terraces (from 5 nm to hundreds of nm) was revealed by the STM and is illustrated in Figure 9. These observations demonstrate the power of the STM, since no other surface-science technique could allow the detailed study of these catalytically important defects. Monolayers of chemisorbed S atoms were imaged in air for the first time with excellent atomic resolution (1.5 Å in the direction parallel to the surface and 0.1 Å in the direction perpendicular to it). An example of the images obtained is shown in Figure 10.

The STM is also being used to study the structure of hard carbon films grown by sputtering techniques that are used for hard disk protection. The origin of the high hardness of these films was investigated in connection with the graphitic,

Fig. 10. Monolayer of chemisorbed sulfur atoms on molybdenum (001). [XBB 886-6470]

Fig. 11A. STM image of a hard carbon surface sputtered onto a hard disk. [XBB 8711-9765]

Fig. 11B. STM image of the basal plane of highly oriented pyrolytic graphite, showing the characteristic honeycomb structure. [XBL 8711-9762]

disordered, or diamond-like structure that has been proposed to explain these properties. In the preliminary images, small graphitic arrangements of C atoms were observed together with domains of less-ordered C atoms. Figure 11A shows an example of these results, along with a pure graphite image for comparison (Figure 11B). The STM will be applied to study the growth and structure of metal and oxide films in the monolayer and multilayer regime in UHV.

The STM was built with the capability to perform spectroscopic imaging. In that way, not only the topography but also the electronic structure of the thin films will be investigated at different points of the surface with atomic resolution. Preliminary experiments under liquids were also performed in the case of graphite and S-covered Re(0001) surfaces with a thin film of silicone oil.

Novel High-Temperature Superconductivity

Principal Investigator: Alex Zettl

Funding: \$66,000

Project Description

The purpose of this study was to synthesize new classes of superconducting materials and to perform transport and mechanical measurements on those materials. It was desired to achieve a material with the highest possible superconducting transition temperature T_c and to understand the superconductivity mechanism. The approach for materials synthesis was to develop new layered metallic oxides, motivated by the earlier observation of superconductivity near 30 K in La-Sr-Cu-O by Bednorz and Muller. Relevant experiments on La-Sr-Cu-O and related materials included infrared reflection and tunneling measurements to determine the magnitude of the gap parameter; elasticity studies to investigate the relation between possible soft phonon modes and high T_c ; electrical conductivity, thermopower, and Hall effect experiments to determine normal-state parameters such as carrier sign and concentration; and isotope substitution to determine the role of phonons in the electron-pairing mechanism.

Accomplishments

The material Y-Ba-Cu-O with an onset of superconductivity near 100 K was synthesized. This transition temperature exceeds the boiling point of nitrogen. This discovery was independent of, but subsequent to, the discovery of Y-Ba-Cu-O by the Houston/Alabama group. High-quality polycrystalline samples of this material and La-based and other rare-earth-based oxides have been produced.

Far-infrared reflection studies of La-Sr-Cu-O and La-Ca-Cu-O indicate anomalous absorption near $E/k_B T = 2.4$. This energy feature has been variously identified as the energy gap or a zero crossing of the dielectric function. A model has been proposed and solved that predicts the infrared reflection for these materials as a function of temperature and frequency. The model is in good agreement with the experiment.

Superconductor-insulator-normal tunneling measurements have been performed on the high- T_c superconductor $YBa_2Cu_3O_7$ at 4.2 and 77 K. The results indicate an energy gap of magnitude $3.9 k_B T_c$ with a temperature dependence consistent with the Bardeen-Cooper-Schrieffer theory of superconductivity.

Young's modulus and internal friction of $La_{1-x}Sr_xCuO_4$ have been measured as a function of temperature and x . For $x = 0.15$, anomalies in the Young's modulus and internal friction at $T_c = 40$ K are preceded by a dramatic decrease in the modulus, indicative of a soft phonon mode beginning near 200 K. For $x = 0.30$, the softening is absent. The magnetic-field dependence of the elastic constants have been investigated, with predictions made for specific-heat anomalies and temperature derivatives of critical field.

Electrical resistivity, Hall effect, and thermoelectric power (TEP) measurements have been performed on $La_{1.85}Sr_{0.15}CuO_4$ in the normal and superconducting states. The transport properties indicate that, in the normal state, the material conducts via holes with a carrier concentration of $6.0 \times 10^{21} \text{ cm}^{-3}$. Evidence is found for unusual phonon-drag effects above T_c and granular or inhomogeneous superconductivity in the vicinity of T_c . Below T_c , the resistivity, Hall constant, and TEP all drop to zero, as expected for a superconducting ground state.

An oxygen-isotope effect has been searched for in $YBa_2Cu_3O_7$ and $La_{1.85}Sr_{0.15}CuO_4$ through substitu-

tion of ^{18}O for ^{16}O . In $\text{YBa}_2\text{Cu}_3\text{O}_7$, no shift in T_c is observed by electrical-resistivity or magnetic susceptibility-measurements, within the experimental accuracy of 0.3 K. With $T_c = M^{-k}$, with M the ion mass, $k = 0 \pm 0.027$ for $\text{YBa}_2\text{Cu}_3\text{O}_7$. For $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, a finite shift is observed, on the order of 0.3–0.4 K. This implies that for $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, $k = 0.15 \pm 0.03$. For $\text{YBa}_2\text{Cu}_3\text{O}_7$, Ba and Cu isotope substitutions have also been performed, with no detectable isotope shifts: for Ba, $k = 0 \pm 0.1$, while for Cu, $k = 0 \pm 0.07$. These results are examined within the framework of phonon-mediated electron pairing. For $\text{YBa}_2\text{Cu}_3\text{O}_7$, the null isotope shifts appear incompatible with phonon-mediated pairing alone. A similar result was obtained for $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, using the small observed value of k .

The above work has prompted continued work in high- T_c oxide superconductors. Single crystals of the oxides are being synthesized to examine anisotropy in transport and elastic properties. New materials based on Bi and Tl are also being produced. The oxygen isotope experiments are being refined in order to obtain a lower error bar on the observed null effect. A systematic search has been initiated for oxide-based superconductors with T_c in excess of 125 K, the current record for Tl-Ba-Ca-Cu-O.

