Title

Annual Report 1989: Electronic Materials High-T{sub c} Superconductivity Polymers and Composites Structural Materials Surface Science and Catalysis Industry Participation

Permalink

https://escholarship.org/uc/item/5k02468n

Author

Lawrence Berkeley National Laboratory

Publication Date

1990-04-01

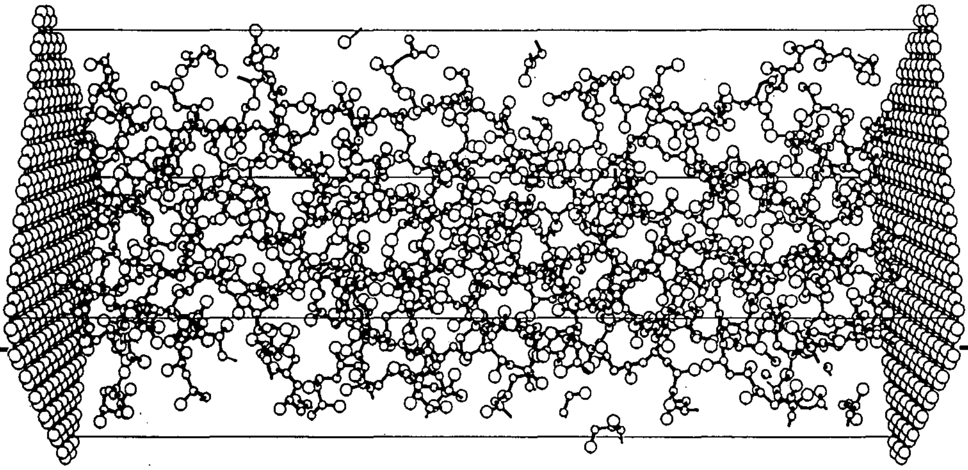
LBL-28495
UC-404

Center for Advanced Materials
CAM

ANNUAL REPORT

1989

Electronic Materials
High-T_c Superconductivity
Polymers and Composites
Structural Materials
Surface Science and Catalysis
Industry Participation



Center for Advanced Materials
Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory • University of California

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

Center for Advanced Materials

Annual Report—1989

Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory
University of California
1 Cyclotron Road
Berkeley, CA 94720

The research described in this report was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under contract No. DE-AC03-76SF00098, and the Divisions and Offices of Chemical Sciences, Energy Biosciences, Conservation and Renewable Energy, Magnetic Fusion and Fossil Energy in the Department of Energy. Portions of this work were also supported by Akzo Corporate Research America, Aluminum Company of America (ALCOA); the Army Research Office; Bell Communications Research, Inc.; Bertram Laboratories; BP America; Cargill Inc.; Chevron Research Company; Cray Instruments; Dow Chemical Company; E.I. DuPont de Nemours & Company; Electric Power Research Institute; Exxon Research and Development; Ford Motor Company; The Harshaw/Filtrol Partnership; IBM; Lockheed Corporation; LTV Steel; Materials Research Corporation; Morris Research; NASA; Naval Air Development Center; The National Science Foundation; Northrop Corporation; Raychem Corporation; Rhône Poulenc; Rouge Steel; Sandia National Laboratories; Shell Development Corporation; 3M; The State of California, California Competetive Technology Program; Union Carbide Corporation; University of Houston; W.R. Grace & Company; and Xerox Corporation.

Cover: Model microstate of glassy atactic polypropylene sandwiched between two basal planes of graphite (see page 73). (XBL 901-114A)

Center For Advanced Materials Personnel

CAM Director
Robert O. Ritchie*

Deputy Director
Mark Alper*

Program Leaders
Morton Denn*
Norman Phillips*
J.W. Morris, Jr.*
Eugene Haller*
Gabor Somorjai*

Deputy Program Leaders
Paul Berdahl †
Wladyslaw Walukiewicz

Project Leaders
Mark Alper*
Alex Bell*
John Clarke*
Rowland Cannon
Lutgard De Jonghe*
Heinz Heinemann
J.W. Morris, Jr.*
Robert O. Ritchie*
Miquel Salmeron
Doros Theodorou*
Jack Washburn*

Scientific Staff
Mehdi Balooch
Mark Bednarski*
Alexis Bell*
Harvey Blanch*
Edith Bourret-Courchesne
Ian Brown §
Arup Chakraborty*
Douglas Clark*
John Clarke*
Marvin Cohen*
Richard Dalven
Thomas Devine*
James Evans*
Leo Falicov*
Robert M. Fisher
Robert N. Fisher
Didier de Fontaine*
Alan Fox
Ronald Gronsky*
Joseph Guitron
Eugene Haller*
William Hansen‡
William Hassenzahl §
Crispin Hetherington
Joseph Jaklevic
Carson Jeffries*
Lutgard De Jonghe*
Roland Keunings
Armen Khatchaturyan
Jack Kirsch*
Vladimir Kresin
Zuzanna Liliental-Weber
Steven Louie*
James Michaels*
Donald Morris **
J.W. Morris, Jr.*
Bruce Novak*
Frank Ogletree
Donald Olander*
Marjorie Olmstead*
Alexander Pines*
Alan Portis*
Clayton Radke*
Jeffrey Reimer*
Paul Richards*
Gerd Rosenblatt
Michael Rubin†
Richard Russo†
Peter Schultz*
Yuen-Ron Shen*
Paul Smith
(University of California,
Santa Barbara)
David Soane*
Angelica Stacy*
Gareth Thomas*
Michel Van Hove
Jack Washburn*
Eicke Weber*
Birgitta Whaley*
Chi-Huey Wong
(Research Institute of
Scripps Clinic, La Jolla, CA)
Kin-Man Yu
Peter Yu*
Alex Zettl*

Postdoctoral Fellows
Angelika Behrooz
Jeffrey Bibbs
Greg Blackman
Lincoln Bourne
Patricia Cioni
Marie-Paule Delplancke
Michael Dixon†
Benoit Ernst
Davide Hill
Christopher Hobbs
Robert Hwang
Mark Johnson
Eric Kvam
Phillippe Lerche
Per Lindberg**
Nancy Missert
Joanne Petithory
Ramamoorthi Ramesh
Thomas Richardson
Philip Rous
Adrian Wander
Cao Wei
Frederick Wellstood
Xiao-dong Xiang
Xiaoguang Zhang

Graduate Students
Stuart Adler
Spencer Anthony-Cahill
Phillip Armstrong
M. Asta
Kiran Atwal
Claudia Bachmann
Reha Bafrali
David E. Bliss
Alex Boffa
Yves Boiteux
Istvan Böszörmenyi
Edwin Bradley, III
Andrew Braisted
Gabriel Briceno
Gillian Brown
Thea Buchanan
Brian Burk
Christopher Burmester
W. Craig Carter
Gerbrand Ceder
Jin Chan
Lydia Chan
Jin-Syung Chen
S. Chi
David Chu
May-Ying Chu
Dean Clarke
Michael Corey
William Creager
Michael Crommie
Douglas Devens, Jr.
Laura Dietsche
Jian-Zhong Duan
Christophe Dumai
Roger Emigh
Boris Fayn**
Mark Fendorf
Mark Ferrari
Mirtha Fernandez
Kim Fortunati
Sabrina Fu
Maria Galiano
Denis Gardin
Massimiliano Ghirlanda
David Giles
David Ginter
Judith Glazer
Janet Griffiths
Mats Gustafsson
William Ham
William Hendricks
Storrs Hoen
Mark Hoinkis
Won-Shick Hong
C. Brad Hopper†
Qing Hu
Craig Jacobson
David Jentz
Glenn Jernigan
Patricia Johnson
Chengfong Jou
Steven Keller
Changmin Kim
Yountai Kim
John Kingston
Colette Knight
Marc Kollrack
Kamala Krishna
David Kapolnek
Anthony Keslinke
Choong-un Kim
Pamela Kramer
Timothy Kueper
Harry Lam
Kenneth Lee
Veronica Lim
Timothy Lindsey
Amy Liu
Stephen Lombardo
Mark McCormack
Brian McIntyre
Leslie McKnelly, Jr.
Peter Macanally
Bruce Malcolm
Michael Mann
Kevin Mansfield
Amit Mararthe**
Carl Mears
Zequn Mei
Alan Michiels
Rebecca Mih
Andrew Miklich
David Miller
Tyrone Mitchell, Jr.
Shelly Miyasato
Amy Moll
Kevin Mon
O.R. Monteiro
Robert Mortlock
Steven Musarra
Chris Mullin
Michael Nahum
Pravin Narwankar**
Pedro Nascente
Nathan Newman
Janice Nickel**
Christopher Noren
Dale Olson
Paul Pinsukanjana
James Powers
Michael Quinlan
Ronald Reade†
Joseph Rosenberg
John Sanchez, Jr.
Michael Schonberg
James Shaffer
Steven Shaffer
Chi Sheu
Robert Shipman
Sara Stoll
Tammy Summers
Anne Sunwoo
Richard Superfine
Rebecca Taylor
Ward Tegrotenhuis
Ruth Ellen Thomson
Dana Tribula
Gilroy Vandentop
Simon Verghese
Stephanie Verzasconi
Gerard Vurens
Albert Wang
Marjorie Went
Gregory Went
Kevin Williams
Sheun Wu
Jeffrey Wolk
Xu-Dong Xiao
Ping Xu
Edward Yin†
David Zeglinski

Technical Support
Whitney Carrico
Sydney Edwards
Wini Heppler
Lynn Oehler
Travis Palomares
Heather Rumsey
Sue Whitfield

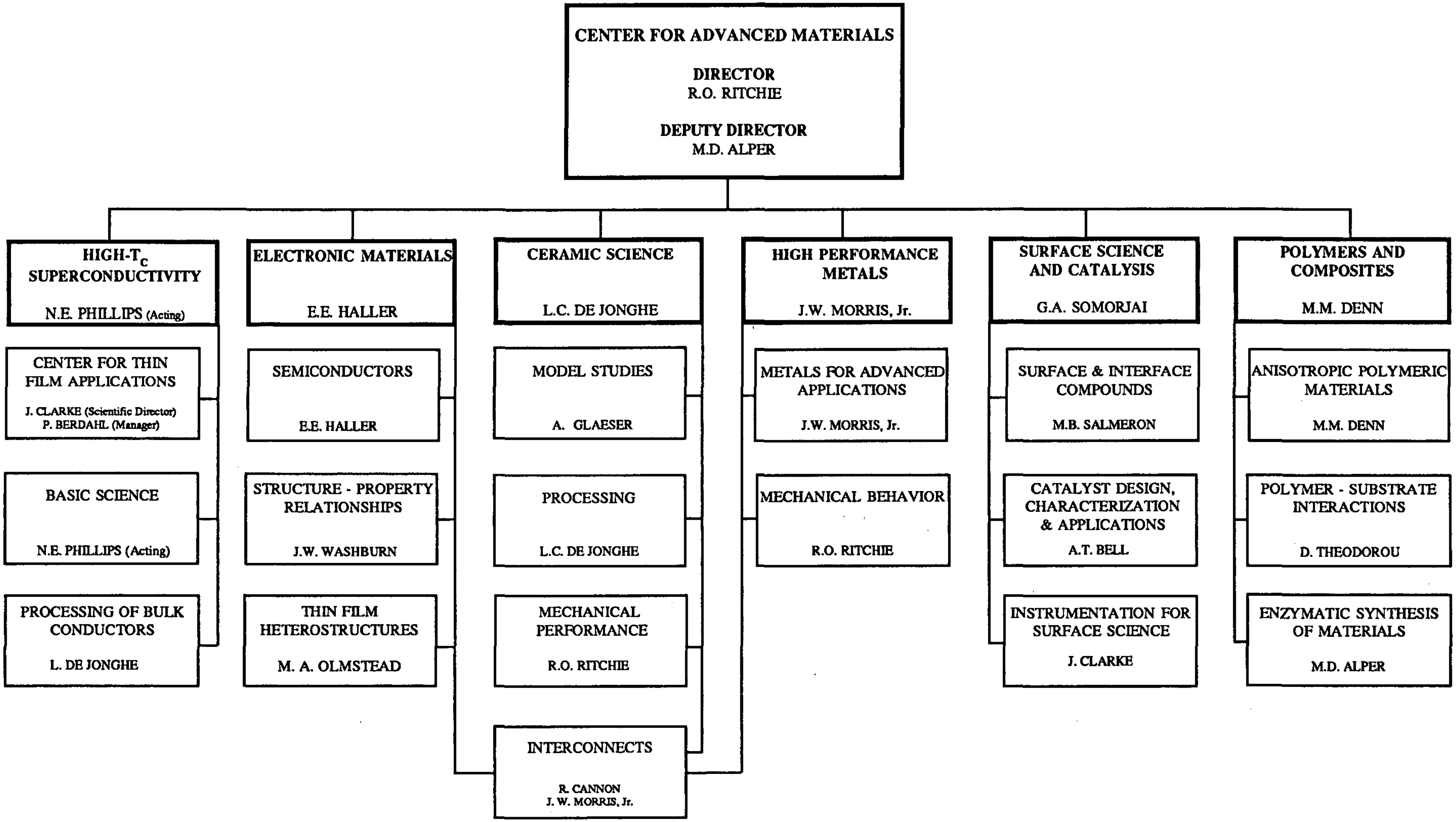
Research Assistants
John Dykema**
Brian Kasper**
William Lewis
Jeffry McMillan†
Andrea Markelz**
Justin Paola**
Michael Powers
Gino Segre **
Victor Shum**
John Surnow**
Ken Takano**
William Vinje**
Troy Wilson

Administrative Support
Learr English
Jane Fortado
Margaret Holm
Linda Kelly
Gloria Osterloh
Madeleine Penton
Margaret Ragsdale
Charlotte Standish†
Brigid Tung
Rebecca Vesterfelt

---

* U.C. Berkeley Faculty
†Applied Science Division,
‡Accelerator and Fusion Research Division
§Engineering Division
** Physics Division

CONTENTS



CENTER FOR ADVANCED MATERIALS

DIRECTOR
R.O. RITCHIE

DEPUTY DIRECTOR
M.D. ALPER

- **HIGH-T_c SUPERCONDUCTIVITY** — N.E. PHILLIPS (Acting)
  - CENTER FOR THIN FILM APPLICATIONS — J. CLARKE (Scientific Director), P. BERDAHL (Manager)
  - BASIC SCIENCE — N.E. PHILLIPS (Acting)
  - PROCESSING OF BULK CONDUCTORS — L. DE JONGHE
- **ELECTRONIC MATERIALS** — E.E. HALLER
  - SEMICONDUCTORS — E.E. HALLER
  - STRUCTURE - PROPERTY RELATIONSHIPS — J.W. WASHBURN
  - THIN FILM HETEROSTRUCTURES — M. A. OLMSTEAD
  - INTERCONNECTS — R. CANNON, J. W. MORRIS, Jr.
- **CERAMIC SCIENCE** — L.C. DE JONGHE
  - MODEL STUDIES — A. GLAESER
  - PROCESSING — L.C. DE JONGHE
  - MECHANICAL PERFORMANCE — R.O. RITCHIE
  - INTERCONNECTS — R. CANNON, J. W. MORRIS, Jr.
- **HIGH PERFORMANCE METALS** — J.W. MORRIS, Jr.
  - METALS FOR ADVANCED APPLICATIONS — J.W. MORRIS, Jr.
  - MECHANICAL BEHAVIOR — R.O. RITCHIE
  - INTERCONNECTS — R. CANNON, J. W. MORRIS, Jr.
- **SURFACE SCIENCE AND CATALYSIS** — G.A. SOMORJAI
  - SURFACE & INTERFACE COMPOUNDS — M.B. SALMERON
  - CATALYST DESIGN, CHARACTERIZATION & APPLICATIONS — A.T. BELL
  - INSTRUMENTATION FOR SURFACE SCIENCE — J. CLARKE
- **POLYMERS AND COMPOSITES** — M.M. DENN
  - ANISOTROPIC POLYMERIC MATERIALS — M.M. DENN
  - POLYMER - SUBSTRATE INTERACTIONS — D. THEODOROU
  - ENZYMATIC SYNTHESIS OF MATERIALS — M.D. ALPER

Center for Advanced Materials

CAM

The Center for Advanced Materials does fundamental research in materials science and helps to train the students and postdoctoral fellows who will become the next generation of materials scientists. In this way it continues the tradition of its internationally recognized parent organizations, the Lawrence Berkeley Laboratory and the University of California at Berkeley.

The mission of the Center represents a departure from that tradition in that it explicitly involves the support of the international competitive standing of US industry. Current research programs look forward— beyond the immediate goals set for corporate research laboratories— to the fundamental science that will serve as the basis of industrial research a decade into the future. Thus, projects at the Center are focused in fields ranging from the next generation semiconductors to the first generation biochips, from light metal alloys for spacecraft to heavy metal oxides for catalysis, from ceramics that fatigue to oxides that superconduct, to polymers that rival steel in their mechanical properties.

CAM management meets regularly with its industrial advisory boards, workshop attendees, and industrial fellows, to identify the basic science questions whose answers are required for the next decade of technological advance. Its programs involve multidisciplinary teams of staff scientists, University of California at Berkeley faculty, students, and postdoctoral fellows. Those teams are provided with the technical support and advanced instrumentation at LBL that built many of the world's great accelerators, designed and fabricated the mirror support and control systems for the Keck 10-meter telescope, and operate among the most advanced atomic resolution and high voltage electron microscopes in the world. This combination of university, laboratory and industry efforts contributes significantly to the success achieved by the Center's research programs.

The cover of this annual report lists the five areas of focus of the Center. The text describes the results of our research in these areas over the past year. The last section describes the modes of interaction with industry that exist at the Center. We are funded primarily by the government and feel it is appropriate to communicate the results of our research to industrial scientists without charge, (except for the recovery of actual costs of our workshops.) The new year is already one third past and next year's report is already taking form. Prominent highlights include the first achievement of thin layer crossovers for devices using the new high-T_c superconductors and the successful fabrication of a self-assembling biochip for bio-electronic sensors.

Electronic Materials

Basic Studies of Defects and Impurities in III-V Semiconductors
Bulk Crystal Growth
Thin Films and Interfaces
Interconnects/Interfaces

Electronic Materials

The CAM Electronic Materials Program concentrates on scientific problems impeding the development of large scale digital integrated circuits and optoelectronic devices based on gallium arsenide and related III–V semiconductors. Research is focused in four main areas.

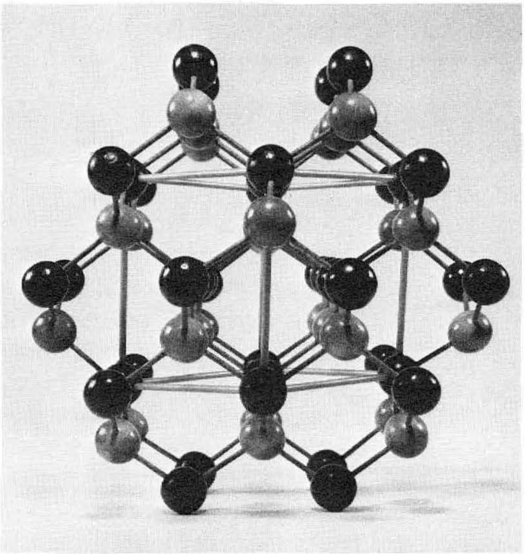
BASIC STUDIES OF DEFECTS AND IMPURITIES IN III-V SEMICONDUCTORS—the study of the structural and electronic properties of defects and impurities and the mechanisms of their incorporation. Many of the properties of compound semiconductors are determined by intrinsic imperfections of the crystal lattice introduced during crystal growth and processing. These must be understood and controlled. Recent results in this area include:

- First measurements of magnetic properties of deep DX donors in $Al_xGa_{1-x}As$ semiconductors. These strongly indicate that the deep donors bind only one electron rather than two.
- Demonstration that native defects play an important role in electron scattering in semiconductor structures. Calculations of the native defect scattering provide for the first unified explanation of an abrupt mobility reduction in heavily, uniformly doped GaAs and in two-dimensional inverted modulation doped GaAs/AlGaAs heterostructures.

BULK CRYSTAL GROWTH—the development of advanced techniques for the growth and characterization of gallium arsenide crystals. Studies rely on the close coupling of crystal growth and the characterization of those crystals in order to gain an understanding of the relationships between growth conditions and the structural and electronic properties of the crystals.

Results achieved during the past year include:

The vertical gradient freeze growth of GaAs crystals using total liquid encapsulation with B_2O_3. The process eliminated detrimental effects of PBN crucible wetting by liquid GaAs.



THIN FILMS AND INTERFACES—the study of dislocations, interfaces and point defect structures in thin films and solid state devices, their origin, processing dependence, and effect on properties. The approach emphasizes high resolution electron microscopy combined with microanalytical techniques. Recent results include:

- Significant reduction of defect densities in MBE-grown GaAs on Si by incorporation of Al; rapid thermal annealing; substrate patterning; use of strained layer superlattice buffers; periodically varying the Ga flux during growth.
- Determination of new phase formation and thermal stability for the Pt/InP metal contact for a range of temperatures.
- Development of a convenient technique for identification of inversion boundaries that arise from growth of a polar film on a nonpolar substrate and of techniques for elimination of such defects for GaAs on Si.

ELECTRICAL INTERCONNECTS/INTERFACES —the study of the microstructural, chemical and mechanical features of interfacial adhesion pertinent to the fabrication and reliability of microelectronic interconnects and packages. These efforts study fundamentals of interfacial decohesion and also seek microstructures that yield more durable interfacial bonds under both sustained and cyclic loading patterns. Related work with thin films addresses microstructures, stress states, degradation and electromigration. Notable results this year include:

- Identification of surprising nature of the plastic deformation field resulting from crack extension at a ceramic-metal interface as reflected by compressive stresses in the crack wake.
- Elucidation of complex delamination mechanism for vapor deposited tantalum thin films caused by tensile and compressive stress components induced by displacive transformation of initial bct phase to the bcc phase. Variants of a simpler mechanism are shown to describe splitting and delamination driven by tensile growth stresses for many other film/substrate combinations.
- New theoretical criteria for damage formation due to interfacial rupture induced by stresses generated while sintering multicomponent materials.

Above: View of GaAs crystal lattice in (110) direction. (CBB 791-812)

BASIC STUDIES OF DEFECTS AND IMPURITIES IN III-V SEMICONDUCTORS

CARRIER SCATTERING BY NATIVE DEFECTS IN UNIFORMLY AND MODULATION-DOPED SEMICONDUCTOR STRUCTURES

W. WALUKIEWICZ

Many device applications of semiconductors require preparation of very low resistivity, high mobility materials. Charge carrier mobilities in semiconductors are limited by intrinsic, or phonon scattering, and extrinsic scattering processes such as ionized impurity and native defect scattering. In most semiconductors the phonon and impurity scattering mechanisms are now well-understood and their contribution to the total scattering can be evaluated. The scattering by native defects, on the other hand, is difficult to calculate since in general, neither the microscopic nature of the defects nor their concentrations are known in semiconductors.