Publications

L.C. Bourne, K.J. Chang, M.L. Cohen, A.M. Stacy, and W.K. Ham, "Elasticity Studies of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$," *Phys. Rev. B* 35, 8785 (1987).

L.C. Bourne, M.L. Cohen, W.N. Creager, M.F. Crommie, A.M. Stacy, and A. Zettl, "Onset of Superconductivity in Y-Ba-Cu-O at 100 K," *Phys. Lett. A* 120, 494 (1987).

L.C. Bourne, M.F. Crommie, A. Zettl, H.C. zur Loye, S.W. Keller, K.L. Leary, A.M. Stacy, K.J. Chang, M.L. Cohen, and D.E. Morris, "Search for Isotope Effect in Superconducting Y-Ba-Cu-O," *Phys. Rev. Lett.* 58, 2337 (1987).

L.C. Bourne, A. Zettl, T.W. Barbee III, and M.L. Cohen, "Complete Absence of Isotope Effect in $\text{YBa}_2\text{Cu}_3\text{O}_7$: Consequences for Phonon-Mediated Superconductivity," *Phys. Rev. B* 36, 3990 (1987).

R.M. Cannon, "Critical Examination of Stress Development During Sintering," First International

Conference on Ceramic Powder Processing Science, Am. Ceram. Soc., Orlando, FL, Nov. 1987.

J.S. Chen, H. Menendez, and T.M. Devine, "The Sensitization Behavior of 308 Duplex Stainless Steel Welds with Lath and Vermicular Ferrite," in *Proc. Third Int. Conf. on Environmental Degradation of Engineering Materials*, The Pennsylvania State University, University Park, PA, 1987.

M.L. Cohen, D.E. Morris, A. Stacy, and A. Zettl, "Oxygen Isotope Effect in the High Temperature Superconductors $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ with ^{18}O Substituted by Diffusion," in *Proc. Workshop on Novel Mechanisms of Superconductivity*, June 22–26, 1987, Berkeley, CA, V. Kresin and S. Wolf, Eds., 1987.

M.L. Cohen, A. Stacy, and A. Zettl, "A Status Report on the Berkeley Research on High T_c Superconductors," in *Proc. Symp. S 1987 Spring Meeting Mat. Res. Soc.*, April 21–25, Anaheim, CA, D. Gubser and M. Schluter, Eds., 1987, p. 93.

M.F. Crommie, L.C. Bourne, A. Zettl, M.L. Cohen, and A. Stacy, "Tunneling Measurements of the Energy Gap in Y-Ba-Cu-O," *Phys. Rev. B* 35, 8853 (1987).

C.N. Cronin and J.F. Kirsch, "The Role of Arg292 in the Substrate Specificity of Aspartate Aminotransferase as Examined by Site-Directed Mutagenesis," *Biochemistry*, in press.

C.N. Cronin, B.A. Malcolm, and J.F. Kirsch, "Reversal of Substrate Charge Specificity by Site-Directed? Mutagenesis of Aspartate Aminotransferase," *J. Amer. Chem. Soc.* 109, 2222 (1987).

T.M. Devine, "Kinetics of Sensitization and Desensitization of Duplex 308 Stainless Steel," *Acta Metall.*, in press.

T.M. Devine, "Electrochemical Measurement of Chromium on Grain Boundaries in Sensitized Stainless Steel," submitted to *Corrosion*.

T.M. Devine, "Influence of the Degree of Sensitization and Dissolved Oxygen on the Intergranular Stress Corrosion Cracking of Stainless Steel," submitted to *Corrosion*.

T.M. Devine, "Mechanism of Sensitization of Austenitic Stainless Steel," submitted to *Corrosion Science*.

T.M. Devine, "Intergranular Stress Corrosion Cracking of Stainless Steels," in *Corrosion '88*, NACE, Houston, TX, 1988, p. 290.

D. Erskine, E. Hess, P. Y. Yu, and A. M. Stacy, "Pressure Dependence of the Superconducting Transition Temperature in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ to 8 GPa," *J. Mat. Res.* 2, 783 (1987).

D. Erskine, E. Hess, P. Y. Yu, A. M. Stacy, A. Zettl, and M. L. Cohen, "Electrical Properties of High T_c Superconductors under High Pressures," LBL-23692 (June 1987).

D. Erskine, P. Y. Yu, and S. C. Freilich, "High Pressure Visible Spectroscopy of Polyimide Film," LBL-24553 (November 1987).

D. Erskine, P. Y. Yu, and G. Martinez, "A New Technique for High-Pressure Electrical Conductivity Measurements in Diamond Anvil Cell at Cryogenic Temperatures," *Rev. Sci. Instrum.* 58, 406 (1987).

A.G. Evans and R.M. Cannon, "Stresses in Oxide Films and Relationships with Cracking and Spalling," in *Proc. Stresses and Degradation of Oxide Coatings*, TMS-AIME, 1987, in press.

S. Fahy, K. J. Chang, S. G. Louie, and M. L. Cohen, "Pressure Coefficients of Band Gaps of Diamond," *Phys. Rev. B* 35, 8196 (1987).

T.A. Faltens, W.K. Ham, S.W. Keller, K.J. Leary, J.N. Michaels, A.M. Stacy, H.C. zur Loye, D.E. Morris, T.W. Barbee III, L.C. Bourne, M.L. Cohen, S. Hoen, and A. Zettl, "Observation of an Oxygen Isotope Shift in the Superconducting Transition Temperature of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$," *Phys. Rev. Lett.* 59, 915 (1987),

R.M. Fisher, "Role of High Voltage and High Resolution Electron Microscopy in Interfacial Adhesion Research," Hawaii Seminar on Electron Microscopy, Honolulu, HI, Sept. 1987.

R.M. Fisher, "The Critical Voltage Effect in Metals, Alloys and Compounds," in *Proc. 1st Beijing Conference and Exhibition on Instrumental Analysis*, Vol. 1, p. 232 (1987).

R.M. Fisher, "Interface and Adhesion Science Research Related to Electronics Packaging and Reliability," seminar, Materials Dept., Ford Research Lab., Dearborn, MI, Jan. 1987.

R.M. Fisher, "Thin Film Delamination," seminar, IBM Advanced Packaging Technology Laboratory, East Fishkill, NY, Jan. 1987.

R.M. Fisher, "Interface and Adhesion Science at CAM," Interdepartmental Colloquium, Rockwell

International Science Center, Thousand Oaks, CA, June 1987.

R.M. Fisher, "Chemical and Microstructural Factors in Interfacial Adhesion," Second Beijing Conference and Exhibition on Instrumental Analysis, Beijing, Peoples Republic of China, Oct. 1987.

R.M. Fisher and R.M. Cannon, "Interface Reliability Issues in VLSI Packaging," Golden Gate Materials Technology Conference, San Francisco, CA, Feb. 1987; Intel Corp., Chandler, AZ, March 1987.

R.M. Fisher and R.M. Cannon, "Fundamentals of Interface Adhesion and Spontaneous Delamination of Thin Films," seminar, Components Research, Intel Corp., Santa Clara, CA, Feb. 1987.

A.G. Fox and R.M. Fisher, "Structure Factors and Debye Temperatures of Al-Li Solid Solution Alloys," *Acta Crystallogr.* 43, 260 (1987).

A.G. Fox and R.M. Fisher, "Low-Angle Atomic Scattering Factors and the Charge Density of Beryllium," *Philos. Mag.*, in press (1987).

A.G. Fox and R.M. Fisher, "A Summary of the Low Angle X-ray Atomic Scattering Factors Which Have Been Measured by the Critical Voltage Effect in High Energy Electron Diffraction (HEED)," invited presentation at the International Symposium on Accuracy in Structure Factor Measurements, Warburton, Australia, Aug. 1987; *Aust. J. Phys.*, in press.

A.G. Fox and R.M. Fisher, "The Origin of the High Elastic Modulus in Al-Li Alloys," *J. Mat. Sci.*, 1987, in press.

M.F. Hundley, A. Zettl, A. Stacy, and M.L. Cohen, "Transport Properties of the Superconducting Oxide $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$," *Phys. Rev. B* 35, 8800 (1987).

J.F. Kirsch, "Mechanism of Action of Aspartate Aminotransferase," invited paper, University of Minnesota, Minneapolis, MN, Feb. 1987.

J.F. Kirsch, "Site-Directed Mutagenesis of Aspartate Aminotransferase," invited paper, University of Wisconsin, Madison, WI, Feb. 1987.

J.F. Kirsch, "Alteration of Charge Specificity of AATase," Gordon Conference on Enzymes, Coenzymes, and Metabolic Pathways, Meriden, NH, July 1987.

J.F. Kirsch, "Site-Directed Mutagenesis and Mechanism of Aspartate Aminotransferase," invited

paper, Florida State University, Tallahassee, FL, March 1987.

J.F. Kirsch, "Specific Alterations of Enzyme Active Sites," invited paper, University of Texas, Austin, TX, Oct. 1987.

J.F. Kirsch, C.N. Cronin, M.D. Toney, and W.L. Finlayson, "Active Site Structure of Aspartate Aminotransferase," 194th National Meeting, American Chemical Society, New Orleans, LA, 1987.

J.F. Kirsch, W.L. Finlayson, M.D. Toney, and C.N. Cronin, "Mechanistic Analysis of the Aspartate Aminotransferase Active Site Mutants—Y70F, K258A, and R292D," in *Biochemistry of Vitamin B6*, Proc. 7th Int. Congress on Chemical and Biological Aspects of Vitamin B6 Catalysis, T. Korpele and P. Christen, Eds., Birkhauser, Basel, 1987, p. 59.

P. K. Lam, M. L. Cohen, and G. Martinez, "Analytic Relation Between Bulk Moduli and Lattice Constant," *Phys. Rev. B* 35, 9190 (1987).

B.A. Malcolm, S. Rosenberg, M.J. Corey, J.S. Allen, A. de Baetselier, and J.F. Kirsch, "Site-Directed Mutagenesis of the Catalytic Residues Asp-52 and Glu-35 of Chicken Egg-White Lysozyme," submitted to *Proc. Natl. Acad. Sci.*

H. Menendez and T.M. Devine, "Sensitization of Duplex Stainless Steel Welds," in *Corrosion '87*, NACE, Houston, TX, 1987, p. 99.

D.E. Morris, U.M. Scheven, L.C. Bourne, M.L. Cohen, M.F. Crommie, and A. Zettl, "Mobile Oxygen and Isotope Effect in the High Temperature Superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$," in *Proc. Symp. S 1987 Spring Meeting Mat. Res. Soc.*, April 21–25, Anaheim, CA, D. Gubser and M. Schluter, Eds., 1987, p. 209.

G.M. Rosenblatt, "Recent Developments in Optical Methods for the Study of Adsorbed Species," Third Annual Meeting on Chemical Analysis, Brussels, Belgium, May 1987; Physics Colloquium, University of California at Riverside, Nov. 1987.

M. Salmeron, "Scanning Tunneling Microscopy: A New Tool for Surface Studies in Vacuum, Liquid and Air Environments," in *Proc. Asia Pacific Symposium on Surface Physics*, April 14–17, 1987, Xie Xide, Ed., World Scientific, Singapore, 1987, p. 148.

M. Salmeron, "Scanning Tunneling Studies of Pyrolytic Carbon Surfaces in Air: Grain Boundaries and Surface Defects," 9th Surface/Interface Re-

search Meeting of the NCCAVS, IBM Almaden, San Jose, CA, Feb. 25, 1987.

M. Salmeron, "Scanning Tunneling Microscopy Studies of Au Films and Pyrolytic Carbon Surfaces in Air," 14th Int. Conf. on Metallurgical Coatings (ICMC 87), San Diego, CA, March 24–31, 1987.

M. Salmeron, "Scanning Tunneling Microscope Studies of Steps Defects and Grain Boundaries in Pyrolytic Carbons in Air," seminar, University of California at Riverside, April 29, 1987.

M. Salmeron, "Scanning Tunneling Microscopy Studies of Surfaces in Air and Liquid Environments: Defects Induced by Electrochemical Action Between Tip and Surface," lecture, Xerox Palo Alto Research Center, Palo Alto, CA, May 29, 1987.