We have demonstrated that our previously proposed amphoteric native defect model provides the basis to identify the microscopic nature and calculate abundances of the defects incorporated in semiconductors. We have shown that the Fermi level induced enhancement of defect incorporation explains the mobility reduction in heavily, uniformly doped n-type GaAs, as well as in modulation doped GaAs/AlGaAs heterostructures.

Uniformly doped GaAs

According to the amphoteric defect model, the upward shift of the Fermi level in heavily doped GaAs n-type induces an increase in the formation of gallium vacancies. These acceptor-like native defects not only compensate intentionally introduced donors but also act as very efficient carrier scattering centers leading to a reduction of the electron mobility. We have used a variational procedure to calculate the electron mobility in n-type GaAs in the presence of ionized gallium vacancies. For electron concentrations exceeding ~ 5×10^{18} cm^{-3}, the electron mobility is abruptly reduced due to the scattering by native defects (Figure 1). The

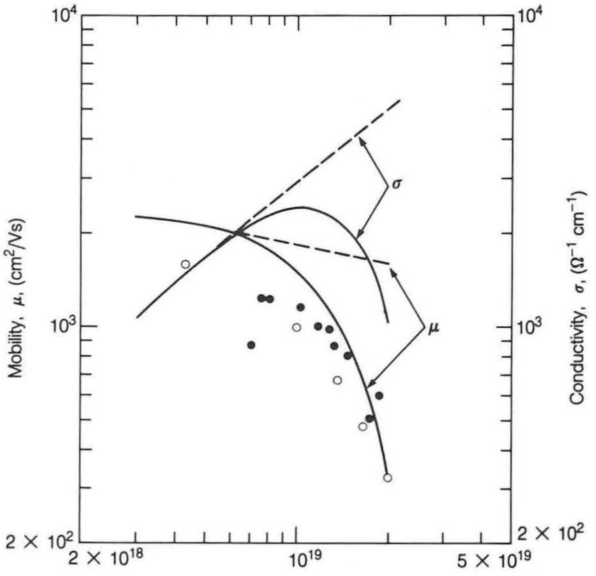


Figure 1
Electron mobility and conductivity in heavily doped n-GaAs. The solid lines represent the calculations in which effects of native defects were included. The broken curves correspond to the standard case in which the concentration of charged scattering centers is equal to the carrier concentration. The points represent typical experimental data. (XBL 885-1895)

reduction of the mobility results in a non-monotonic dependence of the conductivity on the electron concentration. The calculations show that a maximum conductivity of $\sigma \sim 2.5\mathrm{x}10^{-3}\ \Omega^{-1}\mathrm{cm}^{-1}$ is achieved for a carrier concentration of ~ 10^{19} cm^{-3}. This is an important finding since it points out that in order to increase conductivity of n-type GaAs one has to reduce the incorporation of native defects by invoking non-equilibrium incorporation of donor impurities or by inducing agglomeration of the impurities and native defects into neutral complexes which are inefficient as electron scattering centers.

Modulation Doped Heterostructures

In modulation doped heterostructures the donor impurities located in the barrier-forming layer are spatially separated from the 2-dimensional carrier gas in the quantum well. This configuration has been shown to reduce the impurity scattering and lead to ultra-high carrier mobilities. Thus, in n-GaAs/AlGaAs modulation doped heterostructures (MDH) mobilities in excess of 10^7 $\mathrm{cm}^{-2}/\mathrm{V{\cdot}s}$ were reported. This is orders of magnitude higher than the mobility observed for the equivalent carrier densities in uniformly doped GaAs. Such high mobilities could be obtained only in so-called normal modulation doped heterostructures (N-MDH), in which undoped quantum well forming GaAs is grown prior to the heavily doped AlGaAs barrier. In inverted-MDHs in which the growth sequence is reversed, i.e., the heavily doped AlGaAs barrier is grown first, followed by growth of the GaAs well, much lower mobilities are observed. Since I-MDHs are better suited for some device applications, a significant effort was directed towards understanding of the physical mechanism responsible for the mobility reduction in these structures. We have shown that the difference between N-MDH and I-MDH lies in much different conditions for native defect incorporation during preparation of these structures. In I-MDH the quantum well is grown in the presence of electrons transferred from the heavily doped AlGaAs. According to the amphoteric defect model such conditions enhance the formation of native defects in the quantum well. We have calculated the Fermi energy induced enhancement of the native defect formation in a typical I-MDH. It is found that although the concentration of the defects is very low, below 10^{15} cm^{-3}, the fact that the defects are located in the quantum well in the vicinity of 2-D electron gas leads to a substantial reduction of the electron mobility. Calculations of temperature dependent electron mobilities of 2-D electron gas in N- and I-MDH can be seen (Figure 2). In I-MDH low temperature mobility is about one order of

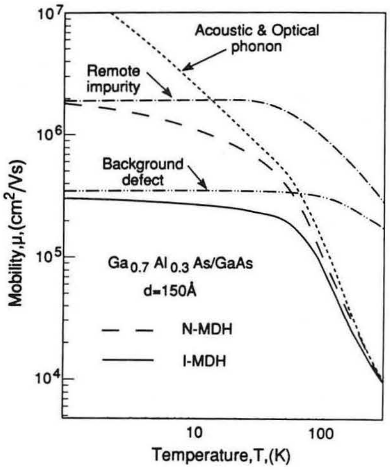


Figure 2

Temperature dependent 2-D electron gas mobilities in $Al_{0.3}Ga_{0.7}As/GaAs$ *MDHs with the spacer width* $d = 150\text{Å}$. *The broken and solid lines represent electron mobilities in normal- and inverted-MDHs, respectively. Contributions to the total mobilities resulting from different scattering mechanisms are also shown. (XBL 899-3381)*

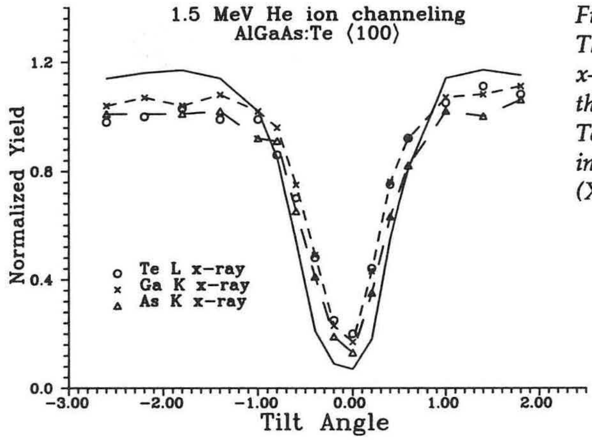


Figure 3
The angular scans of the TeL (o), GaK_{α} (x), and AsK_{β} (Δ) x–rays and the RBS signal (full line) excited by 1.5 MeV $^4He^+$ through a <100> axis for the AlGaAs:Te sample. Note that the Te scan follows the lattice Ga and As scans almost exactly, indicating good substitutionality of the Te atoms in the AlGaAs. (XBL 897-2727)

magnitude lower than the mobility in an equivalent N-MDH. On the basis of the present model of defect formation we have proposed a strategy to reduce the native defect concentration in I-MDH. This can be achieved by reducing the doping level in the AlGaAs barrier, and by controlling the 2–D electron gas density by the gate voltage applied to the structure.

The model presented is quite general and can be applied to any semiconductor system. We have shown that there is no enhancement of defect generation in p-type GaAs. Therefore, we predict the mobilities of 2–D hole gas in p-type I and N-MDHs.

LATTICE LOCATION OF DOPANT ATOMS IN III-V COMPOUND SEMICONDUCTORS

L.Y. Chan, E.E. Haller, J.M. Jaklevic, K. Khachaturyan, H.P. Lee, W. Walukiewicz, E.R. Weber, K.M. Yu

Unlike elemental semiconductors, compound semiconductors in general exhibit lower dopant activation efficiency. In the case of III-V semiconductors, e.g., GaAs and InP, there exist upper limits to the free electron or hole concentrations. Several theoretical models have been proposed to explain this free carrier saturation phenomenon in compound semiconductors. However, experiments directly addressing the local environments of the dopant atoms in highly doped III-V semiconductors are scarce. It is therefore of particular interest to investigate the substitutionality of dopant atoms in III-V semiconductors which are highly doped with dopant concentrations exceeding the free carrier saturation level. Our experiments were carried out on highly doped III-V compound semiconductors using ion channeling methods. N-type (Sn,Te), and p-type (Zn), as well as isoelectronic (In) dopants in GaAs, InP, and AlGaAs substrates were studied.

Highly doped GaAs:Zn and InP:Zn samples were obtained by closed ampoule diffusion with a Zn solid source. Combined Particle Induced X-ray Emission (PIXE) and ion channeling experiments on GaAs:Zn ($\sim 10^{21}cm^{-3}$) show a high level of substitutionality (≥90%) of the Zn atoms in the GaAs lattice. However, for InP:Zn ($\sim 10^{19}cm^{-3}$) only about 50% of the Zn atoms are found to be substitutional. From the channeling results, the nonsubstitutional Zn atoms are believed to form clusters or precipitates. Detailed electron microscopy studies on these Zn precipitates are planned.

The lattice location of Sn atoms in MBE grown GaAs and $Al_xGa_{1-x}As$

(x ≈ 41%) layer (≈ 3.5 µm thick) were also studied by ion channeling. The concentration of Sn in the layers was measured by PIXE to be ≈ $6x10^{18}$ atoms cm^{-3}. Results show that the Sn atoms are all substitutional in both the GaAs and AlGaAs layers with the displacement from the Ga or Al site smaller than 0.1Å. An accumulation of Sn atoms near the surface of the layers is detected. This surface Sn accumulation effect is consistent with previous reports on MBE grown GaAs:Sn layers. Te doped $Al_xGa_{1-x}As$ (x ≈ 42%) with N_{Te} ≈ $3x10^{18}cm^{-3}$ grown by metal organic vapor phase deposition technique was also studied. The Te atoms are found to be 95% substitutional in the layer with no detectable displacement from the As lattice site (Figure 3).

The results of the Te and Sn doped AlGaAs layers have important implications for theoretical models proposed for the formation of DX centers in AlGaAs. Our channeling results with the AlGaAs:Te system do not contradict the recent theoretical calculations on a group VI dopant, S in AlGaAs, which showed that one of the nearest neighbor Ga (or Al) atoms of the S dopant moves by 1.13 Å into the interstitial position. The S atoms remain substitutional in the As sites. The AlGaAs:Sn results, however, do not agree with any theoretical model that predicts a large lattice relaxation involving the movement of the dopant atoms into the interstitial positions.

BISTABLE DONORS ("DX-CENTERS") IN COMPOUND SEMICONDUCTORS

K. KHACHATURYAN, E.R. WEBER, D.O. AWSHALOM*, J.R. ROSEN*

Many donors in compound semiconductors show bistability, connected with a lattice relaxed, deep ground state. The so-called "DX-Centers" in AlGaAs are the most well-known examples for this class of defect. The bistability has detrimental effects on device performance, such as high noise figures and slow transients.

Recent pseudopotential calculations have suggested that the formation and metastable properties of the DX center can be explained by redistribution of electrons according to the reaction $2D^0 \Rightarrow D^+ + D^-$, where rather than all donors being neutral (D^0), half of the donors have two electrons and become negatively charged (D^-) in a lattice relaxed state, whereas the other half have none and are positively charged (D^+) (negative U model) (Figure 4). According to this model, the DX centers should be diamagnetic.

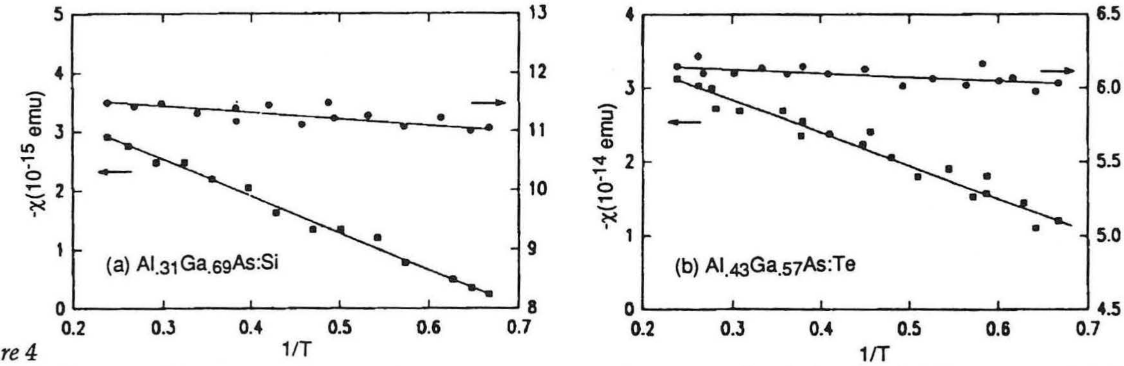


Figure 4

Diamagnetic susceptibilty of the epilayers vs inverse temperature before (squares) and after (circles) illumination in a field of 3.7 G. Illumination was made with 500 µW at E = 1.6 eV. The data offset is arbitrary but the same for the plots before and after illumination. (a) $Al_{0.31}Ga_{0.69-}$ As: ($3x10^{17}$Si). (b) $Al_{0.43}Ga_{0.57}$As:($3.6x10^{18}$Te). Before illumination, the paramagnetism of the bistable donors is visible; after illumination, the much weaker paramagnetism of free electrons producing persistent photoconductivity is measured. (XBL 901-121)

---

* IBM Research Center, Yorktown Heights.

This negative U model is in disagreement with magnetic susceptibility measurements on DX centers in AlGaAs and GaAsP. In these measurements, the concentration of paramagnetic defects was determined from the temperature dependent part of the magnetic susceptibility. Using a wide variety of samples with different doping and composition, the concentrations of paramagnetic impurities were found to be equal to the concentrations of DX centers obtained from electrical measurements. The DX center paramagnetism disappeared after 1.6 eV illumination. Even though DX centers are paramagnetic donors, no electron paramagnetic resonance signal can be detected from the ground state of DX centers in bulk GaAsP:S, grown by chloride vapor phase transport. However, a very large EPR signal from the light induced metastable X-like hydrogenic state of S in GaAsP can be seen. The mechanism of lattice relaxation was further investigated by PIXE-channeling measurements on Sn:AlGaAs. No relaxation of Sn atoms from the substitutional site could be detected. This observation is also in disagreement with the negative U model of the DX center.

ARSENIC ANTISITE DEFECTS IN GaAs

M. HOINKIS, E.R. WEBER

Arsenic antisite defects (As atoms on Ga sites) in GaAs produce the so-called EL2 midgap donor level, which dominates the electrical properties of semi-insulating GaAs. The EL2 defect shows a characteristic metastability: illumination at low temperatures can bring this defect into a metastable state, bleaching all optical absorption due to EL2 and removing the EL2 energy levels from the band gap. The origin of this metastability is not yet unambiguously established; a model developed independently by two groups of theoreticians suggests the atomic motion of the As atom from a Ga substitutional site into an interstitial position.

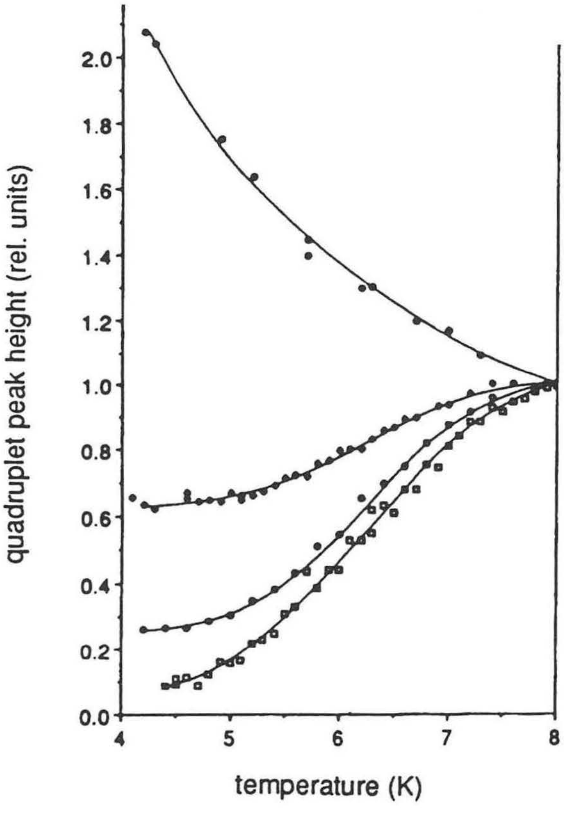


Figure 5
The quadruplet peak height as a function of temperature is shown for the neutron-irradiated sample (filled circle), the optically nonquenchable quadruplet in the plastically deformed sample (diamond), the optically quenchable quadruplet in the plastically deformed sample (open circle) and the quadruplet in the ITC + 800 sample (square). The quadruplet peak height at 8.0K in all four curves has been set equal to unity in order to display their qualitative features. (XBL 901-116)

Our previous work on the characteristic quadruplet Electron Paramagnetic Resonance (EPR) signals of positively charged antisite defects in as-grown GaAs crystals showed unambiguously that these signals arise from the positive charge state of EL2. EPR measurements from plastically deformed or neutron irradiated GaAs showed a strong enhancement of this quadruplet signal. However, the newly formed antisite defects did not show the metastability characteristics of EL2.

Measurements of the temperature dependence of the EPR signals in as-grown, plastically deformed and neutron irradiated GaAs allowed us for the first time to distinguish the EPR quadruplet spectra of arsenic antisite defects producing metastable EL2 levels from those which do not show metastability. Metastable antisite defects show saturation at low temperatures because of long spin-lattice relaxation times indicative for undisturbed defects, whereas antisite defects which are not metastable exhibit less saturation at low temperatures and thus shorter spin-lattice relaxation times (Figure 5). This result allows us to conclude that lattice distortions such as dislocation strain fields can suppress the metastability of antisite defects. Our findings are an important contribution towards the microscopic understanding of the EL2 defect in GaAs.

DONOR EXCITED-STATE SPECTROSCOPY OF ULTRA-PURE GaAs

J. Wolk, E.E. Haller, S.E. Bauser*

The electronic states of defects in semiconductors can conveniently be studied using far-infrared Fourier transform spectroscopy. One of the inherent difficulties in such studies is that there are several effects which broaden the spectral lines produced by transitions between the ground state and excited states. One important cause of broadening is impurity wave-function overlap. This is particularly important in GaAs, where the spatial extent of the donor ground state is $r_d \approx 100$ Å. In order to reduce overlap broadening, spectroscopy is often performed in a magnetic field. This squeezes the donor wave function and therefore reduces overlap, but the magnetic field represents a strong perturbation. If $nr_d^3 << 1$, where n is the concentration of impurities, then impurity wavefunction overlap is no longer important. There are two further types of line broadening, however, that play important roles even in pure samples. Both result from the electric fields due to ionized impurities. These electric fields limit the lifetime of a carrier in a bound excited state, which results in line broadening. The fields also shift the energies of the transitions (Stark shift) and this results in Stark broadening. The effect of Stark broadening is usually not observed in GaAs, because it is less important than lifetime broadening except in extremely pure samples. These last two effects can be diminished by shining "band edge light" on the sample. Light with photon energies just above the bandgap creates large numbers of electrons and holes which can neutralize ionized impurities. To study Stark broadening of shallow donor states we have used ultra-pure n-type GaAs epilayers with mobilities over 200,000 cm^2/Vs at 77 K and electron concentrations ranging from 2-4x10^{12} cm^{-3} grown by liquid phase epitaxy at the Max-Planck-Institute in Stuttgart. These samples are pure enough that no magnetic field is necessary to reduce wavefunction overlap. Stark broadening is expected to be the dominant type of line broadening. We have observed the excited state structure of the shallow donors at high resolution with photothermal ionization spectroscopy using a far-infrared Fourier transform spectrometer. Samples have been studied both with and without band

---

* Max-Planck-Institute for Solid State Research, Stuttgart, FRG.

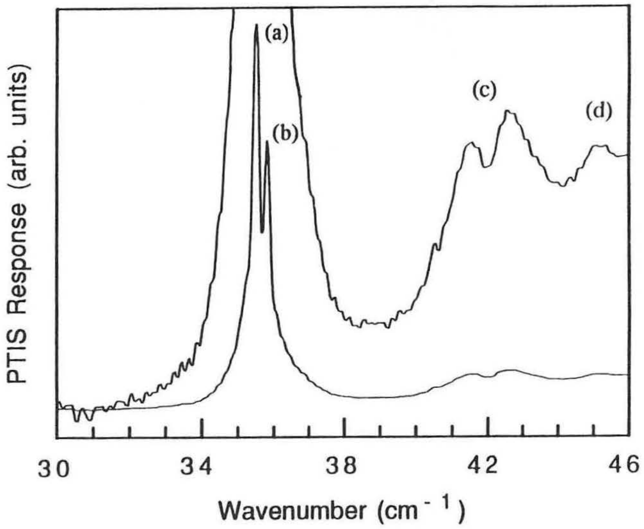


Figure 6
Two different magnifications of the PTIS response of an ultra-pure GaAs epilayer under illumination by band edge light. The features (a) and (b) are the 1s-2p peaks of silicon and sulfur donors, respectively. The double peak of feature (c) is the Stark split 1s-3p peak, and feature (d) is the 1s-4p peak. (XBL 901-122)

edge illumination (BEI). Under BEI, the 1s-2p transitions of S and Si are resolved and have a FWHM as low as 0.025 meV. The extreme narrowness of these lines has stimulated interest in using this material as photoconductors for astronomical observation. Both with and without BEI, the 1s-3p peaks of the two kinds of donors are too broad to be separated. However, the single 1s-3p peak is split (Figure 6). This splitting is in agreement with the theory which predicts that for n odd, the 1s-np transitions would be split by the Stark effect, and that this splitting should increase as $n^{2/3}$. Shining band edge light on the sample reduces the concentration of ionized impurities and therefore should also decrease the splitting. This effect is clearly observed in our study.