M. Salmeron, "Surface Characterization Using the Scanning Tunneling Microscope," 1st Summer Workshop on Surface Characterization of Optical and Electronical Materials, Instituto de Fisica de la UNAM, Ensenada, Mexico, July 27–31, 1987.

M. Salmeron, "Atomic Structure of Clean and Adsorbate Covered Surfaces Studied by Scanning Tunneling Microscopy," lecture, Dow Chemical Company, Midland, MI, Oct. 15, 1987.

M. Salmeron, D.S. Kaufman, B. Marchon, and S. Ferrer, "Structure and Thermal Stability of the Au(334) Surface and Au(111) Thin Films in Air: A Scanning Tunneling Microscopy Study," *Appl. Surf. Sci.* 28, 279 (1987).

M. Salmeron, B. Marchon, P. Bernhardt, M.E. Bussell, G.A. Somorjai, and W. Siekhaus, "Atomic Arrangement of Sulfur Ad-atoms on Mo(001) at Atmospheric Pressure. A Scanning Tunneling Microscopy Study," *Phys. Rev. Lett.*, in press.

M. Salmeron, B. Marchon, S. Ferrer, and D.S. Kaufman, "Scanning-Tunneling-Microscopy Study of the Au(334) Surface in Air," *Phys. Rev B Rapid Commun.* 3, 3036 (1987).

M. Salmeron, B. Marchon, S. Ferrer, D.S. Kaufman, and W. Siekhaus, "The Surface Topography of Pyrolytic Carbons and Au Thin Films by Scanning Tunneling Microscopy: Grain Boundaries and Surface Defects," in *Proc. 14th Int. Conf. on Metallurgical Coatings*, San Diego, CA, March 23–28, 1987; *Thin Solid Films* 154, 65 (1987).

M. Salmeron, B. Marchon, D.F. Ogletree, and W. Siekhaus, "STM Study of the Re(0001) Surface

Passivated by Half a Monolayer of Sulfur in an Atmospheric Environment," *J. Vac. Sci. Technol.*, in press.

M. Salmeron, B. Marchon, F.D. Ogletree, M.E. Bussell, and W. Siekhaus, "STM Study of Sulfur-Covered Re(0001) Surface in Air," Second International Conference on Scanning Tunneling Microscopy/ Spectroscopy, Oxnard, CA, July 20-24, 1987.

P. Schultz, "Active Site Probing Using Semisynthetic Enzymes," lecture, University of Chicago, Chicago, IL, 1987.

P. Schultz, "Alteration of Active Sites Using Non-Natural Amino Acids," lecture, University of Wisconsin, Madison, WI, 1987.

P. Schultz, "Semisynthetic Enzymes," lecture, University of Massachusetts, Worcester, MA, 1987.

P. Schultz, "Synthetic Amino Acid Analogue Incorporation into Protein," lecture, Yale University, New Haven, CT, 1987.

P. Schultz, "New Approaches Towards the Design of Biological Catalysts," E. Bright Wilson Lecture-ship, Harvard University, Cambridge, MA, April 1987.

P. Schultz, "Semisynthetic Enzymes and Catalytic Antibodies," lecture, Massachusetts Institute of Technology, Cambridge, MA, Oct. 1987.

M.S. Sherwin, P.L. Richards, and A. Zettl, "Temperature Dependent Far Infrared Reflectance of La-(Sr,Ca)-Cu-O: BCS Electrodynamics—But

Uncertain Energy Gap," *Phys. Rev. B* 37, 1587 (1988).

H.-C. Tsai, D.B. Bogy, M.K. Kundmann, D.K. Veirs, M.R. Hilton and S.T. Mayer, "Structure and Properties of Sputtered Carbon Overcoats on Rigid Magnetic Media Disks," submitted to *J. Vac. Sci. Technol. A*.

D.K. Veirs, V.K.F. Chia, and G.M. Rosenblatt, "Raman Spectroscopy Applications of an Imaging Photomultiplier Tube," *Appl. Opt.* 26, 3530 (1987).

D.K. Veirs, V.F.K. Chia, and G.M. Rosenblatt, "Applications of Position Sensitive, Photon-Counting Detectors in Raman Spectroscopy," Topical Meeting of the Optical Society of America, Incline Village, NV, Jan. 1987.

U. Walter, S. Fahy, A. Zettl, S.G. Louie, M.L. Cohen, P. Tejedor, and A.M. Stacy, "Probing Density of States and Interactions at the Rare Earth Site in Superconducting $\text{ErBa}_2\text{Cu}_3\text{O}_7$," *Phys. Rev. B* 36, 8899 (1987).

U. Walter, M.S. Sherwin, A. Stacy, P.L. Richards, and A. Zettl, "Energy Gap in the High T_c Superconductor $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$," *Phys. Rev. B* 35, 5327 (1987).

F.C. Wellstood, M.J. Ferrari, J. Clarke, A.M. Stacy, A. Zettl, and M.L. Cohen, "Upper Limit on the Resistivity of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$," *Phys. Lett. A* 122, 61 (1987).

R. M. Wentzcovitch, M. L. Cohen, and P. K. Lam, "Theoretical Study of BN, BP, and BAs at High Pressures," *Phys. Rev. B* 36, 6058 (1987).

Nuclear Science Division

New Detectors for Low-Energy Particles

Principal Investigator: Joseph Cerny

Funding: \$29,800

Project Description

The project supported the development of a particle telescope capable of measuring very low-energy protons in the presence of a high β^+ background in order to search for the first observation of ground-state (g.s.) two-proton radioactivity. The ability to identify protons in a high background is necessary because nuclei that are predicted to decay by two-proton g.s. emission are expected to have half-lives well below 10 ms and to be produced in reactions with very small cross sections. As a result, separation of the multiple reaction products prior to the proton measurements is almost impossible. The detector must be able to measure protons with an energy range of 100 keV to 1 MeV because any proton-rich nucleus with more than 1 MeV of energy available to the g.s. two-proton decay channel will not live long enough to be observed.