BULK CRYSTAL GROWTH RESEARCH

SEMI-INSULATING GaAs SINGLE CRYSTALS

E. Bourret, M. Galiano, R. Mih, J. Guitron

The vertical gradient freeze method for the growth of single crystals of GaAs offers great promise for crystals of improved electrical homogeneity and low dislocation density. Significant research is required before a reliable method can be developed by industry. Defects that still impair the success of this approach are most often generated by nucleation on the crucible wall and/or by very small inhomogeneities in the thermal field. Basic research for identification of the causes for non-reproducibility and means to prevent them has been the recent focus of our program. The electrical properties of the crystals have been further investigated to achieve a complete understanding of the compensation mechanism in these crystals. These studies were conducted for crystals 2" in diameter grown in Pyrolytic Boron Nitride (PBN) crucibles.

PBN crucibles are widely used for the growth of GaAs by the Czochralski technique because they are essentially non-reactive with the GaAs melt, and structurally stable up to high temperatures. In the vertical gradient freeze technique, the crystal grows in contact with the crucible wall. Therefore, in addition to being nonreactive, the crucible must not be wetted by the GaAs melt. Clean PBN is partially wetted by GaAs and reproducible growth cannot be achieved. Total liquid encapsulation with B_2O_3 has been found to be an efficient way to prevent random nucleation

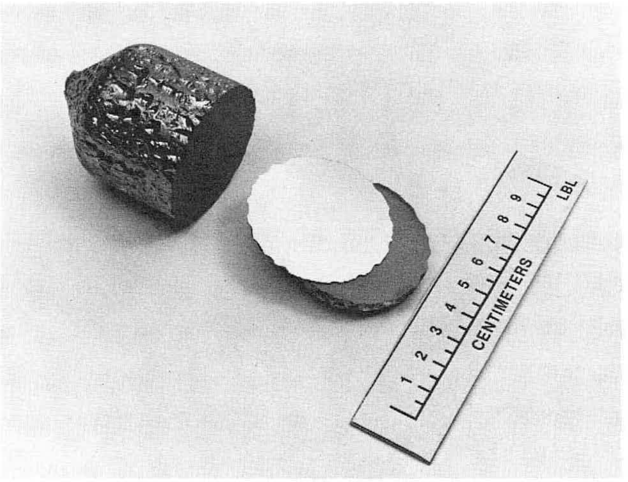


Figure 7
GaAs single crystal 2" in diameter, grown in a Pyrolytic Boron Nitride crucible fully encapsulated in wet B_2O_3 *(about 1200 ppm* H_2O*). Imprints of water vapor bubbles are seen on the surface of the crystal. (BBC 892-899)*

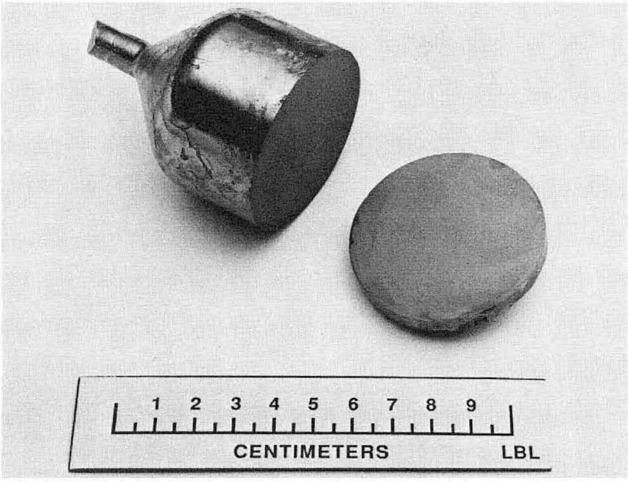


Figure 8
GaAs single crystal 2" in diameter, grown in a Pyrolytic Boron Nitride crucible fully encapsulated in dry B_2O_3 *(about 400 ppm* H_2O*). The surface of the crystal is smooth and shiny. (CBB 893-2639)*

on the PBN crucible wall. A thin layer of liquid B_2O_3 coats the crucible wall and separates the melt and growing crystal from it. Complete wettability between B_2O_3 and PBN is critical. Two processes have been successfully developed to uniformly coat the crucibles with B_2O_3. The residual water content of the B_2O_3 determines its wetting behavior and the surface morphology of the GaAs crystal. High water content increases wetting; however, at high temperatures, water vapors condense into bubbles which are trapped between the crucible and the GaAs melt. Traces of these bubbles appear on the surface of the crystals (Figure 7). They do not induce nucleation even though the resulting holes can be up to 3 mm deep. When dry B_2O_3 is used, the gas bubbles do not form (Figure 8). The smooth surface is advantageous for reducing grinding waste during further processing.

The effects of liquid encapsulation on the electrical properties of the crystals are being investigated. B_2O_3 can getter silicon, and carbon impurities present in the GaAs melt. The gettering ability also depends on the water content of the B_2O_3 encapsulant. Crystals are being grown using partial encapsulation (coated crucible wall only), total encapsulation (coated wall and B_2O_3 layer on top of the melt), and wet and dry encapsulant. Preliminary results indicate that carbon is efficiently gettered by wet B_2O_3. Due to a shift in the balance of donors and acceptors, undoped crystals with very low residual carbon concentration (less than $10^{14}cm^{-3}$) show a relatively low resistivity in the $5x10^5$ to $5x10^6$ Ω cm range. This point is being investigated further. Semi-insulating crystals of a resistivity up to $3x10^8$ Ω cm and a mobility of about 5500 $cm^2/V{\cdot}s$ have been obtained using dry B_2O_3 as the encapsulant.

n-TYPE Te-DOPED CRYSTALS

E. Bourret, R. Mih, J. Guitron, A.G. Elliot*

The vertical gradient freeze technique developed for undoped crystals has been adapted for growth of Te-doped GaAs single crystals. These crystals are used for optoelectronic devices such as high efficiency LED's.

---

* CAM Industrial Fellow, Hewlett-Packard Optoelectronics Division

Low dislocation density and uniformity of dopant concentration must be achieved to assume a high yield for device manufacturing. Two-inch-diameter single crystals have been obtained with dislocation densities about 10 times lower than those in crystals grown by the more traditional Czochralski technique. The crystals are doped at 10^{17} Te cm^{-3}. A new experimental setup is being implemented to grow three-inch-diameter crystals, which is the size needed for competitive manufacturing of the devices. Defect formation in three-inch-diameter crystals will be studied in relation to the new growth conditions.

THIN FILMS AND INTERFACES: METAL CONTACTS TO III-V SEMICONDUCTORS

PHASE FORMATION IN THE Pt/InP THIN FILM SYSTEM

D. A. OLSON, K. M. YU, J. WASHBURN, T. SANDS*

The stability and reproducibility of metal contacts to compound semiconductor devices are critical for proper device operation. These characteristics generally depend on the formation of interfacial phases and their morphology. Binary phase diagrams (e.g., PtIn and PtP) do not fully describe the nature of possible reaction products in these systems. Phase formation for thin Pt films on chemically cleaned InP substrates has been studied as a function of temperature. This information will be useful in predicting the suitability of this metal for use as a contact material.

InP substrates with 40nm metal films of Pt were encapsulated in SiO_2, and isochronally annealed up to 600°C in flowing forming gas. The composition and morphology of the phases that formed were studied using Rutherford backscattering, x-ray diffraction, transmission electron microscopy, and energy-dispersive spectroscopy.

Results show that the Pt/InP system begins interacting at 300°C. The Pt layer has been completely consumed by 400°C, with a uniform reacted layer indicated by RBS. At high temperatures (between 500°C and 600°C), the reaction products are $PtIn_2$ and PtP_2. The two phases are layered, with PtP_2 at the InP/reacted layer interface. The phosphide phase also shows a preferred orientation relationship with the substrate.

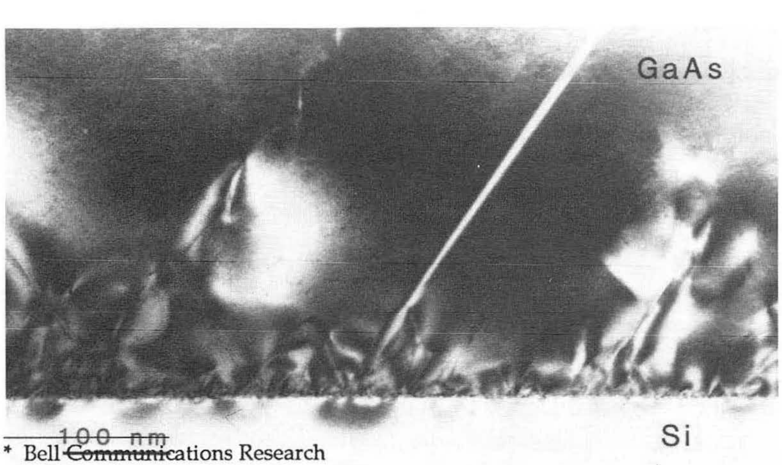


Figure 9
Cross-section TEM micrograph showing an inversion boundary. The boundary is faceted on {110} even though its average orientation is near that of the microtwin, {111}, to its right. (XBB 894-9410)

---

* Bell Communications Research

CHARACTERIZATION OF GaAs EPITAXIAL LAYERS

GaAs/Si Heterostructures

Z. LILIENTALWEBER, J. WASHBURN

Recent developments in the field of GaAs/Si heteroepitaxy have been spurred by the possibility of combining high-speed GaAs material with well-established Si technology, thus gaining better thermal conductivity, higher fracture toughness, smaller weight and larger diameter wafers offering the possibility for integration of optoelectronic and digital devices. Unfortunately, many problems are encountered in growth of GaAs on Si, such as growth of polar crystal on nonpolar substrate, lattice mismatch of 4.1%, and a considerable difference in thermal expansion coefficient between epilayer and substrate. As a consequence of these problems, the quality of GaAs epilayers on Si substrates is very poor. The dominant defects in the GaAs epilayer are misfit dislocations formed at the interface with Si, stacking faults, microtwins and threading dislocations which propagate through the epilayer, and inversion boundaries (IBs).

Inversion Boundaries

Z. LILIENTAL-WEBER, J. WASHBURN, H. KROEMER*

Presence of inversion boundaries was confirmed by transmission electron microscopy (TEM) using the convergent beam electron diffraction method (Figure 9). Electrical and optical properties of the boundaries were investigated using cathodoluminescence, electron beam induced current and scanning deep level transient spectroscopy (in cooperation with Hewlett-Packard). It was found that IBs reduce near-bandgap luminescence and minority carrier lifetime. In contrast to the recombination at threading dislocations in GaAs films, the nonradiative recombination process at IBs is not due to deep traps but rather to a continuum of bandgap states. Drastic changes in IB densities were observed upon changing the growth parameters. After postgrowth annealing IB-free layers even as nominal (100) substrates were found.

Reduction of Defect Density

Z. LILIENTAL-WEBER , J. WASHBURN, S. WANG*, H. KROEMER*, P. UMENO*, H. LEC*

Several methods have been found for reduction of overall defect density. The defect density was determined by TEM. It was found that the cleaning of the Si substrate before GaAs growth played a crucial role in the formation of new defects at the interface (Figure 10). The work showed that high

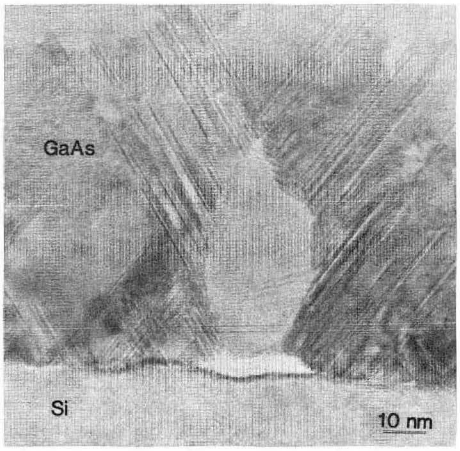


Figure 10
High-resolution image of the GaAs on Si interface taken in {110} projection. Note that interface contamination is the source of polycrystallinity and other defects. (XBB 870-3155)

---

* Department of Electrical and Computer Engineering, University of California, Santa Barbara

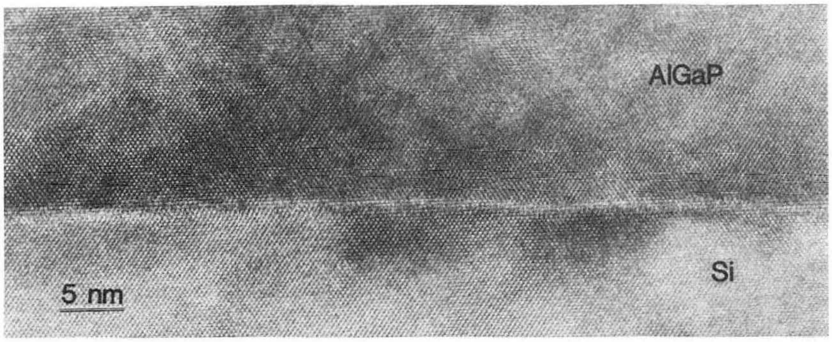


Figure 11
For growth of GaP on Si it has been shown that addition of small amounts of Al promotes perfect layer-by-layer growth resulting in very few defects compared to the more typical island growth mode. (XBB 894-3163)

temperature substrate annealing steps currently used should be avoided. Such high annealing temperatures result in roughening of the Si surface and are incompatible with patterned epitaxy. A promising approach is the use of Ga reduction (proposed by H. Kroemer) or growth of ternary Al-containing buffer layers (in cooperation with P. Umeno). It was shown that addition of small amounts of Al results in perfect two-dimensional growth (Figure 11). This may be due to the high affinity of Al for oxygen, allowing growth of Al-containing compounds on both clean and contaminated surface areas.

Another promising method is migration-enhanced epitaxy in which the Ga and As flux is alternated, or modulation-enhanced epitaxy with continuous As flux but intermittent Ga flux. It was demonstrated that this kind of growth enhances two-dimensional growth and results in very narrow PL lines (in cooperation with H. Lec from S. Wang's group). Post-annealing of GaAs on Si was also shown to improve the quality of the GaAs layer.

Noticeable improvements in the quality of GaAs/Si epilayers grown by MBE were observed after rapid thermal annealing (RTA) at 800°C for 10 seconds by the capless close proximity method in a commercial heat-pulse furnace. The density of stacking faults after this treatment was very low, possibly because of the rapid cooling rate compared to furnace annealing. RTA was found to be beneficial for the removal of stacking faults, but it inhibits stress relief; this was evidenced by cracking of GaAs epilayers. The heterointerface was also observed to be more undulated after RTA, compared to the as-deposited samples. Independent electrical measurements of devices after RTA showed noticeable improvement for forward and reverse bias characteristics. Leakage currents were reduced by more than two orders of magnitude after this treatment.

Patterned or island growth was also shown to be effective for reduction of defect densities. Growth of a mismatched heteroepilayer with a network of misfit dislocations confined to the interface and no threading dislocations in the epilayer requires glide of the threading "arms" of misfit dislocations across the whole wafer without being blocked by other threading dislocations. It is much easier to achieve this goal if the growth areas are confined to small parts of the substrate, e.g., by patterning lines or mesas on the substrate.

Growth of GaAs on Si through openings in an oxide or nitride mask was studied. Above the SiN mask the GaAs was polycrystalline, but in the open areas where the nitride was removed, monocrystalline GaAs was found with much lower dislocation density than in typical two-step growth. The stacking fault density was also much lower in the entire pattern, inceasing only at the border with the nitride. This decrease in defect density was probably connected with stress released at the periphery of patterns in the polycrystalline areas. Post-growth annealing at 850°C in arsenic overpressure resulted in significant grain growth in the polycrystalline GaAs overgrown on the amorphous oxide or nitride, and elimination of the defects at the transition region between polycrystalline and single crystal growth. An increase of Hall mobility of 30% was achieved in these annealed samples.

Another promising method for obtaining device-quality epitaxial GaAs which was investigated is the use of strained-layer superlattices (SLSLs), which increase dislocation annihilation by causing them to bend into the strained interface.This investigation found that by application of SLSLs of InGaAs/GaAs with 10nm-thick periods grown on Si(211), blocking of dislocation propagation occurred almost entirely at the uppermost interface between the strained layers and the final thick GaAs layer. It was concluded that reduction of dislocation density was only weakly dependent on the number of periods of the strained-layer superlattice. InGaAs/GaAs superlattices proved to be more efficient in dislocation bending than InGaAs/InGaP SLSLs. Because it was recognized that only the upper interface of the SLSL was efficient in dislocation bending, packages consisting of 5 periods of SLSL (InGaAs/GaAs) were tried. Indeed, each set of SLSLs was found to cause dislocation bending, but in some areas these dislocations were also formed at the lower interface between the buffer layer and the SLSL. On the average, the dislocation density in this sample was in the $\sim 2\times10^7/\mathrm{cm}^2$ range, which is very low taking into account that all misfit dislocations in the GaAs grown on Si(211) are 60° dislocations with Burgers vectors inclined to the interface.

Further defect reduction strategies, such as thermal cycling during growth, post-growth annealing, and the use of strained-layer superlattices, need to be optimized. Combined use of some of these methods together with the possibilities of pattern epitaxy appear to make high-quality growth of lattice mismatched heterostructures such as GaAs/Si achievable. Only such optimized low-defect material will allow practical use of the numerous devices possible with this technology, including minority carrier devices, the feasibility of which have already been demonstrated in GaAs/Si heteroepitaxy.

Ultra-High-Speed Metal-Semiconductor-Metal Photodetectors

Z. Liliental-Weber, J. Washburn, J. Mariella*

In some applications a high defect density can be an advantage. The possibility of using GaAs grown on Si to fabricate ultra-high-speed metal-semiconductor-metal (MSM) photodetectors was investigated. Optimum performance of such detectors requires a combination of high sensitivity with short minority carrier lifetime. In earlier work, neutron-damaged GaAs has been used in MSM devices but sensitivity was sacrificed for the increased speed. Our approach was to use molecular beam epitaxy (MBE) to grow GaAs on Si substrates. The planar thin film geometry allows good carrier mobility parallel to the GaAs/Si interface, while the expected high density of crystal defects at this interface could reduce the carrier lifetime. Two kinds of samples were compared: GaAs grown on a 15 Å Si epilayer grown on GaAs, and GaAs grown at low temperatures (300°C) on conventional Si substrates. It was shown that the GaAs epitaxial layer grown on a thin Si layer had reverse polarity to the substrate (antiphase relation), which is consistent with preferential bonding of As to Si. The density of

---

* Lawrence Livermore National Laboratory.

defects formed in the GaAs grown on a conventional (001) Si substrate was higher compared to the GaAs/Si/GaAs(001) structure and was found to correlate with increased device speed.

GaAs Grown on InP

Z. Liliental-Weber, J. Washburn

Characterization of 3 µm-thick GaAs films grown on (100) InP substrates by MBE employing different buffer layer structures during the initial deposition was performed. Three buffer layer structures were under study: 1) GaAs layer grown at low temperature; 2) GaAs layer grown at low temperature plus two sets of $In_{0.08}Ga_{0.92}As$/GaAs strained layer superlattices and 3) a transitional compositionally graded $In_xGa_{1-x}As$ layer between the InP substrate and the GaAs film. After the buffer layer deposition, the growth was continued by conventional MBE to a total thickness of 3 µm for all samples. From the 77K photoluminescence (PL) measurement, it was found that the sample with SLSL layers had the highest PL intensity and the narrowest PL line width. Cross-sectional TEM studies showed that the SLSL was effective in reducing the propagation of threading dislocations and explains the observed superior optical quality from the PL measurement. The effect of InGaAs/GaAs SLSL in bending threading dislocations was thus applicable to GaAs/InP heteroepitaxy as in the case of other heteroepitaxial systems such as GaAs/Si, although the average lattice constant of SLSL is not matched with either the films or the substrates.

MBE GaAs Grown at Low Temperatures on GaAs Substrate

Z. Liliental-Weber, E. R. Weber, J. Washburn

GaAs layers grown by MBE at very low substrate temperatures have gained considerable interest as buffer layers for GaAs metal-semiconductor field effect transistors (MESFETs) due to high resistivity and excellent device isolation. However, the structure and the electronic properties of such layers have not yet been investigated in detail. We have studied unannealed low temperature (LT) MBE layers grown at 200°C using TEM, analytical TEM, x-ray diffraction, the Hall effect, and electron paramagnetic resonance (EPR) techniques.

For TEM studies, cross-sectional samples in the (110) orientation were prepared from unannealed LT GaAs MBE layers grown on a Si LEC GaAs substrate at 200°C. Bright and dark field micrographs were taken in the two-beam condition for the (200) reflection, which is the most sensitive to changes in the structure factor. As reported previously, contrast is found at the interface between GaAs substrate and epilayer. This contrast suggests either different stoichiometry of the LT layer as compared with the substrate or stress built into the layer during the low-temperature growth. Analytical electron microscopy showed ~1% to 1.5% excess arsenic for unannealed LT GaAs MBE layers in comparison with the substrate. Moreover, analytical TEM studies revealed nonuniformity of the distribution of excess arsenic within the same layer, varying between 1% and 1.5%. This is a two order of magnitude higher deviation from stoichiometry towards arsenic-rich composition than ever observed for other GaAs crystals.

CHARACTERIZATION OF STRAINED InGaAs SINGLE QUANTUM-WELL STRUCTURES

K.-M. YU, K.T. CHAN*

Pseudomorphic strained single quantum well (SSQW) structures of $In_xGa_{1-x}As$ on both GaAs and InP substrates have demonstrated excellent performance in modulation-doped field effect transistors and optoelectronic devices. Since device characteristics are strongly affected by the SSQW properties, such as strain and well thickness, it is important to be able to measure those parameters in order to understand their correlation with device performance.

$In_xGa_{1-x}As$ SSQW structures on GaAs substrates were investigated using ion beam methods. The SSQWs were fabricated at the Microwave Technology Division of the Hewlett-Packard Corporation by molecular beam epitaxy. The composition and well size were measured with combined Rutherford backscattering spectrometry (RBS) and particle induced x-ray emission (PIXE). The crystalline quality of the SSQW was also investigated using ion channeling methods (Figure 12).

For an InGaAs layer below the critical thickness, the lattice constant perpendicular to the layer will be increased due to the Poisson effect. This distortion in the lattice parameter of the film can be detected when the substrate is aligned with the ion beam at a tilted axis. We have investigated this lattice strain in InGaAs SSQW structures by ion channeling combined with PIXE and RBS across the <112> axis. The In content in the SSQW's was also evaluated from the lattice strain measured according to Vegard's law. The In fractions measured this way agree very well with those obtained by RBS and PIXE.

The structural properties of the InGaAs SSQWs grown by MBE with various growth parameters were studied by the ion beam methods. Results indicate that there is little variation of In mole fraction and SSQW thickness by varying the substrate temperature T_s in the range of 375 to 510°C during film growth. Ion channeling also revealed that the crystal quality of the SSQW degrades as T_s increases. This degradation in crystal quality is accompanied by a decrease in electron mobility measured by Hall effect. The electrical and structural degradation of the SSQW due to high T_s (~510°C) can be prevented by increasing the As_4/Ga beam equivalent pressure ratio during MBE growth. More detailed studies on the relationship between MBE growth parameters and the electrical as well as structural properties of SSQW structures on GaAs are underway.

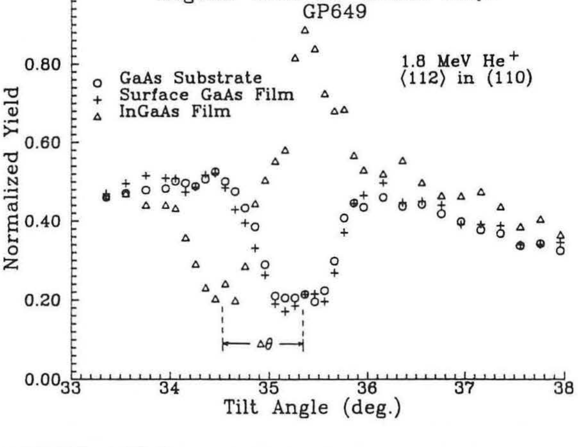


Figure 12
The angular scan profiles of the GaAs substrate, the GaAs capping layer, and the $In_xGa_{1-x}As$ layer obtained by a 1.8 MeV $^4He^+$ beam across the {112} axis along a (110) plane. Note that the profiles for the GaAs substrate and the capping layer follow exactly, indicating that the capping layer is grown without observable strain on the In_xGa1-x As layer. The dip in the $In_xGa_{1-x}As$ profile deviates from that in the substrate profile by Dq=0.84, which arises from the strain in the $In_xGa_{1-x}As$ layer. (XBL 896-2740)

---

* CAM Industrial Fellow, Hewlett-Packard Corporation, Microwave Technology Division.

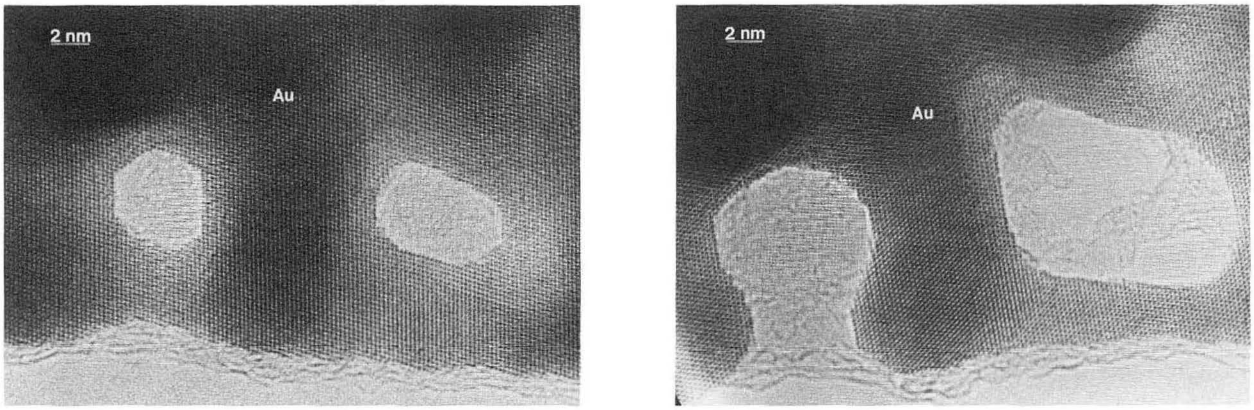


Figure 13
High voltage TEM observation can cause dramatic changes in an image during observation. Extreme care must be taken to be sure that high resolution details have not been altered either in the microscope or during thin foil preparation. This specimen is a gold foil showing successive pictures of the same area. (XBB 893-2487)

INTERCONNECTS

INTERFACIAL FRACTURE ENERGIES

R. Cannon, A. Fox

The events associated with fractures along interfaces between copper thin films and glass substrates were investigated by X-ray diffraction and transmission electron microscopy (TEM). In as-bonded films, the Bragg diffraction lines were shifted and broadened (relative to strain-free Cu) due to residual in-plane tensile strains arising from differences in thermal contraction after bonding; TEM studies showed that these stresses had been relieved somewhat by dislocation densities in the Cu as high as 10^{10}cm^{-2} for Cu/SiO$_2$. The passage of an interfacial crack led to a marked reduction in line shift and a slight reduction in the broadening. Thus, dislocations generated by the fracture "plasticially relaxed" the stresses in the as-bonded Cu by superposing a compressive component onto the pre-existing in-plane tensile strains. This dislocation generation was con-

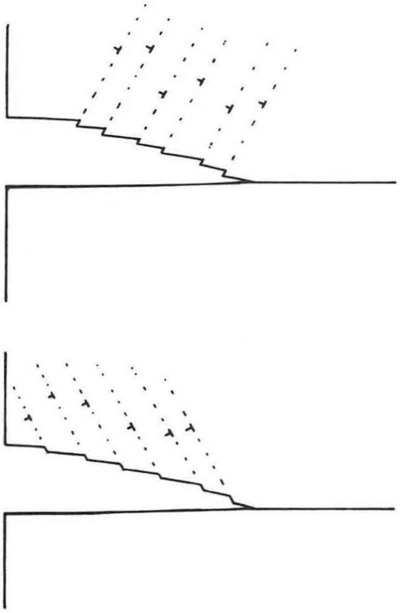
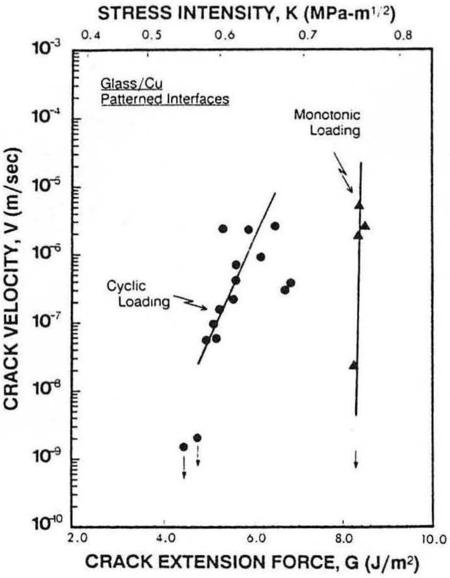


Figure 14
Diagrams showing effects of dislocations emitted from an interfacial crack tip concommitant with crack growth that would yield (a) tensile and (b) compressive in-plane stresses in the crack wake. X-ray diffraction studies of the Cu adjacent to a fractured Cu/glass interface favor a model like the latter. (XBL 902-452)

Figure 15

Subcritical crack growth rates as a function of crack extension force, G, for Cu/glass interfaces with patterned arrays of microcracks within the Cu that induce crack bridging. The growth rates are higher under cyclic loading than sustained loading, but are retarded in both cases relative to those for plain interfaces. (XBL 8910-3599)



firmed using TEM. The results indicated that greater numbers of dislocations were generated in the Cu by fracture along interfaces of higher toughness (i.e., bond strength). These stresses are opposite in sign to those expected from a ductile crack in a metal and provide a basis for developing models for the bond rupture and deformation near an advancing interfacial crack (Figure 14).

Fracture energies of such interfaces and others designed to have enhanced fracture energy by virtue of near-interfacial microstructures that induce crack-tip shielding are being studied in conjunction with R.O. Ritchie of the CAM Structural Materials Program. The fracture resistances, under tensile and mixed mode loading, and under static and cyclic loading, pertain to studies of thin film adherence and reveal methods to increase the integrity in such interface dependent applications (Figure 15).

FRACTURE AND DELAMINATION OF THIN FILMS

R.M. Fisher, J.-Z. Duan, A. Fox

Studies of vapor-deposited chromium films on glass, silicon or polymer substrates, with and without prior deposition of a thin copper layer, have been extended to tantalum. Differences in microstructures, stress states and the events leading to film cracking and spalling have emerged. A very fine dendritic structure forms during Ta deposition, rather than the aligned columnar structure of Cr films. This trend with homologous deposition temperature, which for Ta on a room temperature substrate is even lower than for Cr (0.084 vs 0.127), coincides with trends seen elsewhere and here for Cr films. In Cr, the columnar grains are finer, more branched and less textured crystallographically when deposited on Si than on glass, apparently owing to less film heating with the more conductive Si. More importantly, vapor-deposited Ta forms initially as a bct phase and then transforms to the denser bcc phase at a critical thickness of roughly 100 nm that depends somewhat upon substrate features.

Study of various film/substrate combinations has yielded a coherent understanding of splitting and delamination for films with internal tension and of the several crack morphology regimes, dictated by the relative interfacial, film and substrate fracture resistances that these exemplify. Extant fracture mechanics models plus film stresses and stress gradients deduced by x-ray diffraction are used to compute driving forces for the

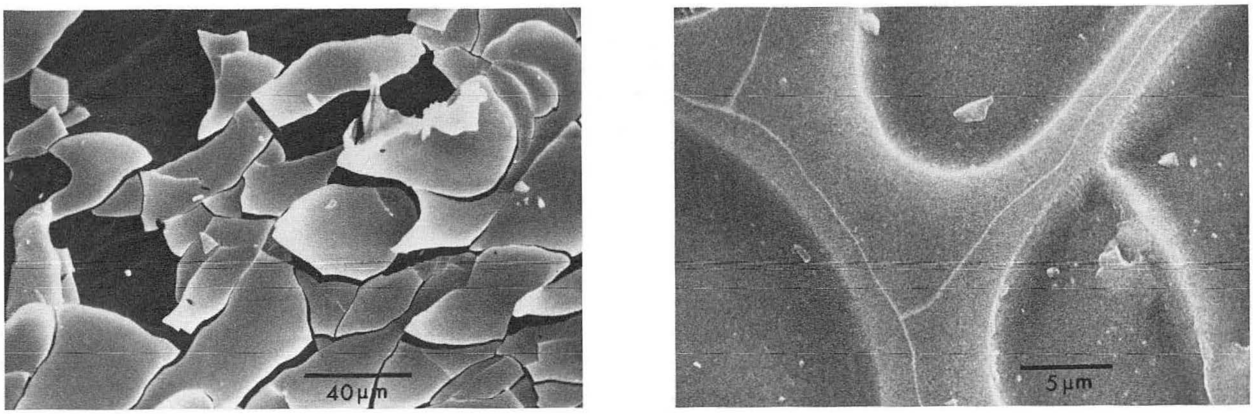


Figure 16
Scanning electron micrographs showing: a) splits and partial delamination for an 180 nm Ta film e-beam deposited onto glass and b) the glass which reveals the degree of substrate fracture. Chromium films delaminate from glass similarly. (XBB 902-1122, XBB 902-1120)

various cracks; these are compared with interfacial fracture energies from macroscopic tests for interfaces that fracture and with bulk fracture energies where appropriate. For Cr deposition, tensile "growth" stresses become high enough as the thickness increases to crack the film into small "islands." If the Cr exceeds a critical thickness, spontaneous delamination occurs as cracks spread from the splits. The delamination can be at an interface that is less tough than the substrate, e.g., Cr with a Cu prelayer on glass, or fully within the substrate several film thicknesses below the interface, as occurs for Cr/Si. A common, intermediate situation, e.g., Cr or Ta on glass, in which the delaminating crack first spreads along the interface and then penetrates into the substrate (Figure 16), results if the environmentally induced subcritical crack velocity curves for the interface and substrate cross, as found from macroscopic tests on Cu/glass interfaces of suitable purity. Several issues, such as the extent that splitting cracks penetrate into the substrate deeper than the delamination cracks, and the role of shear loading on interfacial fracture energies, are subjects of ongoing analysis.

More complex stresses occur in Ta films due to anisotropic strains associated with the martensitic transformation that can yield failure

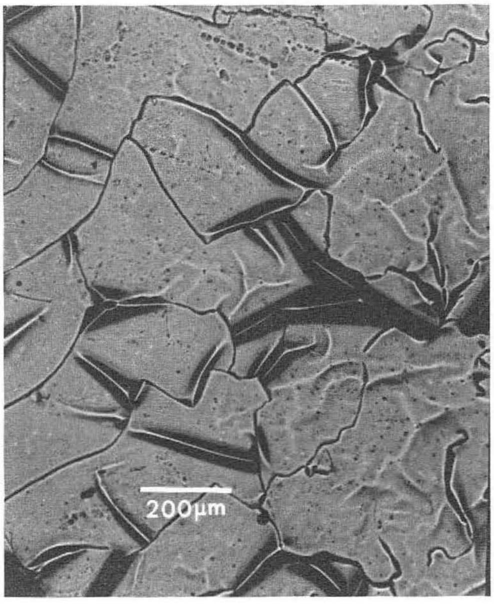


Figure 17
Optical micrograph showing fracture and delamination of a bilayer film of 106 nm Ta film deposited onto a 53 nm precoating of Cu on glass. The lower interfacial adhesion of Cu permits film decohesion at an earlier stage of Ta deposition. The mixture of tensile splits in the film and buckles indicating compression indicate large anisotropic transformation strains. (XBB 902-1121)

modes representative of both tensile and compressive stress components when a Cu sublayer is present and adhesion is reduced (Figure 17). For more adherent films, as on bare glass, the transformation is surpressed and significant cracking does not occur until the film is thicker and stresses are dominantly tensile, leading to failure modes described above.

INTERFACIAL WETTING AND RUPTURE DURING SINTERING

R. Cannon, C. Carter

Mechanisms causing damage, by interfacial rupture, during fabrication by sintering of heterogeneous materials, such as multicomponent electronic packages, are being analyzed theoretically. To establish concepts, a linear row of sintering particles has been used that permits highly precise treatments based on previously computed, equilibrium grain shapes. Under constraint, mechanical forces develop which can induce rupture by a process analogous to differential densification in a three dimensional compact (Figure 18a). The morphological stability analyses address both thermodynamics and kinetics and, thereby, apply to a wide range of constraining conditions. Results delineate loads under which the rod would either extend or shrink. The new feature is that regimes were identified wherein strain would tend to be homgeneous or susceptible to localization leading to grain boundary fracture (Figure 18b). Moreover, much greater loads can apparently be borne without damage, for certain small displacements, than are predicted from solely thermodynamic treatments.

Equilibrium shapes were also calculated for axisymmetric fluid bridges between two solids having arbitrary radii of curvature and contact angles. Results are being used to assess the stability of powder compacts containing liquids, as occur during liquid phase sintering and drying of powder compacts. They also pertain to tribology issues involving the interaction of a protrusion (even an STM tip) with a substrate in the presence of a lubricant or condensate fluid.

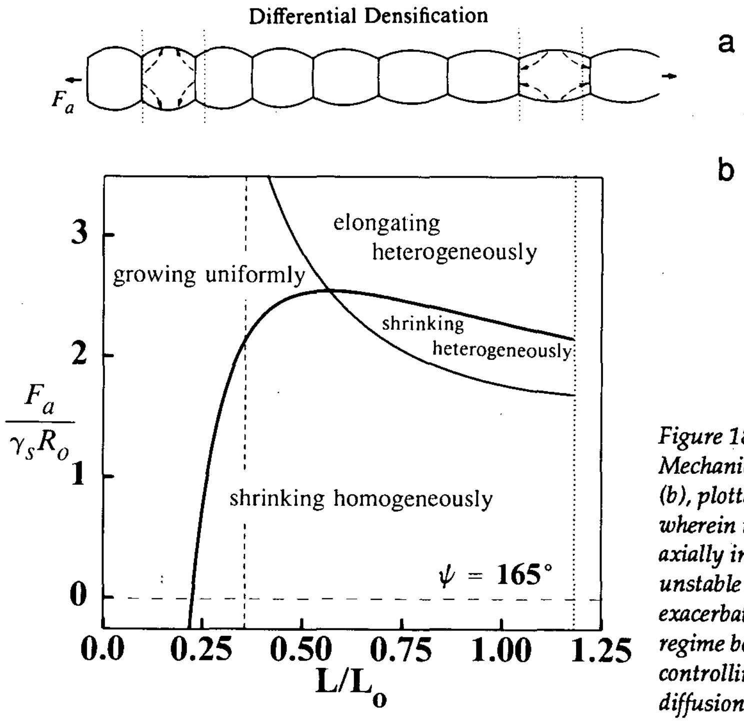


Figure 18

Mechanical stability diagram for a multigrain chain (a), also shown (b), plotted in terms of mechanical load and elongation. Regimes wherein the rod would elongate in response to the load or shrink axially in response to capillary forces are divided into stable and unstable subregimes. In the latter, any heterogeneities would be exacerbated inducing necking and grain boundary rupture. The regime boundaries depend strongly upon the dihedral angle and controlling diffusion mechanism; this diagram is for boundary diffusion control. (XBL 897-2849A, XBL 902-453)

MECHANICAL PROPERTIES OF CERAMIC/METAL INTERFACES

R.M. Cannon, R.H. Dauskardt*, R.O. Ritchie*

Fatigue-Crack Propagation along Ceramic/Metal Interfaces

Fatigue-crack propagation behavior was examined in both glass/copper and alumina/aluminum alloy interfaces with the objective of determining how cyclic loading degrades the toughness of the interface. Results for the glass/copper system where cracking proceeds directly along the interface, show cyclic crack-growth rates to be many orders of magnitude faster than those measured under monotonic loading (stress-corrosion cracking), with fatigue thresholds (below which crack growth is dormant) between 2 and 10 times lower than the interfacial fracture toughness. Similar results were obtained on interfaces containing patterns of microcrack-like voids. In contrast, cyclic crack growth for the Al_2O_3/Al-Mg system occurred in the metal layer close to the interface, although under monotonic loads the crack reverted to the ceramic material, again close to the interface. When compared with fatigue-crack growth results for either bulk aluminum alloys or alumina, interfacial crack-growth rates, characterized in terms of the range of strain-energy release (DG) computed using the appropriate interfacial crack-tip fields, were found to be significantly in excess of those of the bulk ceramic but comparable with behavior in the bulk metallic alloy (Figure 19). Current research is aimed at examining the mechanisms underlying such behavior, including the role of constraint in the metal and the micromechanics of interfacial crack advance under cyclic and monotonic loads.

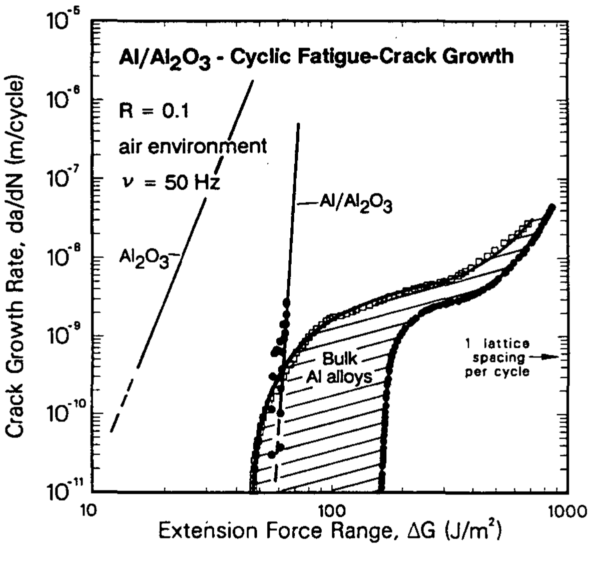


Figure 19

Comparison of cyclic fatigue-crack growth rates, da/dN, as a function of ΔG, for bulk alumina ceramic, bulk aluminum alloys, and alumina/aluminum-alloy interface. Interfacial crack growth tests were performed on compact tension samples in a room-air environment. (XBL 899-3147)

---

* CAM Structural Materials Program.

STAFF

Program Leader	*Deputy Program Leader*
Eugene E. Haller	Wladyslaw Walukiewicz

Project Leaders
Jack Washburn—Structure-Property Relationships
Rowland Cannon—Interconnects

Investigators and Scientific Staff	*Graduate Students*
Edith Bourret-Courchesne	David E. Bliss
Robert Fisher	W. Craig Carter
Alan Fox	Lydia Y. Chan
Joseph Guitron	Jian-Zhong Duan
William Hansen	Maria Galiano
Joseph Jaklevic	Mark D. Hoinkis
Zuzanna Liliental-Weber	Rebecca D. Mih
Marjorie Olmstead	Amy Moll
Eicke Weber	Dale A. Olson
Kin-Man Yu	Jeffrey A. Wolk

Student Assistant
Richard Hashimoto

Administrative Assistant
Margaret Ragsdale

AWARDS

- David Bliss received an IBM Fellowship.
- Amy Moll received a Fellowship from the Office of Naval Research.

INDUSTRY INTERACTIONS

Industrial Fellows

- Grant Elliot, Hewlett-Packard Optoelectronics Division, collaborated on a study of the growth of n^+ type GaAs single crystals in vertical gradient freeze furnaces. The focus is on low defect density crystals for optoelectronic applications. The furnaces in use were donated to CAM by Hewlett-Packard.
- Kam T. Chan, Hewlett-Packard Microwave Technology Division, is collaborating with the Semiconductor Processing and Characterization Project on studies of structural defects in epitaxially grown GaAs and GaInAs strained heterostructures and on investigations of defects in GaAs grown at low temperatures.
- Roy Crooks, Rockwell International Science Center, is working with the Interconnects Project on the adhesion of thermal barrier coatings for advanced aircraft. The focus of the work is on mechanisms to limit delamination and spalling during supersonic flight.

Advisory Board

Robert A. Burmeister, Chairman	Hewlett Packard Laboratories
Robert S. Bauer	Xerox Corporation PARC
Walter Brown	ATT Bell Laboratories
John Carruthers	Intel Corporation
Richard A. Reynolds	Department of Defense
R. Noel Thomas	Westinghouse R & D Center
August Witt	Massachusetts Institute of Technology

Contracts

- IBM provided support for the Interconnects project for research on ceramic-metal interfacial fracture resistance and thin film adhesion.

Gifts

- Gifts from Bertram Laboratories and AKZO Corporate Research America, Inc., to the Semiconductors Project were used to intensify research in the area of crystal growth by the vertical gradient freeze method.

Technology Transfer

- A patent application was filed for a process to prepare non-melting surface of pyrolytic boron nitride crucibles for vertical Bridgeman growth of GaAs.

BIBLIOGRAPHY

Semiconductor Processing and Characterization Project

Refereed Journal Articles

Chadi, D.J., D.J. Chang, and W. Walukiewicz, "Reply to: Evidence Against Negative Charge State Model for the DX Center in n-type GaAs," *Phys. Rev. Lett.*, vol. 62, p. 1923, 1989.