Accomplishments

The particle-identification telescope that has been designed to meet these criteria is shown in Figure 1. It consists of a gas ΔE counter and a silicon E counter. In the telescope, the signals from the ΔE counter are used in conjunction with the silicon E counter for particle identification, but the final energy signal for protons is taken solely from the silicon E counter. The forerunner of the detector shown in Figure 1 was first tested off-line with 0.5- and 1-MeV protons from a Van de Graaff generator to determine the optimum operating parameters. In the first telescope, the active volume of the gas ΔE counter was defined by the silicon E counter and an aluminized entrance window rather than by the two grounding wire grids shown in Figure 1. The first telescope was tested on-line at the 88-Inch Cyclotron and it was found that, although the telescope could readily identify low-energy protons in a high-background environment, the gas ΔE counter broke down and did not recover when it was operated in the "in-beam" configuration illustrated in Figure 2 (the configuration necessary to search for g.s. two-proton radioactivity). The grounding grids shown in Figure 1 were then added to the gas ΔE counter to give a well-defined active volume for the gas ΔE counter, and the telescope performed well when tested on-line

Fig. 1. Cross-section view of the low-energy particle telescope. [XBL 891-139]

Fig. 2. Rapidly rotating wheel used for proton-decay measurements of very-short-lived species. [XBL 887-2661]

and "in-beam." This design has been incorporated into an array consisting of twelve of these gas ΔE counters and silicon E counters. The detector was able to measure the 389-keV proton group from ^{28}Si β -delayed proton decay in a β background of $\sim 10^5$ cps with 4 μA of pulsed ^3He beam incident on a 1.59 mg/cm 2 ^{26}Mg target. The search for g.s. two-proton radioactivity is now under way.

Although the new particle telescope was designed to measure low-energy protons, it is clear from the recent measurement of the β -delayed proton decay of ^{28}Si that this new detector also works well for measuring high-energy protons. In previous proton measurements, solid-state particle-identification telescopes have been used. The new detector has the advantage over these solid-state detectors in that it can measure a wider range of proton energies, and the resolution of the telescope is limited only by the resolution of the silicon E counter and the entrance-window thickness, as the protons lose only a few keV of energy in the gas ΔE counter. As a result, this new detector will be used in a majority of future proton measurements at the 88-Inch Cyclotron.

Large Einsteinium Activation Program (LEAP)

Principal Investigator: Darleane C. Hoffman

Funding: \$76,000 (second year of funding)

Project Description

Experiments continued using available actinide targets, especially ^{249}Bk and ^{251}Es , and neutron-rich heavy ion projectiles such as ^{16}O and ^{22}Ne , to determine the best production methods for new heavy-element isotopes and to devise the best experiments and techniques to be used when a large ^{251}Es target is produced. The currently available ^{251}Es target was used in experiments in which the new, unexpectedly long-lived ^{261}Lr and ^{262}Lr isotopes were discovered and characterized.

Accomplishments

The alpha-spontaneous fission (SF) system has been completed, including new electronics so that

alpha and SF spectra can be taken simultaneously. This system gives enhanced capability for off-line measurements of actinides produced in the reactions of heavy actinide targets and heavy projectiles. This capability is essential to the continuing effort to understand the reaction mechanisms to optimize the conditions for production of actinide and transactinide isotopes to study their nuclear and chemical properties.

Special Si(Au) surface barrier detectors have now been obtained for the rotating-wheel system at the 88-Inch Cyclotron, and these have been used in studies of the chemical and nuclear properties of the heaviest elements. In addition, a system of 12 alpha-SF detectors has been set up; the signals can be fed into the real-time data acquisition and graphics system (RAGS) for data acquisition and complete data analysis, including alpha-alpha correlation analysis, which is most valuable in identifying heavy-isotope decay chains. Using these systems, measurements have been completed of the ionic radius of lawrencium, element 103, and preliminary experiments have been performed to try to reduce lawrencium to the +1 or +2 oxidation state. Colleagues from the University of Mainz and the Gesellschaft für Schwerionenforschung in Germany came to collaborate in these studies, and also in experiments to measure the hydration enthalpies of Md(III) and Lr(III).

Using these facilities and a newly installed hood system near Cave 0 at the 88-Inch Cyclotron, the first aqueous-chemistry studies of element 105, hahnium, have been performed. These studies attracted national attention and were written up in several publications.

Collaborations have continued with the Heavy Element Chemistry Group of the Lawrence Livermore National Laboratory's Nuclear Chemistry Division to produce and study the spontaneous-fission properties of the newly discovered 39-minute ^{261}Lr and 216-minute ^{262}Lr . The half-lives of these isotopes are even longer than predicted in the original LEAP proposal and confirm the extra stability toward SF of isotopes containing an odd number of protons and/or neutrons.

Development work on SASSY-II has continued. Data-reduction programs and calculations concerning the magnetic trajectories of recoil particles through the spectrometer were made. Tests of the detector and magnet systems were performed.

Fig. 3. Gamma-ray spectra observed from samples of Norwegian goat cheese and American cheddar cheese. [XBL 8711-4615]

Low-Background Counting System

Principal Investigator: Eric B. Norman

Funding: \$37,700

Project Description

A system for studying rare-decay processes of interest in nuclear astrophysics and tests of fundamental symmetries was developed.

Accomplishments

To date, the new counting system has been used in five different experiments. Experiments have

begun to measure the β -decay half-life of ^{54}Mn and the β -decay half-life of ^{56}Ni . These parameters are of interest for the problems of cosmic-ray lifetimes and of the time interval between the production and acceleration of cosmic-ray nuclei. This system has also been used in a search for the isospin-forbidden Fermi decay of ^{56}Ni . This experiment will provide a measurement of the isospin purity of the ^{56}Ni ground-state wave function. A search for supermassive, long-lived negatively charged (X^-) particles bound to lead nuclei was also carried out using the data acquisition system.

Finally, radioactive fallout from the Chernobyl nuclear reactor accident was measured in imported food products. Figure 3 shows the gamma-ray spectra observed from samples of Norwegian goat cheese and American cheddar cheese. The clear $^{134,137}\text{Cs}$ γ -ray peaks seen in the Norwegian cheese are fingerprints of the Chernobyl accident. The observed activities are well below the ceiling of 10 picocuries per gram set by the U.S. Department of Agriculture. Analysis of the data obtained in the above-mentioned experiments is now in progress.

Calorimeter Development

Principal Investigator: Hans-Georg Ritter

Funding: \$48,600

Project Description

The purpose of the project was the development of sampling calorimeters that can be used for a dilepton experiment with heavy ions at the Alternating Gradient Synchrotron (AGS) at Brookhaven National Laboratory. Calorimeters will be needed for the energy determination of the high-energy electrons (energies greater than a few GeV) and for electron identification in the huge number of relatively soft hadrons emitted at mid-rapidity in relativistic heavy-ion collisions. Under those conditions, the traditional depth segmentation into two parts (electromagnetic and hadronic) is not sufficient for a good separation between electromagnetic and hadronic showers. Calorimeters with good energy resolution and high granularity will be needed. The same characteristics will be required for other AGS experiments and for experiments at the planned Relativistic Heavy Ion Collider (RHIC).

Accomplishments

The project was started by working in collaboration with scientists from Oak Ridge National Laboratory on the analysis and development of the response function for the calorimeters used in the CERN experiment WA80. The experience gained in WA80 led to the design of finely granulated lead scintillator test calorimeters. These utilize a conventional readout via wavelength shifters and photomultipliers on two sides, giving two signals from two different regions along the particle path. Additional depth information will be obtained by using scintillators with different decay times along the particle path and by doing pulse-shape analysis. A similar method has been successfully used in the Plastic Ball spectrometer. This will reduce the number of photomultipliers and related equipment needed, reducing the total cost substantially.

The design of the test calorimeters has been completed, all materials have been ordered and received, and the calorimeters are now ready to be assembled. As a first step, the depth segmentation and energy resolution will be optimized in test beams at the Bevalac.

Publications

D.A. Bennett, H. Nitsche, R.J. Silva, and D.C. Hoffman, "Studies on the Hydrolysis and Carbonate Complexation of Dioxoplutonium(V)," *Proceedings of the 194th National ACS Meeting*, New Orleans, LA, Aug. 31-Sept. 4, 1987.

W. Bröchle, M. Schädel, U.W. Scherer, J.V. Kratz, K.E. Gregorich, D. Lee, M. Nurmia, R. Chasteler, H. Hall, R. Henderson, and D.C. Hoffman, "The Hydration Enthalpies of Md^{3+} and Lu^{3+} ," *Inorg. Chim. Acta* 146, 267 (1988).

J. Cerny, J.D. Robertson, J.E. Reiff, D.M. Moltz, and T.F. Lang, "The β -delayed Proton Decay of ^{26}Si ," submitted to *Phys. Rev. C*; LBL-26335 (1988)

R.M. Chasteler, R.A. Henderson, D. Lee, K.E. Gregorich, M.J. Nurmia, R.B. Welch, and D.C. Hoffman, "Excitation Functions for Production of Heavy Actinides from Interactions of ^{16}O with ^{249}Cf ," *Phys. Rev. C* 36, 1820 (1987).

M.M. Fowler, W.R. Daniels, H.R. von Gunten, H. Gaggeler, D.C. Hoffman, K.J. Moody, M. Lerch, G. Herrmann, and N. Trautmann, "Radiochemical

Separation of Actinides from Copper and Gold Catcher Foils from Heavy Ion Reactions with Actinide Targets," *Radiachim. Acta* 46, 75 (1986).

C.M. Gannett, D.A. Bennett, R.B. Chadwick, R.M. Chasteler, K.E. Gregorich, H.L. Hall, R. Henderson, D.M. Lee, J. Leyba, M. Nurmia, and D.C. Hoffman, "Cross Sections for Production of Above Target Nuclides," *Proceedings of the 194th National ACS Meeting*, New Orleans, LA, Aug. 31-Sept. 4, 1987.

A. Ghiorso, "Recoil Spectrometer for the Detection of Single Atoms," presented at the International Conference on Methods and Applications of Radioanalytical Chemistry, Kona, HI, April 5-10, 1987; *J. Radioanal. Nucl. Chem.* 124, 407 (1988).

A. Ghiorso, S. Yashita, M.E. Leino, L. Frank, J. Kalnins, P. Armbruster, J.-P. Dufour, and P.K. Lemmerts, "SASSY, A Gas Filled Magnetic Separator for the Study of Fusion Reaction Products," *Nucl. Instrum. Meth.* A269, 192 (1988).

K.E. Gregorich, R.A. Henderson, D.A. Bennett, R.B. Chadwick, R.M. Chasteler, C.M. Gannett, H.L. Hall, D. Lee, J.D. Leyba, M.J. Nurmia, G.T. Seaborg, and D.C. Hoffman, "Non-Eka-Tantalum Behavior in Ha (Element 105)," *Proceedings of the 194th National ACS Meeting*, New Orleans, LA, Aug. 31-Sept. 4, 1987.

K.E. Gregorich, R.A. Henderson, D.M. Lee, M.J. Nurmia, R.M. Chasteler, H.L. Hall, D.A. Bennett, C.M. Gannett, R.B. Chadwick, J.D. Leyba, and D.C. Hoffman, "Aqueous Chemistry of Element 105," *Radiachim. Acta*, 41, 223 (1988).

H.A. Hall, R.A. Henderson, K.E. Gregorich, D.C. Hoffman, and D.M. Lee, " β -Delayed Fission from ^{256}Es and the Level Scheme of ^{256}Fm ," *Proceedings of the 194th National ACS Meeting*, New Orleans, LA, Aug. 31-Sept. 4, 1987.

D.C. Hoffman, "Heavy Ion Reactions with Trans-plutonium Elements," *Proceedings of the 194th National ACS Meeting*, New Orleans, LA, Aug. 31-Sept. 4, 1987.

D.C. Hoffman and L.P. Somerville, "Spontaneous Fission," published as a chapter in *Charged Particle*

Emission from Nuclei, Vol. III, CRC Press, Inc., Boca Raton, FL (1988), p. 1.