Hamera, M., W. Walukiewicz, D.D. Nolte, and E.E. Haller, "Dependence of Transition Metal Impurity Levels on Host Composition in III-V Semiconductors," *Phys. Rev. B*, vol. 39, p. 114, 1989.

Hoinkis, M. and E.R. Weber, "Differentiation of Electron Paramagnetic Resonance Signals of Arsenic Antisite Defects in GaAs," *Phys. Rev. B*, vol. 40, p. 3872, 1989.

Hoinkis, M., E.R. Weber, W. Walukiewicz, J. Lagowski, M. Matsui, H.C. Gatos, B.K. Meyer, and J.M. Spaeth, "Unification of the Properties of the EL2 Defect in GaAs," *Phys. Rev. B*, vol. 39, p. 5538, 1989.

Hurd, J.L., D.L. Perry, B.T. Lee, K.M. Yu, E.D. Bourret, and E.E. Haller, "Polycrystalline Hexagonal Boron Nitride Films on SiO_2 for III-V Semiconductor Applications," *J. Mater. Res.*, vol. 4, p. 350, 1989.

Khachaturyan, K.A., D.D. Awschalom, J.R. Rozen, and E.R. Weber, "Magnetic Studies of Persistent Photoconductivity in n-AlGaAs," *Phys. Rev. Lett.*, vol. 63, p. 1311, 1989.

Khachaturyan, K., M. Kaminska, E.R. Weber, P. Becla, and R.A. Street, "Lattice Relaxation and Negative U of DX-like Donors in ZnCdTe," *Phys. Rev. B*, vol. 40, p. 6304, 1989.

Lee, B.-T., E.D. Bourret, R. Gronsky, and I. Park, "Annealing of GaAs Single Crystal: Relationship between Electrical Properties and Structural Defects," *J. Appl. Phys.*, vol. 65, p. 1030, 1989.

Li, M.F., P.Y. Yu, W. Shan, W. Hansen, and E.R. Weber, "Effect of Boron on the Deep Donors (DX-Centers) in GaAs:Si," *Appl. Phys. Lett.*, vol. 54, p. 1344, 1989.

Nolte, D.D., "Band Offsets for Pseudomorphic InP/GaAs," *Appl. Phys. Lett.*, vol. 54, p. 259, 1989.

Nolte, D.D., "Band Offsets for Pseudomorphic InP/GaAs: Addendum," *Appl. Phys. Lett.*, vol. 54, p. 2277, 1989.

Walukiewicz, W., "Amphoteric Native Defects in Semiconductors," *Appl. Phys. Lett.*, vol. 54, p. 2094, 1989.

Walukiewicz, W., "Dislocation Density Reduction by Isoelectronic Impurities in Semiconductors," *Appl. Phys. Lett.*, vol. 54, p. 2009, 1989.

Walukiewicz, W., "Doping-Induced Suppression of Dislocation Formation in Semiconductors," *Phys. Rev. B*, vol. 39, p. 8776, 1989.

Refereed Conference Proceedings

Brown, I.G., M.D. Rubin, K.M. Yu, R. Mutikaimen, and N.W. Cheung, "Ion Beam Modification of the Y-Ba-Cu-O System with the MEVVA High Current Metal Ion Source," *Mater. Res. Soc. Symp. Proc.*, vol. 147, p. 391, 1989.

Walukiewicz, W., "Defect Reactions at Metal-Semiconductor and Semiconductor-Semiconductor Interfaces," *Mat. Res. Soc. Symp. Proc.*, vol. 148, p. 137, 1989.

Yu, K.M., B. Katz, I.C. Wu, and I.G. Brown, "Formation of Buried Iridium Silicide Layer in Silicon by High Dose Iridium Ion Implantation," *Mat. Res. Soc. Symp. Proc.*, vol. 147, p. 229, 1989.

Theses

Galiano, M.L., *Vertical Gradient Freeze GaAs: Growth and Electrical Properties*, May 1989. (M.S. Thesis, Department of Materials Science and Mineral Engineering, U.C. Berkeley. Advisor: E.E. Haller.)

LBL Reports (including journal articles submitted or in press)

Bliss, D.E., D. Nolte, W. Walukiewicz, E.E. Haller, and J. Lagowski, LBL 27780, "Absolute Pressure Dependence of the Second Ionization Level of EL2 in GaAs," *Appl. Phys. Lett.* (Submitted.)

Bourret, E.D., J.B. Guitron, M.L. Galiano, and E.E. Haller, LBL 26949, "Vertical Seeded Melt-Growth of GaAs," *J. Cryst. Growth.* (Submitted.)

Chan, K.T., M.J. Lightner, G.A. Patterson, and K.M. Yu, "Some Growth Studies of Pseudomorphic GaAs/InGaAs/AlGaAs Modulation-Doped Field Effect Transistor Structures," *Appl. Phys. Lett.* (Submitted.)

Walukiewicz, W., LBL 27828, "Carrier Scattering by Native Defects in Heavily Doped Semiconductors," *Phys. Rev. B.* (Submitted.)

Walukiewicz, W., LBL 28105, "Electron Scattering by Native Defects in Uniformly and Modulation Doped Semiconductor Structures," *Proc. MRS Fall Meeting, 1989.* (In press.)

Yu, K.M. and K.T. Chan, "Characterization of Strained InGaAs Single Quantum Well Structures by Ion Beam Methods," *Appl. Phys. Lett.* (In press.)

Yu, K.M., K. Khachaturyan, E.R. Weber, H.P. Lee, and E.G. Colas, LBL 27952, "Substitutionality of Te and Sn Related Dx Centers in $Al_xGa_{1-x}As$," *Phys. Rev. Lett.* (Submitted.)

Yu, K.M., H.P. Lee, and S. Wang, "Lattice Location of Sn Atoms in MBE GaAs by Ion Channeling Methods," *Appl. Phys. Lett.* (Submitted.)

Invited Talks

Chan, K.T. and K.M Yu, *Ion Beam Studies of Strained InGaAs Single Quantum Well Grown by Molecular Beam Epitaxy*, Electrical Engineering Colloquium, Department of Electrical Engineering, University of California, Irvine, CA, April 1989.

Khachaturyan, K., *DX-Like Negative-U Behavior in Semiconductors*, Gordon Research Conference on Point Defects, Line Defects and Interfaces, Plymouth, NH, July 1989.

Walukiewicz, W., *Amphoteric Native Defects in Semiconductors*, Presented at the Gordon Research Conference on Point and Line Defects on Interfaces, Plymouth, NH, July 1989; and Xerox, PARC, Palo Alto, September 1989.

Walukiewicz, W., *Defect Reactions at Metal-Semiconductor and Semiconductor-Semiconductor Interfaces*, Presented at the MRS Spring Meeting, San Diego, CA, April 1989; and the Gordon Conference on Inorganic Thin Films and Interfaces, Plymouth, NH, July 1989. (Published in the Proceedings of the MRS Spring Meeting, v. 148, p. 137, 1989)

Weber, E.R., *The Mechanism of Transition Metal Gettering in Silicon*, Seminar, San Francisco Section of the Electrochemical Society, San Francisco, CA, April 1989.

Weber, E.R., *Metastable Defects in Semiconductors*, Solid State Seminar, Department of Materials Science, UC Santa Barbara, February 1989.

Weber, E.R., *Metastable Point Defects in Semiconductors*, 4th International Conference on Semiconductor Physics, Belo Horizonte, Brasil, February 1989.

Weber, E.R., *Metastable Deep/Shallow Donors in Compound Semiconductors*, Seminar, Naval Research Laboratory, Washington, DC, January 1989.

Weber, E.R., *The Identification of Defects in Semiconductors*, American Physical Society March Meeting, St. Louis, MO, March 1989. (Bull. Am. Phys. Soc., vol. 34, pg. 1527, 1989.)

Weber, E.R., *Gettering Mechanism of Transition Metals in Silicon*, 3rd International Autumn Meeting, Gettering and Defect Engineering in Semiconductor Technology - GADEST '89, Castle Garzau, East Germany, October 1989.

Weber, E.R., *Gettering of Transition Metals in Semiconductors*, International Conference on the Science and Technology of Defect Control in Semiconductors, Yokohama, Japan, September 1989.

Yu, K.M., *Near Surface Profiling Using MeV Ion Beam Techniques*, Greater Silicon Valley Implanter User Group Meeting, Palo Alto, CA, February 1989.

Contributed Talks

Bliss, D.E., W. Walukiewicz, D.D. Nolte, and E.E. Haller, *Absolute Pressure Dependence of the Second Ionization Level of EL2 in GaAs*, Presented at the March 1989 Meeting of the American Physical Society, St. Louis, MO; and the Fall Meeting of the Materials Research Society, November1989, Boston, MA.

Bourret, E.D., M.L. Galiano, R.D. Mih, J.B. Guitron, and E.E. Haller, *Vertical Seeded Melt-Growth of GaAs*, Ninth International Conference on Crystal Growth, Sendai, Japan, August 1989.

Merk, E., J. Heyman, and E.E. Haller, *Infrared Absorption Study of Zinc-Doped Silicon*, MRS Meeting, Boston, MA, November 1989.

Walukiewicz, W., *Mechanism of Doping Induced Dislocation Suppression in Semiconductors*, March 1989 Meeting of the American Physical Society, St. Louis, Missouri, March 1989.

Structure - Property Relationships Project

Refereed Journal Articles

Kaminska, K., Z. Liliental-Weber, E.R. Weber, T. George, J.B. Kortright, and A.R. Calawa, "Structural Properties of As-Rich GaAs Grown by Molecular Beam Epitaxy at Low Temperatures," *Appl. Phys. Lett.*, vol. 54, p. 1881, 1989.

Kaminska, K., E.R. Weber, Z. Liliental-Weber, and R. Leon, "Stoichiometry-Related Defects in GaAs Grown by Molecular Beam Epitaxy at Low Temperatures," *J. Vac. Sci. Tech.*, vol. B7, p. 710, 1989.

Kvam, E.P., "A Model for Low Temperature Dynamic Recrystalization in Highly Strained Pore Cu and Cu *in situ* Composites," *Scripta Met.*, vol. 23, p. 1341, 1989.

Leon, R.P., N. Newman, Z. Liliental-Weber, E.R. Weber, J. Washburn, and W.E. Spicer, "Mechanisms for Nearly-Ohmic Behavior in Annealed Au/n-GaAs Schottky Diodes," *J. Appl. Phys.*, vol. 66, p. 711, 1989.

Liliental-Weber, Z., N. Newman, J. Washburn, E.R. Weber, and W.E. Spicer, "Influence of Interfacial Contamination on the Structure and Barrier Height of Cr/GaAs Schottky Contacts," *Appl. Phys. Lett.*, vol. 54, p. 356, 1989.

Liliental-Weber, Z. and M. O'Keefe, "Atomic Arrangement at the Cr/GaAs Interface," *J. Vac. Sci. Technol.*, vol. 7, p. 1022, 1989.

Liliental-Weber, Z. and M.A. O'Keefe, "Inversion Boundaries in GaAs Grown on Si," *Ultramicroscopy*, vol. 30, p. 20, 1989.

Refereed Conference Proceedings

Caron-Popowich, R., J. Washburn, and T. Sands, "Phase Formation in the Pol/InP Systems," *Mat. Res. Soc. Symp. Proc*, vol. 148, 1989.

Ding, J., B. Lee, K.M. Yu, R. Gronsky, and J. Washburn, "Investigation of the Interface Integrity of the Thermally Stable WN/GaAs Schottky Contacts," *Mat. Res. Soc. Symp. Proc.*, vol. 148, p. 41, 1989.

Liliental-Weber, Z., "Methods to Decrease Defect Density in GaAs/Si Heteroepitaxy," *Mat. Res. Soc. Symp. Proc.*, vol. 148, p. 205, 1989.

Liliental-Weber, Z. and R.P. Mariella, Jr. , "Growth and Characterization of GaAs/Si/GaAs Heterointerfaces," *Mat. Res. Soc. Symp. Proc.*, vol. 148, p. 241, 1989.

Liliental-Weber, Z. and R. Marielle, Jr., "Characterization of the GaAs/Si/GaAs Heterointerfaces," *Mat. Res. Soc. Symp. Proc.*, vol. 148, p. 205, 1989.

Liu, X., H.P. Lee, S. Wang, T. George, E.R. Weber, and Z. Liliental-Weber, "Growth and Characterization of GaAs on InP with different Buffer Structures by Molecular Beam Epitaxy," *Mat. Res. Soc. Symp. Proc.*, vol. 148, p. 297, 1989.

Newman, N., W.E. Spicer, E.R. Weber, and Z. Liliental-Weber, "Electrical Study of Metal/GaAs Interfaces," *Mat. Res. Soc. Symp. Proc.*, vol. 148, p. 117, 1989.

Olson, D., K.M. Yu, J. Washburn, and T. Sands, "Phase Formation in the Pt/InP Thin Film System," *Mat. Res. Soc. Symp. Proc.*, vol. 148, p. 47, 1989.

Spicer, W.E., R. Cao, K. Miyano, C. McCants, T.T. Chiang, N. Newman, T. Kenelewicz, I. Lindau, E. Weber, and Z. Liliental-Weber, "Disruption, Metalization, and Electrical Properties of Metal GaAs and InP Semiconductor Interfaces," *Proc. of the NATO Advanced Research Workshop on Metalization and Metal/Semiconductor Interfaces*, p. 139, Plenum Publishing, 1989.

Other Publications

Liliental-Weber, Z., "Point and Extended Defects in Semiconductors," in *Influence of Residual Contamination on the Structure and Properties of Metal/GaAs Interfaces*, ed. G. Benedek, A. Cavallini and W. Schroter, p. 165, Plenum Publishing, 1989.

Liliental-Weber, Z., E.R. Weber, J. Washburn, T.Y. Liu, and H. Kroemer, "Supression of Defect Propagation in Heteroepitaxial Structures by Strained Layer Superlattices," in *Heterostructures on Si: One Step Further with Silicon*, ed. Y.I. Nissim, E. Rosencher, vol. 160, p. 19, Kluwer Academic Publishers, NATO ASI Series, 1989.

Theses

Caron, R.P., *Pd and Ni Thin-Film Reactions with InP: Possibilities for Metal Contacts*, April 1989. (Ph.D. Thesis, Department of Materials Science and Mineral Engineering, U.C. Berkeley. Advisor: J. Washburn.)

Ding, J., *Thermally Stable Metal/GaAs Contacts*, June 1989. (Ph.D. Thesis, Department of Materials Science and Mineral Engineering, U.C. Berkeley. Advisor: J. Washburn.)

LBL Reports (including journal articles submitted or in press)

George, T., Z. Liliental-Weber, E.R. Weber, and F.H. Pollack, "Characterization of Polish-Induced Damage in (100) GaAs; A Comparison of Transmission Electron Microscopy and Raman Spectroscopy," *J. Appl. Phys.* (Submitted.)

Liliental-Weber, Z., "The Influence of Residual Contamination on the Structure and Properties of Metal/GaAs Interfaces," *Proc. International School of Materials Science and Technology.* (In press.)

Liliental-Weber, Z., W.R. Weber, and J. Washburn, "Heteroepitaxy of GaAs on Si: Methods to Decrease Defect Density in the Epilayer," *Proc. Int. Conf. on the Science and Tech. of Defect Control in Semiconductors.* (In press.)

Liliental-Weber, Z., C.W. Wilmsen, K.M. Geib, P.D. Kirchner, J.M. Balico, and J.M. Woodal, "Structure and Chemical Composition of Water-Grown Oxides of GaAs," *J. Appl. Phys.* (Submitted.)

Nauka, K., G.A. Reid, and Z. Liliental-Weber, "EBIC and CL Imaging of the Antiphase Domain Boundaries in GaAs Grown on Si," *Appl. Phys. Let.* (In press.)

Shin, J., K.M. Geib, C.W. Wilmsen, and Z. Liliental-Weber, "The Chemistry of Sulfur Passivation of GaAs Surfaces," *J. Vac. Sci. Technol.* (In press.)

Spicer, W.E., N. Newman, C.J. Spindt, Z. Liliental-Weber, and E.R. Weber, *Pinning and Fermi Level Movement at GaAs Surfaces and Interfaces.*

Waddill, G.D., I.M. Vitomirov, C.M. Aldov, S.G. Anderson, C. Capasso, J.H. Weaver, and Z. Liliental-Weber, "Abrupt Interfaces with Novel Structural and Electronic Properties: Metal Cluster Deposition and Metal Semiconductor Functions," *Phys. Rev. B.* (In press.)

Washburn, J. and Z. Liliental-Weber, LBL 27500, "On the Dynamic Nature of Microscopy Specimens at Lattice Resolution," *J. de Physique.* (In Press.)

Invited Talks

Liliental-Weber, Z., *Methods to Decrease Defect Density in GaAs/Si Heteroepitaxy,* Materials Research Society Meeting, San Diego, California, April 1989.

Liliental-Weber, Z., *The Influence of Residual Contamination on the Structure and Properties of Metal/GaAs Interfaces,* International School of Materials Science and Technology, Erice, Italy, November 1989.

Liliental-Weber, Z., E.R. Weber, and J. Washburn, *Heteroepitaxy of GaAs on Si: Methods to Decrease Defect Density in the Epilayer,* Int. Conf. on the Science and Tech. of Defect Control in Semiconductors, Yokohama, Japan, September 1989. (To be published in the Proceedings.)

Newman, N., W.E. Spicer, E.R. Weber, and Z. Liliental-Weber, *Electrical Study of Metal/GaAs Interfaces,* Mat. Res. Soc. Symp., San Diego, CA, April 1989.

Contributed Talks

Caron-Popowich, R., J. Washburn, and T. Sands, *Phase Formation in the Pol/InP Systems,* Mat. Res. Soc. Symp., San Diego, CA, April 1989.

Ding, J., B. Lee, K.M. Yu, R. Gronsky, and J. Washburn, *Investigation of the Interface Integrity of the Thermally Stable WN/GaAs Schottky Contacts,* Mat. Res. Soc. Symp., San Diego, CA, April 1989.

Lee, H.P., X. Liu, S. Wang, G. George, E.R. Weber, and Z. Liliental-Weber, *Improvement in Crystalline Quality of Heteroepitaxial GaAs on Sil Films Grown by Modulated Molecular Beam Epitaxy,* Electronic Materials Conference, Boston, MA, June 1989.

Liliental-Weber, Z. and R. Marielle, Jr., *Characterization of the GaAs/Si/GaAs Heterointerfaces,* Mat. Res. Soc. Symp., San Diego, CA, April 1989.

Liliental-Weber, Z., N. Newman, E.R. Weber, and J. Washburn, *Structural Analysis of Metal Schottky contacts on GaAs,* Electronic Materials Conference, Boston, MA, June 1989.

Liu, X., H.P. Lee, S. Wang, T. George, E.R. Weber, and Z. Liliental-Weber, *Growth and Characterization of GaAs on the InP with different Buffer Structures by Molecular Beam Epitaxy,* Mat. Res. Soc. Symp., San Diego, CA, April 1989.

Olson, D., K.M. Yu, J. Washburn, and T. Sands, *Phase Formation in the Pt/InP Thin Film System,* Mat. Res. Soc. Symp., San Diego, CA, April 1989.

Interconnects Project

Refereed Journal Articles

Cannon, R.M. and W.C. Carter, "On the Interplay of Sintering Microstructures, Driving Forces, and Mass Transport Mechanisms," *J. Am. Ceram. Soc.*, vol. 72, p. 8, 1989.

Fisher, R.M., J.Z. Duan, and A.G. Fox, "Structures and Stresses in Nanograin Thin Metal Films," *Mat. Sci. and Eng.*, vol. A117, p. 3, 1989.

Fox, A.G., M.A. O'Keefe, and M.A. Tabbernor, "A Set of High-Angle Relativistic Hartree-Fock X-ray and Electoron Atomic Scattering Factors," *Acta Cryst.*, vol. A45, p. 786, 1989. (M.A. Tabbernor, The Polytechnic, Wolverhampton, UK.)

Refereed Conference Proceedings

Fisher, R.M., J.-Z. Duan, and A.G. Fox, "Stress Gradients and Anisotropy in Thin Films," *Mat. Res. Symp. Soc. Proc.*, vol. 130, p. 249, 1989.

Fisher, R.M. and J.Z. Duan, "Chemical and Structural Characterization of Cr Films by Advanced Analytical and E M Instrumentation," *Proc. 3rd Beijing Conf. and Exhib. on Instrum. Analysis*, p. 13, 1989.

Fisher, R.M. and J.Z. Duan, "Influence of Substrate on Cracking of Vapour-Deposited Thin Films Due to Residual Stresses," *Proc. Mat. Res. Soc. Symp.*, vol. 153, 1989§.

Fisher, R.M., J.Z. Duan, C.J. Hetherington, and N. Fowler, "Image Processing to Delineate Defect Structures in HREM Images of Vapor-Deposited Thin Films," *Proceedings of the 47th Annual Meeting of the Electron Microscopy Society of America*, p. 128, 1989§. (N. Fowler, Tracor Northern/ R.J. Lee Group Inc., Berkeley, CA.)

Fox, A.G., M.A. Tabbernor, and R.M. Fisher, "Bonding Charge Densities of Al and Cu Determined by Electron Diffraction," *Proc. 47th Annual Meeting of the Electron Microscopy Society of America*, p. 492, 1989. (M.A. Tabbernor, The Polytechnic, Wolverhampton, UK.)

Oh, T.S., R.M. Cannon, and R.O. Ritchie, "On Optimizing the Toughening of Ceramic/Metal Interfaces using Implanted Microcracks," *Joints of Metals and Ceramics, Mat. Res. Soc. Intl. Symp. Proc.*, vol. 8, 1989*.

Oh, T.S., R.M. Cannon, and R.O. Ritchie, "Tailored Microstructures to Control Interfacial Toughness," *Thin Films: Stress and Mechanical Properties, Mat. Res. Soc. Symp. Proc.*, vol. 130, p. 219, 1989*.

Tribula, D., D. Grivas, D.R. Frear, and J.W. Morris, Jr., "Observations on the Mechanisms of Fatigue in Eutectic Pb-Sn Solder Joints," *J. Electronic Packaging; Proceedings of the ASME Winter Conference*, vol. 3 , p. 83, 1989.

Theses

Carter, W.C., *Capillary-Induced Microstructural Development in Porous Materials.* (Ph.D. Thesis, Department of Materials Science and Mineral Engineering, U.C. Berkeley. Advisor: R.O. Ritchie.)

LBL Reports (including journal articles submitted or in press)

Fisher, R.M. and J.Z. Duan, LBL 28383, "Cracking and Decohesion of Vapour-Deposited Tantalum Films," *Thin Solid Films.* (Submitted.)

Fox, A.G. and R.M. Cannon, LBL 28381, "X-ray Diffraction and TEM Studies of the Delamination of Copper Thin Films from Glass and Silica Substrates," *Proc. Mat. Res. Soc.* (Submitted.)

Fox, A.G., M.A. Tabbernor, and R.M. Fisher, LBL 28382, "Low Angle Atomic Scattering Factors and Charge Density of Aluminum," *Phys. Rev. B.* (Submitted.) (M.A. Tabbernor, The Polytechnic, Wolverhampton, UK.)

Invited Talks

Cannon, R.M., *Fracture Resistance of Ceramic-Metal Interfaces,* Presented at IBM Research Center, Yorktown Heights, NY, May 1989; Seminar, Central Research and Development, DuPont, Wilmington, DE, August 1989; and Solid State Sciences Seminar, Sandia National Laboratories, Albuquerque, NM, December 1989.

Cannon, R.M., *Decohesion of Ceramic-Metal Interfaces,* Workshop on Microstructure of Materials Applied in Electronic Packaging Technology, Bad Honnef, Germany, April 1989.

Cannon, R.M., *Fracture Energy of Ceramic-Metal Interfaces,* Packaging Group, IBM, East Fishkill, NY, April 1989.

Cannon, R.M., *Stress and Damage Generation During Sintering,* Mech. Eng. Dept. Colloquia, University of Rochester, NY, April 1989.

Cannon, R.M., *Stress Development and Damage Resistance During Sintering,* Powder Met. Lab., Max-Planck-Institute, Stuttgart, Germany, April 1989.

Fisher, R.M., *Structures, Stresses, Fracture and Decohesion of Thin Cr Films,* Presented at University of Washington, Seattle, WA, Lecture Series, Materials Science and Engineering Department, April 1989; and IBM Packaging Group, East Fishkill, NY, April 1989.

Contributed Talks

Cannon, R.M., *Fracture Resistance of Ceramic/Metal Interfaces,* Acta/Scripta Met. Conf. on Bonding, Structure and Mechanical Properties of Metal/Ceramic Interfaces, Santa Barbara, CA, January 1989.

Cannon, R.M., G.S. Blackman, M.R. Hilton, M. Salmeron, and G.A. Somorjai, IIn Situ *UHV Testing of Fracture Toughness and Chemistry of Ceramic/Metal Interfaces,* Annual Mtg. Am. Ceram. Soc., Indianapolis, IN, April 1989.

Cannon, R.M. and W.C. Carter, *Microstructural Instabilities for a Row of Sintering Particles,* Annual Mtg. Am. Ceram. Soc., Indianapolis, IN, April 1989.

Cannon, R.M. and R.M. Fisher, *Effects of Loading Mode on Mechanical Delamination of Thin Films from Substrates,* MRS Spring Meeting, San Diego, CA, April 1989.

Carter, W.C. and R.M. Cannon, *The Mechanics of Particle-Fluid-Particle Interactions for Liquid Phase Sintering and Drying,* Annual Mtg. Am. Ceram. Soc., Indianapolis, IN, April 1989.

Carter, W.C. and R.M. Cannon, *The Evolution of Sintering Microstructures,* TMS/ASM Fall Meeting, Indianapolis, IN, October 1989.

Crooks, R. and R.M. Fisher, *Characterization of Thermal Barrier Coatings on Titanium Aluminides,* TMS Northeast Regional Meeting, Hoboken, NJ, May 1989. (R. Crooks, CAM Industrial Fellow, Rockwell Science Center, Thousand Oaks, CA.)

Dalgleish, B.J., V. Jayaram, and R.M. Cannon, *Strength, Toughness and Microstructure of Noble Metal/*Al_2O_3 *Joints*, Annual Mtg. Am. Ceram. Soc., Indianapolis, IN, April 1989. (B.J. Dalgleish and V. Jayaram, University of California, Santa Barbara.)

Dalgleish, B.J., V. Jayaram, and R.M. Cannon, *Microstructure and Strength of Noble Metal/*Al_2O_3 *Bonds*, Acta/Scripta Metal. Conf. on Bonding, Structure and Mechanical Properties of Metal/Ceramic Interfaces, Santa Barbara, CA, January 1989.

Duan, J.Z., *Microstructure of Chromium Films Grown on Glass and Silicon Substrates*, 47th Annual Meeting of Elect. Micro. Soc. Am., San Antonio, TX, August 1989.

Fisher, R.M., S. Ahmad, and C.G. Shirley, *Interfacial Failure Modes During Tests of Wire Bond Strength*, MRS Spring Meeting, San Diego, CA, April 1989. (S. Ahmad and C.G. Shirley, Intel Corporation, Chandler, AZ)

Fisher, R.M. and J.Z. Duan, *Influence of Substrate on Cacking of Vapour-Deposited Thin Films Due to Residual Stresses*, MRS Spring Meeting, San Diego, CA, April 1989. (To be published in the Proceedings.)

Fisher, R.M., J.Z. Duan, C.J. Hetherington, and N. Fowler, *Image Processing to Delineate Defect Structures in HREM Images of Vapor-Deposited Thin Films*, 47th Mtg. Elect. Micro. Soc. Am., San Antonio, TX, August 1989. (N. Fowler, Tracor Northern/R.J. Lee Group, Inc., Berkeley, CA.)

Fox, A.G., M.A. Tabbernor, and R.M. Fisher, *Bonding Charge Densities of Al and Cu Determined by Electron Diffraction*, 47th Annual Mtg. Elect. Micro. Soc. Am., San Antonio, TX, August 1989. (M.A. Tabbernor, The Polytechnic, Wolverhampton, UK.)

*Joint study with R.O. Ritchie of the CAM Structural Materials Program.

High-T_C Superconductivity

Basic Science
Thin Film Applications
Electron Microscopy

High-T_C Superconductivity

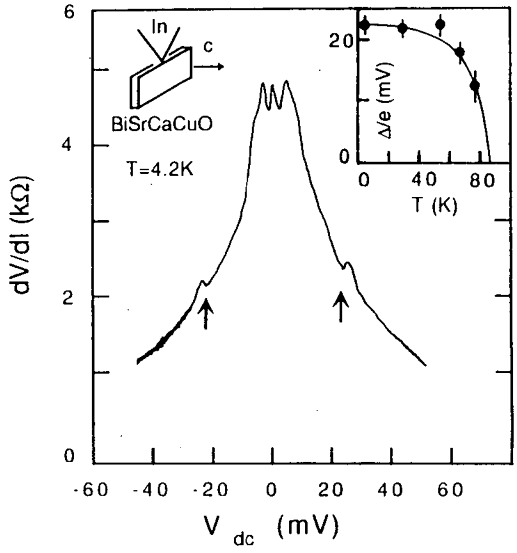
The CAM High-Temperature Superconductivity Program is directed to the development of a fundamental understanding of the new high-critical-temperature (high-T_C) superconductors, by both experimental and theoretical investigations, and to the development of the knowledge necessary for the utilization of these materials in applications in electronics and electrical power systems.

The current research areas are:

- *BASIC SCIENCE,* which includes theory, measurement of physical properties, and materials synthesis.
- *THIN FILMS AND THIN-FILM DEVICES*
- *ELECTRON MICROSCOPY*
- *CERAMIC PROCESSING*

Notable accomplishments during the past year include:

- Calculations for high-pressure metallic hydrogen indicating that it should be superconducting with T_C=230 K.
- Thermodynamic modeling of oxygen ordering.
- Tunneling spectroscopy on 80 K Bi-Sr-Ca-Cu-O single crystals which gave an a-b plane gap of 6.2 k_BT_C, confirming earlier photoemission spectroscopy results, and showing a much smaller 3.3 k_BT_C gap in the c-axis direction.
- Interpretation of the linear term in the low-temperature specific heat in $YBa_2Cu_3O_z$ in terms of localized magnetic moments which form pair-breaking centers.



- Development of $YBa_2Cu_3O_7$-$SrTiO_3$-$YBa_2Cu_3O_7$ crossovers, development of planar spiral coils for SQUID input circuits, and development of a new electrical pulse technique for production of Josephson weak links.
- Design analysis of a high-T_C bolometer and invention of an antenna-coupled high-T_C microbolometer.
- Development of a new high-T_C film deposition technique for forming a film with a single long (millisecond) laser pulse.
- Atomic Resolution Microscope studies of Y-Ba-Cu-O films showing the presence of a new 224 ($Y_2Ba_2Cu_4O_x$) structure.

The majority of the research is conducted by the staff of the Materials and Chemical Sciences Division of the Laboratory, but the effort involves very significant participation by investigators in the Applied Science Division (Berdahl, Rubin, Russo), the Physics Division (D. Morris), and the Accelerator and Fusion Research Division (Brown). Funding sources are likewise diverse: Division of Materials Science in the Office of Energy Research of the US Department of Energy (DOE); Office of Energy Storage and Distribution, Conservation and Renewable Energy at DOE; Electric Power Research Institute; Office of Naval Research; Defense Advanced Research Projects Agency; California Competitive Technology Program; and private sources.

Above: Tunneling data from an indium tip into the a-b plane of a $Bi_2Sr_2CaCu_2O_8$ *crystal.*
(XBL 903-997)

BASIC SCIENCE

M. Cohen, D. de Fontaine, L. Falicov, C. Jeffries, V. Kresin, J. Michaels, D. Morris, N. Phillips, A. Pines, A. Portis, P. Richards, A. Stacy, G. Thomas, E. Weber, P. Yu, A. Zettl

THEORY

The theoretical work includes fundamental microscopic calculations and phenomenological calculations of superconducting properties, as well as computations of oxygen ordering in $YBa_2Cu_3O_7$. Close collaborations with experimentalists are maintained, particularly with regard to oxygen isotope effect research.

Prior work by Kresin, in collaboration with H. Morawitz (IBM, Almaden), on the phonon-plasmon mechanism for electron pairing, was extended. According to this approach, high T_c in the oxides is due to the coexistence of strong electron-phonon coupling and the plasmon mechanism connected with the formation of the unusual low-lying plasmon branches of these layered systems. The importance of the phonon-plasmon mechanism is connected with uniquely small values of the Fermi energy and the Fermi velocity. For the lattice dynamics phonon anharmonicity and the effect of hybridization of acoustic and optical branches have been considered. In addition, the existence of double-well potentials for certain modes was also considered. Both effects lead to strong electron-phonon coupling. Within this model, the non-monotonic dependence of T_c on the carrier concentration is interpreted as a phase-space effect on the attraction between electrons mediated by optical phonons.

First principles calculations, utilizing the standard Eliashberg extension of the BCS theory, resulted in the prediction that metallic hydrogen should exhibit high-temperature superconductivity (Cohen). While the possibility of a metallic structure for hydrogen at high pressures has been investigated for decades, including the possibility of a superconducting transition, only recently has it become possible to perform a first principles calculation of the electron-phonon coupling constant in a hexagonal high-pressure phase. The band structures for both electrons and phonons are computed as inputs to the computation of the electron-phonon coupling. This first-principles approach has successfully predicted superconductivity in compressed silicon. The superconducting transition temperature is estimated to be 230 K, with an uncertainty of 85 K. Thus if metallic hydrogen were to be formed in the laboratory in the proposed hexagonal phase, at pressures of about 400 GPa, it should be superconducting at the highest temperature yet known.

Many authors believe that an electronic mechanism is required to explain the high transition temperatures in certain oxides. In order to constrain the various high-T_c theories, the effects of these electronic pairing mechanisms upon both the transition temperature and the isotope effect was considered (Cohen). The calculations utilize the Eliashberg theory for an isotropic Fermi liquid. For the highest transition temperature compounds (e.g., Y-Ba-Cu-O), the small isotope effect and high T_c can be accounted for only by an unrealistically small value of the electron-phonon coupling parameter. Therefore, an electronic pairing mechanism with characteristic energy above 100 meV can be excluded for a wide class of models.

The phenomenological theory of deformable superconductors was investigated by Falicov. The solution of the Ginzburg-Landau equations for a system that can sustain both superconductivity and a structural transition was obtained. It was found that the interaction between superconductivity and deformation can lead to weak first-order superconducting transitions and to fascinating spatially dependent phenomena: (1) an unexpected magnetostriction at the surface caused by the diamagnetic response of the superconductor and its attendant change in the structural properties; (2) metastable surface superconductivity produced by unreleased stresses at the surface. It was found that while the deformation relaxes over short distances, the superconductivity may extend much deeper into the bulk of the deformable superconductor.

The major normal and superconducting parameters of the high-T_c oxides were evaluated by an analysis based on Fermiology, that is, by a momentum-space analysis which accounts for the topology and shape of the Fermi surface. This phenomenological work is a collaboration of V. Kresin with S. Wolf of the Naval Research Laboratory. The compound $La_{1.8}Sr_{0.2}Cuo_4$ is particularly amenable to this analysis because it has a relatively simple structure and the available experimental data are particularly reliable. Based on the approximation of the Fermi surface as a cylinder, it has been shown that the effective mass of the charge carriers is directly proportional to the Sommerfeld constant (electronic heat capacity divided by the absolute temperature). This constant can be estimated from experimental data, and the effective mass of the charge carriers is thereby determined to be about 5 times the mass of a free electron. A related argument gives the value 0.1 eV for the Fermi energy, based on Hall effect data. More complex analysis, based on the temperature dependence of the heat capacity, the upper critical field, and other data, indicates that the dimensionless electron-phonon coupling constant is about 1.9 for $La_{1.8}Sr_{0.2}CuO_4$. This value shows that the pairing interaction due to phonon exchange is strong, but insufficient to account for critical temperatures as high as the observed 40 K. The needed additional interaction is ascribed to the exchange of acoustic plasmons.

The variability in oxygen concentration in $YBa_2Cu_3O_z$ leads to various phases which are distinguished by ordering of the mobile oxygen atoms (in the crystallographic plane between the two Ba planes in the unit cell). De Fontaine's group proposed a thermodynamic model of this phenomenon in 1987 and has since elaborated and extended it to form a consistent, unified, theoretical picture. The tetragonal phase labeled T in Figure 1 is characterized by a random distribution of oxygen atoms, whereas the

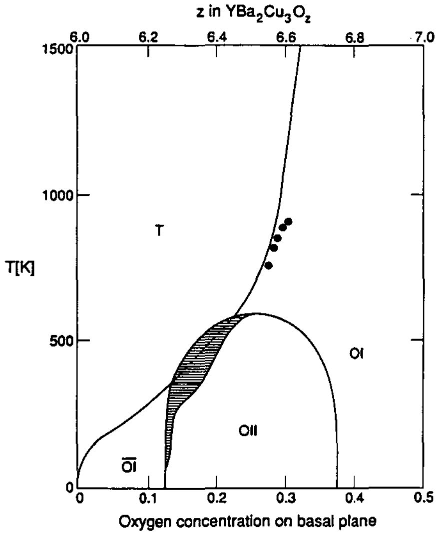


Figure 1

Oxygen ordering phase diagram of $YBa_2Cu_3O_z$ calculated from the cluster variation method. All transitions are second order except where indicated by the shaded region. The lower oxygen content scale denotes oxygen concentration (fractional coverage) c; the upper scale denotes oxygen stoichiometric index z = 2c+6. Filled circles are experimental values from Oak Ridge National Laboratory. (XBL 8910-6326) various orthorhombic phases contain parallel "chains" of oxygen atoms, which are themselves ordered in 1-dimensional arrays depending on oxygen concentration. The 90 K phase is "Ortho I" (OI) and has alternating full and vacant rows of oxygen atoms, at $z = 7$ and zero temperature. The 60 K phase often observed near $z = 6.5$ is identified as the doubled-cell "Ortho II" (OII), in which alternate rows of oxygen atoms of the OI phase are omitted. Input parameters for the theory, such as the attractive second neighbor interaction of the oxygen atoms, are obtained from first principles calculations. The theory utilizes the cluster variation method to perform the statistical mechanical calculations. Still more complex phases, also comprised of ordered rows of oxygen atoms, are expected due to the long-range coulomb repulsion between rows of oxygen atoms. Recent experimental results from electron diffraction and micrography studies confirm the existence of these phases, which are most readily observed between $z = 6.55$ and 6.85.

MEASUREMENT OF PHYSICAL PROPERTIES

Extensive measurements of physical properties of superconductors are performed. These include superconducting energy gap measurements by tunneling, photoemission, and far-infrared spectroscopies. Transport measurements include resistivity as a function of crystallographic direction, pressure, frequency, etc, as well as Hall effect and thermoelectric power. Electrodynamic properties of crystalline and granular materials are examined at rf and microwave frequencies. Still further physical properties measurements include specific heat, Raman scattering, and nuclear magnetic resonance.

Tunneling spectroscopy has been used by Zettl and Briceno to characterize the superconducting energy gap in $Bi_2Sr_2CaCu_2O_8$. Both the anisotropy and the temperature dependence has been investigated. Single crystals were carefully annealed in oxygen and used to form both break junctions and point contact junctions. The current-voltage characteristics suggest zero-temperature energy gap values of 6.2 k_BT_c for tunneling in the a-b plane and 3.3 k_BT_c for tunneling in the c-axis direction. (k_B is Boltzmann's constant and T_c is the critical temperature.) Figure 2 shows data for tunneling from an indium tip into the a-b plane of the crystal; the minima indicated by arrows identify half the energy gap as 22.5 meV. The inset of this figure shows the observed and theoretical dependences of the gap on temperature, which are in agreement. These new measurements of the gap for electron motion in the a-b plane are also in good agreement with measurements, discussed in last year's annual report, by high-resolution photo-emission spectroscopy.

Raman scattering investigations have been carried out (D.E. Morris) in collaboration with H.J. Rosen, M.C. Krantz, and R.M. Macfarlane of IBM Almaden Research Center. The scattering from single crystals of $Tl_2Ca_2Ba_2Cu_3O_{10}$ and $YBa_2Cu_4O_8$ exhibit the characteristic phonon spectra of these compounds. The thallium-compound data were also used to investigate the broad background continuum interpreted as electronic scattering. This continuum decreases substantially below T_c for frequency shifts of smaller than 400 cm^{-1}, which indicates the formation of a superconducting gap. The gap does not show the expected abrupt onset but a linearly rising electronic scattering background similar to observations in $YBa_2Cu_3O_7$, possibly indicating a distribution of gaps or the presence of electronic excitations within the gap.

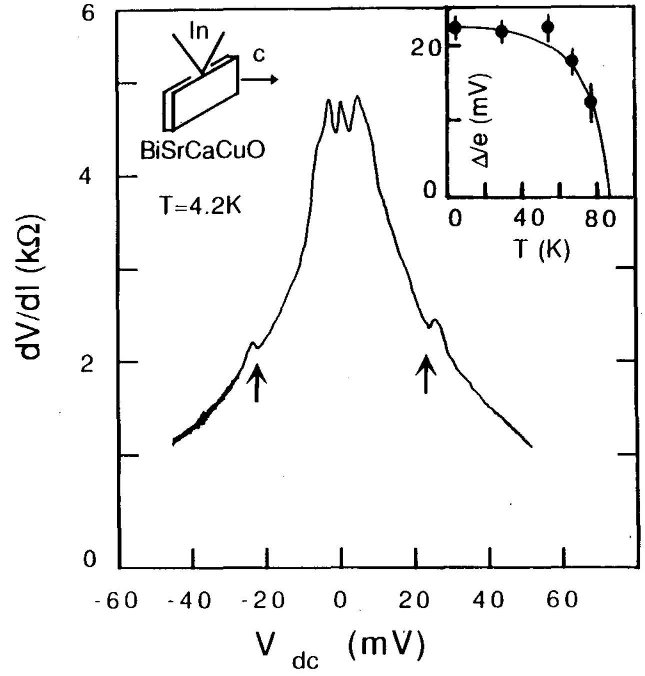


Figure 2
Tunneling data from an indium tip into the a-b plane of a $Bi_2Sr_2CaCu_2O_8$ crystal. The differential resistance is plotted versus bias voltage; the minima indicated by arrows are located at one half of the gap energy. The inset show the temperature dependence of the gap, which is in good agreement with the curve based on the theory of Bardeen, Cooper, and Schrieffer. (XBL 903-997)

Specific heat data were obtained (D.E. Morris) in collaboration with J.S. Urbach, D.B. Mitzi, and A. Kapitulnik at Stanford University, on crystals of $Bi_2CaSr_2Cu_2O_8$ and $Tl_2Ca_2Ba_2Cu_3O_{10}$. Measurements covering the range of 2 to 15 K showed no measurable linear term in the specific heat as a function of temperature. Deviations from the Debye T^3 law were attributed to spin-glass behavior of a small concentration of isolated impurity copper moments.

The well-known, and controversial, linear term in the specific heat of the compound $YBa_2Cu_3O_7$ has been the subject of a continuing investigation by the Phillips group. The data from a number of samples is interpreted as showing the existence of localized magnetic moments on the crystal lattice that suppress the transition to the superconducting state. Both the extent of the transition, as measured by the jump in specific heat at T_c, and the magnitude of the low-temperature "linear" term are correlated with the concentration of these moments in the way expected for pair-breaking centers. That is, the linear term increases and the specific heat jump decreases with increasing moment concentration. The effect of the pair-breaking centers, together with that previously recognized as arising from impurity phases, accounts completely for the observed linear component of the specific heat. Pair-breaking by localized magnetic moments implies singlet-spin pairing in the superconductor state, and also that the large volumes of non-superconducting material produced by low concentrations of magnetic moments pose a problem that will have to be overcome in processing for practical applications.

The lattice and electronic specific heat of $YBa_2Cu_3O_7$ was investigated in the temperature range 78 to 284 K (Phillips). In the high temperature region, the data fall on a smooth curve with no evidence of the anomalous behavior which has been reported near 215 K. Near T_c, the data are consistent with the specific heat of a BCS superconductor that has a contribution from 3-dimensional Gaussian fluctuations; that is, there is a discontinuity at T_c and also contributions proportional to the reciprocal square root of T_c-T. The temperature region near T_c was further explored in a study in which Cr and Zn were substituted in place of Cu. Figure 3 shows how the specific heat "jump" near T_c declines as Cr is added and the superconducting fraction of the material declines. Specific heat measurements on the same samples at lower temperatures, in both zero and 7 tesla magnetic fields, gave evidence for localized magnetic moments, due to the chromium, which are responsible for the elimination of the superconductivity.