D.C. Hoffman, R.A. Henderson, K.E. Gregorich, D.A. Bennett, R.M. Chasteler, C.M. Gannett, H.L. Hall, D.M. Lee, M.J. Nurmia, S. Cai, R. Agarwal, A.W. Charlop, Y.Y. Chu, and R.J. Silva, "Atom-at-a-Time Radiochemical Separations of the Heaviest Elements: Lawrencium Chemistry," International Conference on Methods and Applications of Radioanalytical Chemistry, Kona, Hawaii, April 5-10, 1987; *J. Radioanal. Nucl. Chem.* 124, 135 (1988).

E.K. Hyde, D.C. Hoffman, and O.L. Keller, Jr., "A History and Analysis of the Discovery of Elements 104 and 105," *Radiachim. Acta* 42, 57 (1987).

D.T. Jost, H.W. Gäggeler, Ch. Vogel, M. Schädel, E. Jäger, B. Eichler, K.E. Gregorich, and D.C. Hoffman, "Search for Lawrencium as a P-Element Using Gas Chromatography Techniques," *Inorg. Chim. Acta* 146, 255 (1988).

J.V. Kratz, U.W. Scherer, E. Brühlle, M. Schädel, K.E. Gregorich, R. Chasteler, H. Hall, R. Henderson, D.C. Hoffman, D. Lee, and M. Nurmia, *Proceedings of the 194th National ACS Meeting*, New Orleans, LA, Aug. 31-Sept. 4, 1987.

E.B. Norman, "Influences of the Astrophysical Environment on Nuclear Decay Rates," to be published in *Proc. Symp. Origin and Distribution of the Elements*, 194th National ACS Meeting, New Orleans, LA, Aug. 31-Sept. 4, 1987; LBL-23037 (1987).

U.W. Scherer, J.V. Kratz, M. Schädel, W. Brühlle, K.E. Gregorich, R.A. Henderson, D. Lee, M. Nurmia, and D.C. Hoffman, "Lawrencium Chemistry: No Evidence for Oxidation States Lower than 3+ in Aqueous Solution," *Inorg. Chim. Acta* 146, 249 (1988).

G.T. Seaborg and W. Loveland, "Superheavy Elements," *Contemp. Phys.* 28, 34 (1987).

R.B. Welch, K.J. Moody, K.E. Gregorich, D. Lee, and G.T. Seaborg, "Dependence of Actinide Production on the Mass Number of the Projectile," *Phys. Rev. C* 35, 204 (1987).

Physics Division

Advanced Semiconductor Devices for High-Energy Physics

Principal Investigator: Luciano Bosio

Funding: \$75,100

Project Description

It is well known that the Superconducting Super Collider (SSC) will present a particularly difficult environment to experimenters that will require new detector techniques to match the luminosity, background levels, and physics signatures. Over the past year, new studies have been made that show that background effects, especially for neutrons, appear to be worse than previously anticipated. A conclusion of these studies is that the case for developing semiconductor pixel detectors appropriate to the SSC physics program has been made stronger. During the past year, effort has been directed toward the goal of developing new processing techniques for semiconductor detectors that ultimately will permit the fabrication of circuitry and detector on the same wafer.

Accomplishments

Radiation damage studies. High background levels anticipated for the SSC will introduce radiation damage in detectors and readout electronics. Techniques for the amelioration of the effects of this damage are possible in both design and fabrication processes. The damage in silicon devices has a variety of effects. Excess current flow in both detectors and circuitry, increased noise, and the generation of offsets in the voltages associated with control elements are among the most prominent symptoms.

While there exists considerable literature on the basic mechanisms of radiation damage in semiconductors, the impact of specific process steps is very great, making the applicability of generalized results uncertain. An electron beam irradiation apparatus has been designed and brought into operation for the study of the hardness of interesting devices. This machine can be computer con-

trolled to deliver a raster-scanned beam over an area of interest. The energy of the machine is high enough to penetrate the entire depth of typical integrated circuitry. This will allow the study of the effects of gate oxide charge buildup separately from the bulk damage effects. Preliminary work with this apparatus has already been useful.

Process studies for improved detectors and fully integrated readout systems. In this work, a variety of problems have been studied. One major effort has been the attempt to reduce radiation damage induced during aluminum metalization; the radiation damage can come from UV photons, x rays, or the electrons associated with the sputtering process. Comparative studies of MOS capacitors fabricated by three different methods are underway. The methods are evaporation from a tungsten boat, DC magnetron sputtering, and ion-beam sputtering. It is anticipated that the ion beam will be the most promising.

Another important aspect of this work is the study of gettering processes. Incorporation of gettering steps in the fabrication process can be expected to increase generation lifetime, allow more complicated processing sequences for detectors (e.g., permitting the inclusion of active circuitry), and contribute to higher yield. Initial work with backside polysilicon gettering has been very promising. Other approaches under consideration are ion implantation and deposition of phosphosilicate glass.

A third general direction of effort is improved passivation to increase reliability and lifetime. Avenues under study are the deposition of phosphosilicate glass, silicon nitride (plasma enhanced CVD), and certain organics such as polyimide.

Development of Low Threshold Bolometers for Dark Matter Detection

Principal Investigator: Bernard Sadoulet

Funding: \$97,800

Project Description

Bolometric techniques have been developed to measure energy deposition of a few hundred electron-volts with detector elements of 100 grams or so. This development is motivated by the exciting possibility of detecting dark matter from the halo of the galaxy, if it is made of weakly interacting massive particles (WIMPs). The goal of the study is eventually to demonstrate the feasibility of thresholds as low as 100 eV with crystals of at least a few grams.

The detection of phonons has been explored with highly doped semiconductor thermistors and compensated semiconductor crystals in which electric conduction occurs by phonon-assisted hopping. These can be operated in two modes. The resistance depends very sensitively on the temperature, and these devices can be used as proper thermistors to measure the temperature rise induced by absorption of infrared radiation or by a particle interaction. In principle, because of the decreasing heat capacity, the sensitivity of the method should increase with decreasing temperature. The technique had been demonstrated down to 100 mK, but already at that temperature parasitic effects began to appear and limit, for instance, the biasing power and therefore the sensitivity.