The specific heat of the high-T_c superconductor ($Bi_{1.66}Pb_{0.34}Ca_2Sr_2Cu_3O_{10}$ was measured in magnetic fields of 0 and 7 tesla in the temperature ranges 0.4 to 20 K and 65 to 125 K, in a collaboration of Phillips with H.M. Ledbetter of the National Institute of Standards and Technology, and K. Togano of the National Research Institute for Metals (Tsukuba, Ibaraki, Japan). The coefficient of the low-temperature linear term in the specific heat is unmeasurably small. On initial cooling, an anomaly was observed at T_c, but there were dramatic temperature hysteresis effects present. Hysteretic anomalies were also observed in the magnetic susceptibility and, earlier, in elastic constant measurements.

Transport measurements on the high-T_c superconductors, and their theoretical interpretation, may provide important clues to the origin of their remarkable superconducting properties (Zettl, Yu, Cohen). Measurements on crystals of $Bi_2Sr_2CaCu_2O_{8-x}$ show a metal-insulator transition induced by variable oxygen concentration. "Universal" empirical equations are determined for the electrical resistivity, Hall effect, and thermoelectric power. The same expressions hold for different oxygen concentrations, and possibly for all high-T_c superconductors. Figure 4 shows the nature of the relationship for the resistance (divided by $T^{0.7}$) for several samples. Despite varying oxygen concentration, sample orientation, and even sample composition, the data for each sample falls on a straight line. As another example, the thermoelectric power tends to assume the form

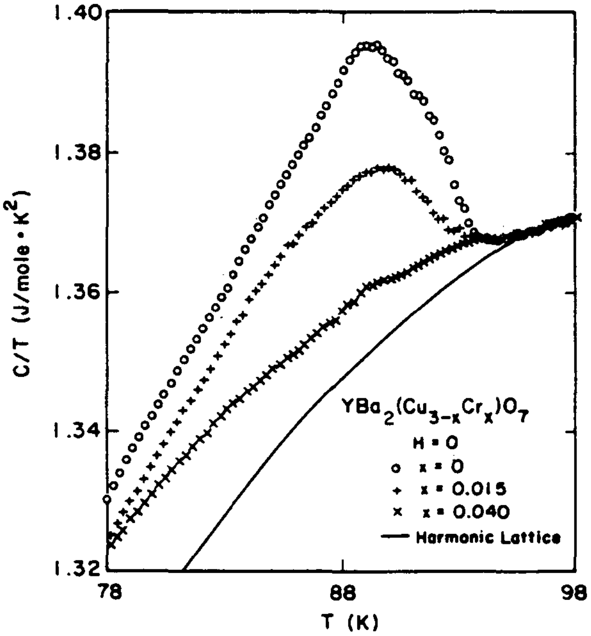


Figure 3

Specific heat data (divided by absolute temperature) for Cr-doped samples in zero magnetic field, showing the suppression of superconductivity by the chromium. The smooth curve is a fit to data at higher temperatures. (XBL 903-995)

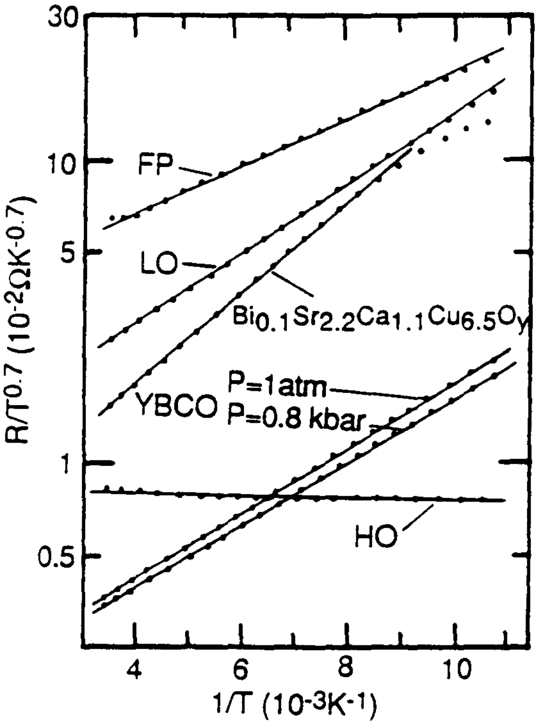


Figure 4
Plots of sample resistance for various high-T_c oxides. FP (freshly prepared), LO (low oxygen), and HO (high oxygen) label data for the a-b plane of several samples of the variable oxygen concentration Bi 2212 compound. The other data are c-axis resistances for the compounds listed. (XBL 903-996)

$S = A + BT$, where the constants A and B vary, e.g. with oxygen concentration, but are independent of T. The fundamental reason the transport properties tend to assume simple empirical forms is not known, but the model of "quantum percolation" due to J.C. Phillips may be useful in this regard.

High pressure electrical conductivity measurements in Cu_2O and CuO were performed (Yu, Zettl, Cohen). The properties of these compounds, in their various phases, may shed light on the nature of conduction in the high-T_c cuprates. The high pressure phase of Cu_2O (above 130 kbar) has a resistive thermal activation energy of a few meV and localization behavior below 7 K. In CuO, no phase transitions were observed at temperatures and pressures up to 700 kbar and 3000 K, but its thermal activation energy decreases linearly with pressure and extrapolates to zero at about 1 Mbar.

The granular nature of ceramic samples of the high-temperature superconductors leads to complex non-linear electrodynamic behavior, which are under investigation by the Jeffries group. The experimental method consists of observing and processing the voltage induced into a copper "receiver" coil wound around a cylindrical ceramic YBCO sample, subject to applied dc and ac fields. Up to 41 harmonics of the fundamental ac excitation have been observed. The theoretical model under study for interpreting these data is an extension and revision of the critical-state model of Bean, Anderson, and Kim ("BAK"), originally proposed as an *ad hoc* and phenomenological explanation of the magnetic properties of type II low-temperature superconductors. According to this model, the local critical current density J_c is a function of the local magnetic field H_{loc}, namely that J_c is proportional to $(H_{loc}+H_0)^{-2}$, where H_0 is a parameter. (The original BAK theory has the exponent -1 rather than the value -2 found necessary here from fits to the data.) Extensive data for the harmonic power for all harmonics up to the tenth are found to be in good agreement

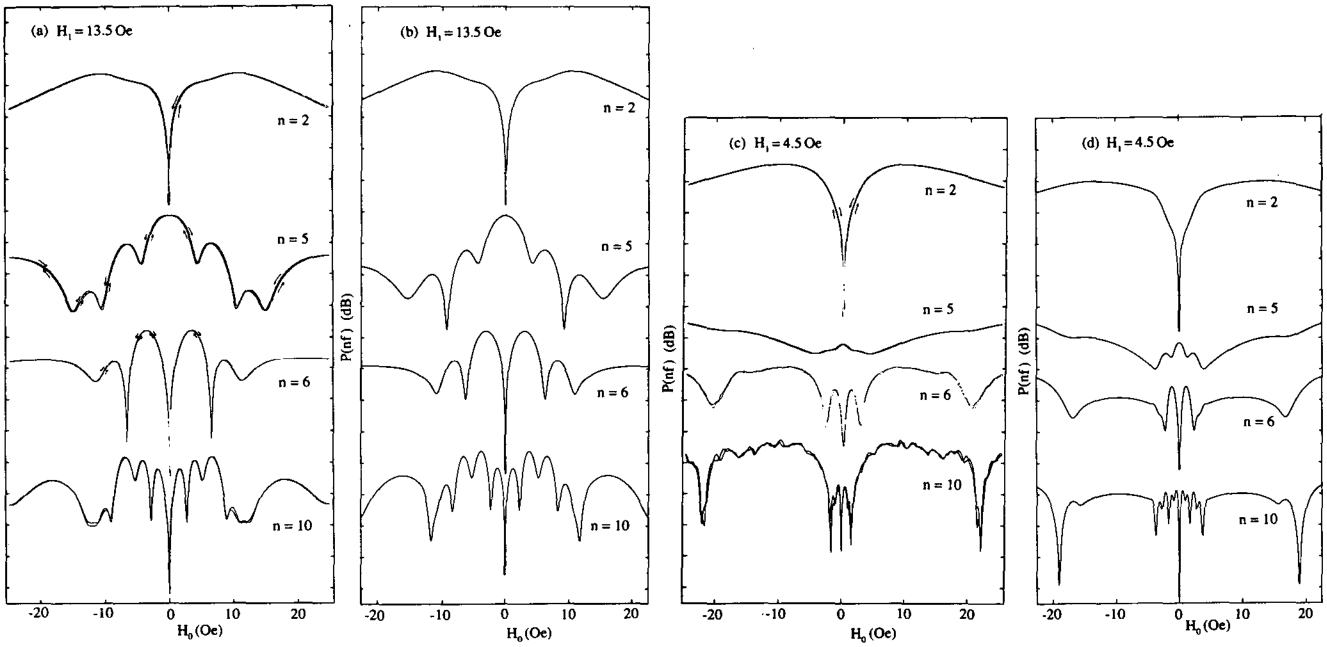


Figure 5
Experimental data at 77 K on harmonic generation power at harmonic n and frequency f, P(nf) (10 dB/div.), in a cylindrical ceramic rod of YBCO. Parts (a) and (b) show experimental and theoretical values, respectively, for the ac magnetic field amplitude H_1=13.5 Oe; parts (c) and (d) show the same information for H_1=4.5 Oe. H_{dc} is the applied dc field. (XBL-902-346)

with the model, as shown in Figure 5. Further, more detailed measurements, of the phase and amplitude of the fundamental ("zeroth harmonic") response show that for applied dc fields below 20 Oe, the intergranular critical current controls the response, whereas at fields above 100 Oe the intragranular region becomes dominant.

The microwave susceptibility of natural SQUID structures in single crystals of $YBa_2Cu_3O_{7-x}$ has been investigated by Portis and Weber, in a collaboration with Z.Z. Wang and N.P. Ong of Princeton University. The microwave absorption exhibits periodic peaks as the applied magnetic field is varied. Both the absorption and dispersion signals are interpreted with an rf SQUID model that associates the absorption signal with hysteresis (due to change in trapped flux), and associates the dispersive signal with constant flux. Hysteresis leads naturally to the observed constancy of the absorption amplitude with increasing rf power. Also readily explained by the SQUID model is the nature of the dispersion.

Magnetic-field-modulated microwave absorption was used to investigate Pb-modified Bi-Ca-Sr-Cu-O, in a collaboration with S.M. Green and H.L. Luo of the University of California at San Diego (Portis, Weber, Thomas). The absorption was observed with a Bruker 200D Electron Spin Resonance spectrometer. At high levels of the modulation field amplitude, the output of the spectrometer is expected to be proportional to the first derivative of the absorption. Figure 6 shows the temperature dependence of the normalized signal strength. High-resolution transmission electron microscopy (HRTEM) has established that the samples are mostly composed of the 115 K polytypoid structure with the 80 K polytypoid found at grain boundaries and at planar defects within grains. The addition of Pb eliminates the lower temperature transition. The observed microwave absorption is consistent with the HRTEM observations and

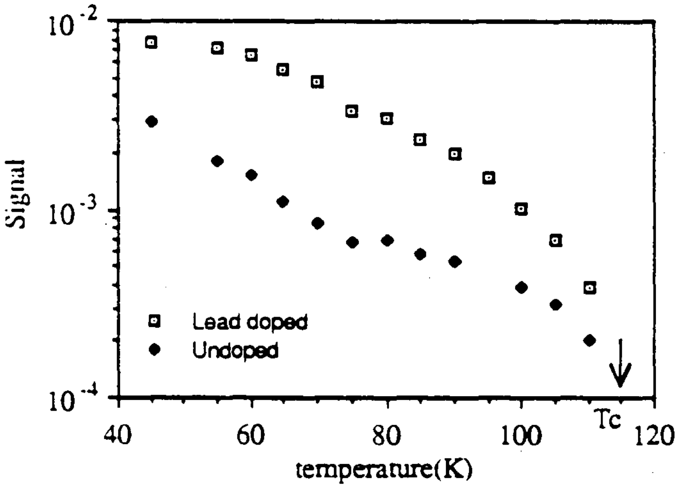


Figure 6
Normalized modulated microwave absorption from two samples of Bi-Ca-Sr-Cu-O. (XBL 903-999)

supports the general view that microwave absorption arises primarily from grain boundaries and planar defects.

The microwave surface impedance of granular superconductors has been investigated in collaboration with D.W. Cooke of Las Alamos National Laboratory and H. Piel at Wuppertal, Germany (Portis). The intergranular medium is modeled by an inductor representing tunneling supercurrents and a resistor representing the effects of microshorts between grains, as proposed by Halbritter. The resulting microwave surface resistance is expected to be proportional to the square of the frequency and to the square of the critical current density at the surface. An estimate of the critical current density of a bulk ceramic specimen, based on microwave impedance measurements, gives 1,800 A cm^{-2}, in good agreement with low-field magnetization measurements.

The oxygen-17 nuclear magnetic resonance spectrum of $La_{1.85}Sr_{0.15}CuO_4$ has been studied at temperatures ranging from 12 K to 295 K (Reimer). Three resonances observed are assigned to planar oxygen sites, axial oxygen sites, and a satellite peak of the La-139 resonance. Temperature-dependent studies of the resonance frequency associated with the axial site show that this resonance moves to higher frequency just above the critical temperature and then rapidly shifts to lower frequency upon formation of the superconducting state. It is suggested that the spin susceptibility of this oxygen site is affected by the onset of superconductivity. Spin-lattice relaxation of this resonance appears to be dominated by quadrupolar mechanisms at temperatures above T_c; the relaxation rate is nearly constant below T_c.

Synthesis

The synthesis research includes the search for new superconducting materials as well as the growth of single crystals.

The oxygen content of $Bi_2CaSr_2Cu_2O_{8-x}$ has been found to affect T_c (D. Morris). In contrast with the shift seen in $YBa_2Cu_3O_{7-x}$, T_c shifts downward for increased oxygen content. The highest T_c = 78.5 K is obtained by treating at 600 C in 10^{-2}-bars oxygen. T_c shifts down to 65.4 K after treatment at 137 bars. The transitions remain sharp, with no evidence of significant structural change by x-ray powder diffraction. The 110 K Bi-compound phase showed a much smaller shift (about 4 K) after treatment in O_2 at 134 bars.

The stability of the 124, 123, and 247 Y-Ba-Cu-O superconductors was investigated in a collaboration with J.E. Post of the Smithsonian Institution (D. Morris). (The notation 124, for example, refers to the compound $YBa_2Cu_4O_x$.) The 124 phase is synthesized by solid state reaction at 930 C in oxygen pressure, $P(O_2)$, above 30 bar, while the 247 phase is favored in the narrow range of $P(O_2)$ between 10 and 30 bar. The 123 phase forms at $P(O_2)$ below 10 bar. Similar results are found for the analogous compounds with rare earths substituted for Y. The pressure ranges for stability of 123/247/124 are nearly independent of starting stoichiometry, but increase with temperature, such that the oxygen content of 123 at the phase boundary is nearly constant. This suggests that superconducting 123 (with oxygen > 6.6) may be thermodynamically unstable to decomposition into 124 (plus non-superconducting compounds) at all temperatures, with synthesis of 124 at low temperatures and oxygen pressure limited only by kinetics. Since very high oxygen pressures are not required, synthesis of the 124 and 247 phases is relatively easy, which may have considerable practical importance.

The 247 compound consists of alternating layers of 123 and 124. Thus it is surprising that 247 has a lower T_c (45-55 K) than either of the parent compounds. The basal plane areas of 247 are larger and orthorhombic distortions smaller than the corresponding 123 and 124, suggesting weaker bonding in the CuO_2 layers. Though the 247 compounds were processed in pressurized oxygen, they may contain less than the 15 oxygens of 124 + 123. This lower oxygen concentration would reduce the hole concentration and could explain the low T_c.

Two new superconductors in the Ca-Y-Ba-Cu-O system have been synthesized by solid state reaction at 930 C at elevated $P(O_2)$ (D.E. Morris): tetragonal $Ca_xY_{(1-x)}Ba_2Cu_3O_y$ (123) prepared at $P(O_2) = 16$ bar (T_c=87 K for x=0.2), and $Ca_xY_{(1-x)}Ba_2Cu_4O_y$ (124) prepared at 50-200 bar (T_c=89 for x=0.1). Calcium substitution shifts the phase stability boundary between 123, 247, and 124 phases to higher $P(O_2)$, and Ca stabilizes the tetragonal structure of 123 at elevated $P(O_2)$ without substantial decrease in T_c. The results confirm that high T_c in 123 does not require orthorhombic distortion; the low-T_c observed in unsubstituted tetragonal 123 is due to oxygen deficiency. Ca-substituted 123 may prove technologically useful because of improved stability as a result of elimination of the tetragonal-orthor-

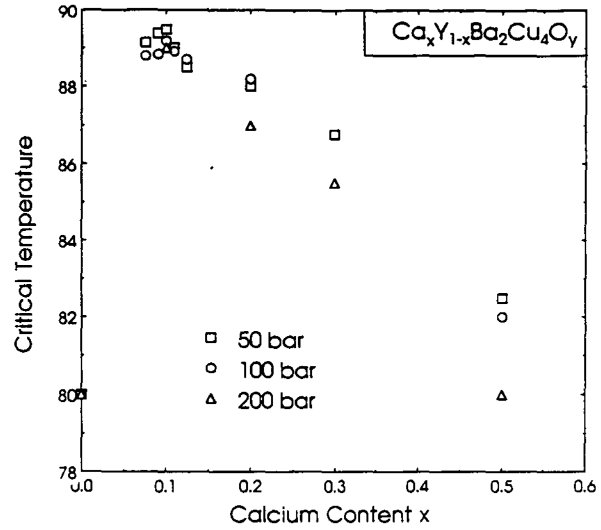


Figure 7

The variation of T_c as a function of x in calcium substituted 124 ($Ca_xY_{(1-x)}Ba_2Cu_4O_y$) synthesized at 930 C in $P(O_2) = 50, 100, 200$ bar, as indicated by the onset of diamagnetism. Note that $T_c = 80$ K for x=0.
(XBL 903-998)

hombic transition and associated twinning. The Ca-substituted 124 phases, as shown in Fig. 7, exhibit an increased T_c at x=0.1 of 89 K, which is larger than the unsubstituted (x=0) phase with T_c of 80. However, at larger Ca concentrations, and larger oxygen pressures, T_c gradually decreases, possibly indicating hole concentration increased beyond the optimum value.

THIN FILMS AND THIN-FILM DEVICES

P. Berdahl, I. Brown, J. Clarke, E. Haller, D. Olander, P. Richards, M. Rubin, R. Russo

The thin-film research includes film synthesis, film characterization, and the investigation of thin-film devices such as bolometers and SQUIDs (Superconducting QUantum Interference Devices), for applications in electronics. Also underway is the development of thin films for tape conductors, for applications to electric power systems. President Reagan designated Lawrence Berkeley Laboratory as a Superconductivity Research Center for Thin-Film Applications in 1987.

Virtually all electronic circuits require insulating crossovers, without which devices and interconnections that can be fabricated are severely limited. Clarke's group has developed YBCO-$SrTiO_3$-YBCO crossovers (YBCO = $YBa_2Cu_3O_7$), which should be suitable for a variety of applications in superconducting microelectronics at 77 K. These tri-layer structures are grown *in situ* by excimer laser deposition onto a heated (100) MgO substrate. The geometrical configuration of each layer is defined by a metal mask; the vacuum chamber is opened between depositions to allow the targets and masks to be changed. The upper and lower YBCO films in the best trilayer structure had transition widths of 1 and 3 K (10-90%), respectively and transition temperatures (zero resistance) of 87 K. The resistance between the YBCO films at 77 K was 10^8 ohm for an overlapping area of 0.2 mm^2, corresponding to a $SrTiO_3$ resistivity of 4 x 10^9 ohm-cm.

A critical technique for a successful high-T_c electronics technology is fabrication of the Josephson junction. A new technique has been devised (Clarke) for growing junctions in microbridge structures. First, a microbridge is patterned in a thin YBCO film grown by laser ablation. Such bridges, immersed in liquid nitrogen, exhibit critical currents ranging from 1 to 50 mA, but as expected, fail to induce constant voltage steps on the current-voltage characteristic, signifying the absence of a Josephson effect. To form a Josephson junction, current pulses are applied to the microbridge one by one. The amplitude of the current spike is increased until the critical current is reduced to about one-half of its initial value. The pulsing and thermal cycling are repeated until the critical current is reduced to tens or hundreds of microamperes. It is then possible to observe microwave-induced steps, implying that Josephson-like behavior has been induced. This method is a straightforward and convenient way of making small junctions with a fair degree of reproducibility that promises to be important for both fundamental studies of high-T_c Josephson junctions and for devices such as SQUIDs.

Very low magnetic flux noise has been observed in laser-deposited *in situ* films of $YBa_2Cu_3O_y$, in a collaboration of Clarke's group with A. Inam and X.D. Wu of Rutgers and L. Nazar and T. Venkatesan of Bellcore. Many applications of SQUIDs demand high sensitivity at low frequencies f (below 1 Hz) and thus require films with low intrinsic "1/f" magnetic flux noise. Although the level of 1/f noise in $Tl_2Ba_2Ca_2Cu_3O_x$ SQUIDs is significantly lower than that in earlier YBCO SQUIDs, it remains higher

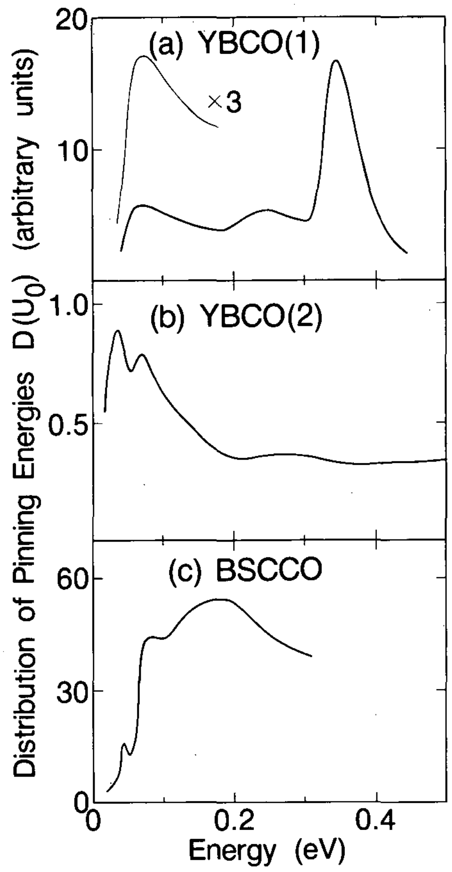


Figure 8

Density of zero-temperature activation energies $D(U_0)$ v. energy U_0 for two YBCO films (a,b) and a thin Bi-2212 crystal (c). Film (1) has been post-annealed, while film (2) was formed in situ by sputtering. Arbitrary units on the vertical scale are the same for each sample. (XBL-897-5154)

than that in low-T_c devices. In post-annealed films of YBCO, the magnitude of the 1/f noise was shown last year to decrease dramatically as the quality of the films is improved. This year we report measurements of flux noise in a film of YBCO grown *in situ* by pulsed laser deposition (but not patterned into a SQUID). The 1/f noise level was 2 orders of magnitude lower than in our best post-annealed film. This noise is low enough to have significant implications for SQUID magnetometers. Expressed as a noise energy for a SQUID with an inductance of 100 pH, it has the value (at 1 Hz, 77 K) of 1.7×10^{-29} J Hz^{-1}. Compared with the noise energies of commercially available devices operated at 4.2 K, this value is only a factor of six greater than dc SQUIDs and a factor of two less than rf SQUIDs. Of course, low flux noise is not in itself sufficient for low noise in a SQUID; one has to make sufficiently low-noise junctions as well. Finally, these results imply that flux transformers made from high-quality films should not induce significant levels of low-frequency noise into the SQUID.