A second detection mode is potentially interesting for particle detection in large crystals, where ballistic phonon effects may become dominant. It is theoretically possible that high-energy phonons couple directly to electrons in the highly doped semiconductor, which may then act as an effective ballistic phonon detector. In that case, the heat capacity of the crystal would be unimportant. It will act as a phonon guide, and the problem is one of phonon collection efficiency.

Accomplishments

Two experimental set-ups have been used that provided quite interesting results.

- **1.4-K dewar.** NTD bolometers have been used to detect alpha particles. Figure 1 shows typical pulses that were obtained. After serving as a training ground, this set-up is now mostly used for development of low noise FET amplifiers working in a 4-K environment. Although the low noise goal has not yet been reached, the first prototype works satisfactorily at low temperature.

Fig. 1. Pulses observed with alpha particles of 5.8 MeV in a bolometer of 6×10^{-3} gram at 1.4 K. Vertical scale: 10 μ V/div. Horizontal scale: 100 μ s/div. BW = 100 kHz; $\Delta E = 5.8$ MeV [XBB 892-834]

- **Dilution refrigerators.** This first experience at very low temperature showed many of the potential problems in set-up—in particular all the problems with RF shielding—and it has been an essential component of a design of a low-temperature laboratory.

It has been possible to characterize precisely the behavior of the NTD bolometer at very low temperature (20 mK), including the dependence of the resistance versus temperature, the optimal biasing conditions, and the effective heat capacity and heat conductance. The responsivity of these devices, shown in Figure 2, is quite impressive (0.3 volts per kelvin, thus allowing the measurement of a temperature rise of less than 10^{-7} K).

At these very low temperatures, the parasitic effects are rather obvious, and preliminary measurements at 20 mK show that the phenomenon may be due to the decoupling of electrons from low energy phonons. Attempts are currently underway to refine the experimental evidence.

This careful ground work allowed the successful detection of 60-keV x rays at 22 mK. This observation in a thermally clamped device seems to confirm the expectation that heavily doped semiconductors are sensitive to ballistic phonons.

Fig. 2. Responsivity of a NTD thermistor as a function of the biasing power for temperatures between 19 and 32 mK. Note that very small biasing power is necessary for these very sensitive devices. [XBL 892-6902]

Publications

B. Sadoulet, "Cryogenic Detection of Particles: Development Effort in The United States," in *Low Temperature Detectors for Neutrinos and Dark Matter*, Rigberg Castle, Tegernsee, March 12-13, 1987, K. Pretzl, N. Schmitz, and L. Stodolsky, editors, Springer-Verlag, Berlin, Heidelberg, 1987, p. 86.

B. Sadoulet, "Is Dark Matter Made out of Particles? Current Searches and Detector Developments," *Proceedings of the VII Moriond Workshop on Searches for New and Exotic Phenomena*, Les Arcs, France, Jan. 24-31, 1987.

B. Sadoulet, "Prospects for Detecting Dark Matter Particles by Elastic Scattering," in *Proceedings of the 13th Texas Symp. Relativistic Astrophysics*, Chicago, Dec. 14-19, 1986, M.L. Ulmer, Ed., World Scientific, Singapore, 1987, p. 260.

B. Sadoulet, "Cryogenic Detectors: Hope and Challenges," invited talk at the Nuclear Symposium, Oct. 1987; *IEEE Trans. Nucl. Sci.* 35, 47 (1988).

N. Wang, B. Sadoulet, T. Shutt, J. Beeman, E. Haller, A. Lange, I. Park, R. Ross, C. Stanton, and H. Steiner, "A 20 mK Temperature Sensor," *IEEE Trans. Nucl. Sci.* 35, 55 (1988).

Acronyms and Abbreviations

Å	angstrom
ADR	absorber-coupled double-effect regenerative
AEM	analytical electron microscopy
AGS	Alternating Gradient Synchrotron
BSA	bovine serum albumin
CEC	California Energy Commission
CERN	European Organization for Nuclear Research
COP	coefficient of performance
cpm	counts per minute
CVD	chemical vapor deposition
DNA	deoxyribonucleic acid
DOE	U.S. Department of Energy
ECM	extracellular matrix
EDM	electric dipole moment
epo	erythropoietin
ESR	electron synchrotron resonance
FEL	free-electron laser
FET	field effect transistor
FY	fiscal year
GML	galvanomagnetic luminescence
GID	grazing-incidence diffraction
GIXS	grazing-incidence x-ray scattering
HME	hemopoietic microenvironment
HMEC	human mammary epithelial cells
HVED	high-voltage electron diffraction
IBS	intrabeam scattering
ICFA	International Conference for Future Accelerators
IGSCC	intergranular stress corrosion cracking
KLH	keyhole limpet hemocyanin
KTBA	keto thiomethyl butyric acid
LBL	Lawrence Berkeley Laboratory
LDL	low-density lipoproteins

LEAP	Large Einsteinium Activation Program
LEED	low-energy electron diffraction
LLNL	Lawrence Livermore National Laboratory
LVDT	linear variable differential transformer
MIT	Massachusetts Institute of Technology
MOS	metal oxide silicon
NMR	nuclear magnetic resonance
NOE	nuclear Overhauser effect
NTD	neutron transmutation doped
PDF	Program Development Fund
PDGF	platelet-derived growth factor
PES	photoemission spectroscopy
PG&E	Pacific Gas & Electric
PHZ	phenylhydrazine
R&D	research and development
RAGS	real-time data acquisition and graphics system
RF	radio frequency
RFLP	restriction fragment length polymorphisms
RHIC	Relativistic Heavy Ion Collider
SEM	scanning electron microscope
SEXAFS	surface extended x-ray absorption fine structure
SOD	superoxide dimutase
SRRC	Synchrotron Radiation Research Center (Taiwan)
SRS	surface Raman spectroscopy
SSC	Superconducting Super Collider
SSRL	Stanford Synchrotron Radiation Laboratory
STM	scanning tunneling microscopy
TEP	thermoelectric power
TGSCC	transgranular stress corrosion cracking
TNF	tumor necrosis factor
UC	University of California
UCSF	UC San Francisco
UHV	ultrahigh vacuum
WAXS	wide-angle scattering
Wimps	weakly interacting massive particles