The distribution of flux pinning energies in YBCO and $Bi_2Sr_2CaCu_2O_8$ has been determined from flux noise measurements, in collaboration with D. Mitzi, P.A. Rosenthal, C.B. Eom, T.H. Geballe, A. Kapitulnik, and M.R. Beasley of Stanford (Clarke). Flux noise offers a novel probe of flux pinning energies which complements studies of resistive transitions in a magnetic field. In particular the region of low and zero magnetic field is readily investigated. The spectral density of the flux noise was found to scale approximately as the inverse of the frequency; it also increases with increasing temperature. The temperature and frequency dependence of the noise is used to determine the pinning energies of individual flux

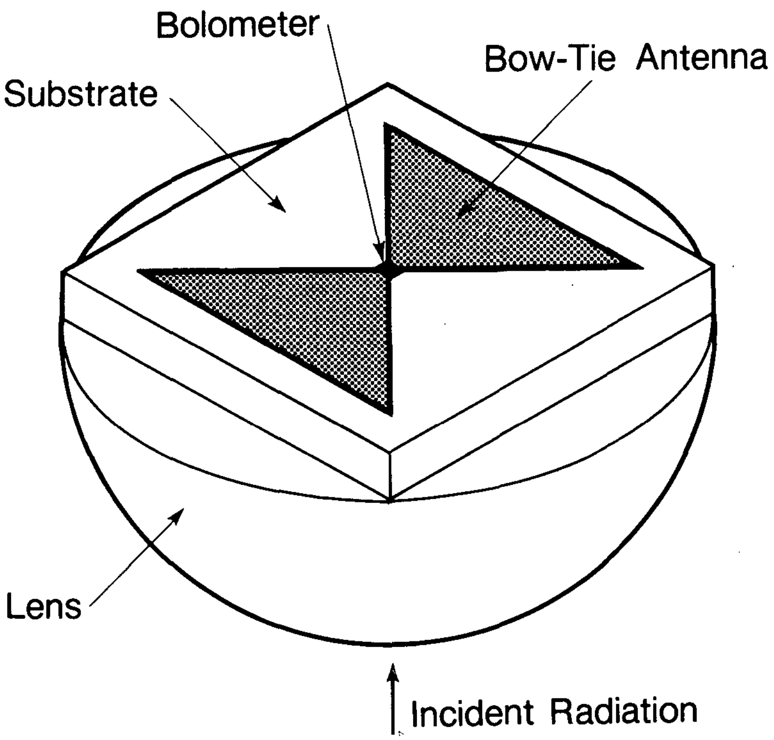


Figure 9
Architecture of a bow-tie antenna-coupled microbolometer on the back side of a hemispherical lens. Radiation is coupled to the antenna more efficiently through the lens and substrate. Spiral and log-periodic antennas will also be useful for such bolometers. Because of its small area, the response of the microbolometer extends to frequencies above 10^5 Hz. (XBL-897-5127)

vortices in thermal equilibrium. The distribution of pinning energies peaks below 0.1 eV in YBCO and near 0.2 eV in $Bi_2Sr_2CaCu_2O_8$, as shown in Figure 8. The noise power is proportional to the ambient magnetic field, indicating that the vortex motions are uncorrelated.

Infrared absorptivity measurements on thin films of $YBa_2Cu_3O_7$ are underway in the Richards group, in a collaboration with Bellcore/Rutgers (S. Etemad, T. Venkatesan, L. Nazar, B. Dutta, X.D. Wu, A. Inam) and Stanford (S.R. Spielman, T.H. Geballe). These measurements are useful as a measure of film quality and may eventually clarify the intrinsic infrared optical properties. The absorptivity measurements cover the range 5 to 700 cm^{-1} and are made at 2 K. C-axis oriented films are grown epitaxially on $SrTiO_3$, $LaAlO_3$, and MgO substrates by off-axis sputtering and a laser deposition technique. In the measurement the film acts as the absorbing element in a composite bolometric detector and is used with a Fourier transform infrared spectrometer. In contrast to the interpretation of many reflectivity measurements, the absorptivity is found to be non-vanishing down to the lowest frequencies. The absorptivity is approximately linear with frequency in the 30 to 300 cm^{-1} range, and its magnitude is less than 0.01 for all frequencies less than about 200 cm^{-1}.

A new type of bolometer ("microbolometer") has been invented by Q. Hu (Richards group); a design analysis of this bolometer indicates high performance at frequencies up to 10 kHz. This new development builds on prior work on the feasibility of high-T_c bolometers, which indicated that high-T_c thin-film bolometers would provide at least an order of magnitude improvement over the sensitivity of commercial pryoelectric detectors which are widely used for laboratory spectroscopy. Figure 9 shows that the new microbolometer design uses a thin film, perhaps 1 by 5 micrometers in size, coupled to a metal-film antenna which intercepts the far-infrared or millimeter-wave radiation. This type of detector can be mechanically stronger, more easily fabricated, and much faster than conventional bolometric infrared detectors. The design analysis shows that a noise equivalent power of 2.5×10^{-12} W $Hz^{-1/2}$ is achievable for modulation frequencies up to 10 kHz.

Both conventional high-T_c bolometers and high-T_c microbolometers are being fabricated by optical lithography and tested for response and noise. Very high quality films from Conductus, Inc. on substrates of Al_2O_3 and Y-stabilized zirconia (YSZ) are used for these devices. Excess voltage noise due to thermally activated flux motion is seen in films deposited directly on Al_2O_3, but not in films on a $SrTiO_3$ buffer layer on Al_2O_3 or YSZ.

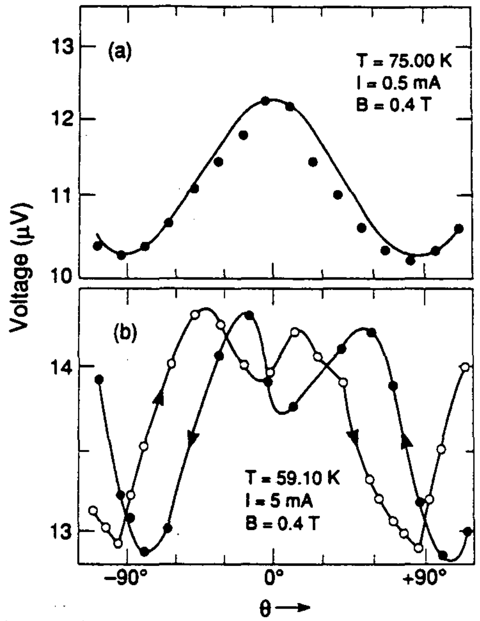
Sputtered high-T_c films and buffer layers for tape conductors are under investigation by Rubin. Using high-pressure d.c. magnetron sputtering his group can deposit YBCO films on a variety of single-crystal substrates with c-axis orientation and near-optimal critical temperatures. Having achieved this prerequisite, they are now concentrating solely on development of tape conductors. A complete tape structure might consist of a metal tape substrate, superconducting film, and current shunt film, separated by appropriate buffer layers. One promising substrate is Hastalloy, a strong Ni alloy, well matched to YBCO in thermal expansion coefficient. Buffer layers of $SrTiO_3$ and Ag have been used to permit formation of superconducting YBCO films on Hastalloy. Increasing the buffer layer thickness reduces the Ni signal seen with Auger spectroscopy at the YBCO surface, but degrades the c-axis orientation. Diffusion at interfaces is a key problem in these multilayer structures. Efforts to further characterize the Ag-YBCO interface with high-resolution electron microscopy are underway in collaboration with R. Gronsky. Also, efforts to lower growth temperatures utilizing low-energy ion bombardment are proving promising.

High energy ion-implantation of YBCO films was investigated (Brown, Rubin), using the metal vapor vacuum arc ion source invented at LBL. This special miniature broad spectrum ion source produces a uniform depth distribution in the implanted film. By implanting a Cu-deficient, insulating, YBCO film with a Cu beam, followed by an oxygen anneal, a superconducting film was produced. This technique could be used to write superconducting patterns in insulating films.

Pulsed laser deposition is also being employed to develop thin superconducting films for tape conductor applications (Russo). Using excimer-laser ablation, excellent as-deposited YBCO superconducting thin films have been fabricated on various substrates. Ablation of various metal buffer layers was studied, followed by deposition of YBCO films. For example YBCO was deposited on stainless steel using a Ag buffer layer. The T_c for zero resistance was 84 K, and the critical current was 1,000 A cm^{-2} at 67 K. However these films had low critical currents in a magnetic field; they are nearly unoriented as shown from x-ray diffraction and from electrical measurements as a function of magnetic field orientation. Thus, thin films for tape conductors are promising, and the 10^6 A cm^{-2} critical currents readily achievable with ablated films on single crystal substrates show the margin available for improvement.

A new long-laser-pulse technique was developed for depositing superconducting thin films (Olander, Russo). The conventional short pulse technique utilizes pulses only a few nanoseconds in length. In this work, however pulses on the order of a millisecond were obtained from a Nd-glass laser with 50 J/pulse. The deposition rate was approximately 100 nm/pulse, and the film stoichiometry was close to that of the target. Scanning electron microscopy revealed spherical inclusions in the film; scanning tunneling microscopy in air revealed a terrace-ledge structure on the uniform portion of the film. A film produced by four pulses on a

Figure 10
Voltage drop as a function of the direction of an applied magnetic field, for a granular, nearly unoriented film deposited on SrTiO$_3$. The points show the measured data. The upper curve is a cosine function; the lower curves are guides for the eye. (XBL 8910-6328)



SrTiO$_3$ substrate held at 540 C and post-annealed in O$_2$ exhibited an onset transition at 85 K and zero resistance at 82 K. This new approach can provide fast deposition rates and broad-area film coverage.

Electrical characterization measurements on films have been performed as a function of the angle θ of an applied magnetic field (Berdahl), as shown in Fig. 10. Here the field is always perpendicular to the current flow; θ is zero when the field is perpendicular to the film. Measurements of this type clarify the nature of resistive losses in the presence of a magnetic field. They also give evidence for orientation of the crystallites of which the film is composed. This film is only slightly oriented; high-quality epitaxial films show a much sharper variation of voltage drop with magnetic field direction when the field is almost parallel to the film (θ near 90 degrees). At the lower temperature of 59 K, a strong hysteresis is observed. The hysteresis is due to the presence of circulating supercurrents induced by the magnetic field, which interact with the transport current used to make the measurement. This figure illustrates the complexity of energy losses which can occur in conductor applications.

ELECTRON MICROSCOPY

J. Evans, R. Gronsky, G. Thomas, J. Washburn

The electron microscopy research features atomic resolution imaging of cations, which enables defects, grain boundary structure, and composition to be analyzed and related to synthesis conditions and to physical properties. The state-of-the-art facilities of the National Center for Electron Microscopy, including the Atomic Resolution Microscope, are extensively used in this research.

The defect structure of in-situ pulsed-laser-deposited thin films of the Y-Ba-Cu-O superconductor has been observed directly by atomic resolution electron microscopy (Thomas), in a collaboration with Bellcore (R. Ramesh, D.M. Hwang, L. Nazar, T.S. Ravi, A. Inam, X.D. Wu, B. Dutta, T. Venkatesan) and Stanford (A.F. Marshall, T.H. Geballe). In a thin film with nominal composition YBa$_2$Cu$_3$O$_7$ (123), stacking defects corresponding to the cationic stoichiometry of "248," "247," and "224" have been observed. Other defects observed include edge dislocations and anti-phase boundaries. These defects, which are related to the non-equilibrium processing conditions, may well be responsible for the higher critical currents observed in these films compared to single crystals.

The transformation interface between the 124 phase and the 123 phase in the Y-Ba-Cu-O system has been resolved, indicating that there are both low-angle boundary configurations and planar faults with mobile partial dislocations (Gronsky). These defects bring about the transformation between these structurally significant phases. Due to the recent success of S. Jin et al. (Bell Labs) in producing a higher critical current phase 123, by starting with a 124 precursor, this transformation interface assumes special importance. Computer modeling of the transformation sequence has been initiated, and the study has now been extended to thin films, where there is a natural 124 precursor to the 123 phase due to the deposition process.

In situ observations of the orthorhombic-tetragonal phase transformation in $YBa_2Cu_3O_{7-x}$ (Evans), have been performed in collaboration with S. Johnson of SRI International. Heat treatments at temperatures between 25 and 500 C at oxygen pressures of 10 torr have been carried out in an environmental cell of a high voltage transmission electron microscope. Phase identification is performed by examination of electron diffraction patterns. It was found that the original orthorhombic OI form transforms into the OII phase (still orthorhombic, but with a doubling of the a-axis, and with $x=0.5$) at about 250 C. As the temperature is increased further the tetragonal phase forms; this phase is evident at 350 C. As the tetragonal phase is slowly cooled to room temperature, the orthorhombic phase OI reappears. Cycling the temperature repeatedly has indicated the regenerability of the OI phase.

Silver metal contacts to YBCO films are under investigation (Gronsky). They exhibit semicoherent structural interfaces, sharply faceted along close-packing planes, with "threading dislocations" nucleating at the MgO substrate interface, passing through the YBCO film, and penetrating the Ag overlayers. Optimum deposition conditions have been identified, and the necessity of a serious cleansing of the YBCO surface (via ion milling) before Ag deposition has been unambiguously proven.

Structural imaging of polytypoids of high-T_c superconductors continued this year, in collaboration with E. Wang and J.M. Tarascon of Bellcore (Thomas). The newly discovered system $Pb_2Sr_2(Ca,Y)Cu_3O_y$ has been examined by high-resolution electron microscopy (HREM), electron diffraction, and x-ray microanalysis. High-resolution imaging has shown the presence of $Pb_2Sr_2Cu_2O_y$ at the grain boundaries. By analogy to the Bi-Ca-Sr-Cu-O system, it is suggested that this polytypoid could have a lower transition temperature compared to the matrix. This finding may explain the steps in the resistivity plot. Figure 11(a) shows a HREM image of the matrix phase in the [100] zone-axis orientation. The cationic stacking sequence in this image consists of two layers of PbO between which is located a Cu atom in the +1 state (as identified by XPS studies). Between the PbO bi-layers, the stacking sequence consists of Sr-Cu-(Ca,Y)-Cu-Sr repeat units. Figure 11(b) shows the stacking sequence adjacent to a grain boundary. In this case the last unit cell at the grain boundary corresponds to $Pb_2Sr_2Cu_2O_y$, which by analogy to the Bi-Ca-Sr-Cu-O system, may be a superconductor with a low T_c, or even a semiconductor. This situation correlates well with the resistivity plot, which exhibits an onset at 60 K, while zero resistance is obtained only at 20 K.

An electron microscopy study has been carried out to characterize the microstructure of a sintered Gd-Ba-Cu-O superconductor alloy. This

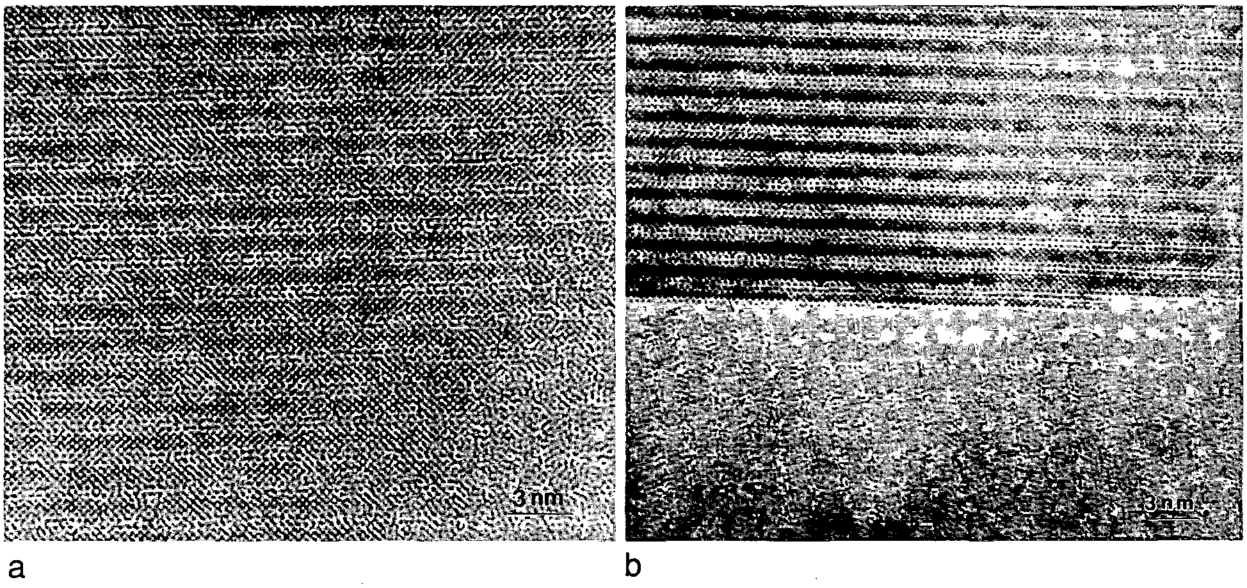


Figure 11(a)
[100] zone axis HREM image of the superconducting phase with the composition $Pb_2Sr_2(Ca,Y)Cu_3O_y$. (b) [110] zone axis image of the superconducting phase, showing the formation of one unit cell of $Pb_2Sr_2Cu_2O_y$ adjacent to the grain boundary. (XBB 902-1228, XBB 902-1229)

work is a collaboration of Thomas with the University of Houston (R.L. Meng, P.H. Hor, and C.W. Chu). The $GdBa_2Cu_3O_7$ phase in an oxygen-annealed sample is orthorhombic, while in a vacuum-annealed sample it is tetragonal. The details of the fine structure in the [001] zone-axis convergent-beam patterns can be used to distinguish between the orthorhombic form and the tetragonal form. In addition to this matrix phase, an amorphous phase is frequently observed at the triple gain junctions. Gd-rich inclusions have also been observed inside the matrix phase.

CERAMIC PROCESSING

ALUMINUM CLADDING OF HIGH-T_C SUPERCONDUCTOR BY THERMOCOMPRESSION BONDING

T.J. Richardson, L.C. De Jonghe

Thermocompression bonding of aluminum to $YBa_2Cu_3O_{7-x}$ (YBCO) has been demonstrated. The superconductor is protected by a thin barrier layer of silver. The specific resistivity of the Al/Ag/YBCO interface was measured at 77 K as a function of current density and is below 3.2×10^{-5} Ωcm^2 for electrode current densities of at least 400 Acm^{-2}. This technique provides a convenient means of cladding bulk superconducting ceramics with a strong, inexpensive, and highly conductive metal.

STAFF

Program Leader
Norman Phillips

Deputy Program Leader
Paul Berdahl [*]

Investigators
Ian Brown [†]
Marvin Cohen
John Clarke
James Evans
Leo Falicov
Didier de Fontaine
Lutgard De Jonghe
Ronald Gronsky
Eugene Haller
William Hassenzahl [†]
Arlon Hunt
Carson Jeffries
Lutgard De Jonghe
Vladimir Kresin
James Michaels
Donald Morris [§]
J.W. Morris, Jr.
Donald Olander
Alexander Pines
Alan Portis
Jeffrey Reimer
Paul Richards
Michael Rubin [*]
Richard Russo [*]
Angelica Stacy
Gareth Thomas
Jack Washburn
Eicke Weber
Peter Yu
Alex Zettl

Scientific Staff
Mehdi Balooch
Richard Dalven
Robert N. Fisher
William Hansen [‡]
Crispin Hetherington

Visiting Scientists
Xiang-lei Mao—University of Science and Technology, Hefei, PRC
Ian Parker—University of Cambridge, England
Didier Robbes—Cannes, France
A.P.B. Sinha—National Chemical Laboratory, Pune, India
Henrik Svensmark—Danish Technical University

Postdoctoral Fellows
Angelika Behrooz
Lincoln Bourne
Michael Dixon [*]
Mark Johnson
Eric Kvam
Phillippe Lerche
Per Lindberg [§]
Nancy Missert
Ramamoorthi Ramesh
Thomas Richardson
Cao Wei
Frederick Wellstood
Xiao-dong Xiang

---

[*] Applied Science Division
[†] Accelerator and Fusion Research Division
[‡] Engineering Division
[§] Physics Division

Graduate Students
Stuart Adler
M. Asta
K. Atwal
Gabriel Briceno
Brian Burk
C. Burmester
G. Ceder
William Creager
Michael Crommie
Boris Fayn §
M. Fendorf
Mark Ferrari
K. Fortunati
William Ham
Storrs Hoen
C. Brad Hopper *
Qing Hu
C.J. Jou
Steven Keller
Yountai Kim
John Kingston
Harry Lam
Amy Liu
M.E. Mann
Amit Mararthe §
Carl Mears
Andrew Miklich
David Miller
O.R. Monteiro
Michael Nahum
Pravin Narwankar §
Nathan Newman
Janice Nickel §
P. Pinsukanjana
Ronald Reade *
Sara Stoll
Simon Verghese
Edward Yin *

Research Assistants
John Dykema §
Brian Kasper §
William Lewis
Jeffry McMillan *
Andrea Markelz §
Justin Paola §
Michael Powers
Gino Segre §
John Surnow §
Ken Takano §
Victor Shum §
William Vinje §

Administrative Support
Learr English
Charlotte Standish *

INDUSTRY INTERACTIONS

Contracts

- A grant from the California Competitive Technology Program supports much of the effort to develop commercial high-T_c SQUID magnetometers. This work includes collaborations with Stanford and Conductus, Inc.

Industrial Collaborations

- H. Morawitz of IBM Almaden is collaborating with V. Kresin on the phonon-plasmon mechanism of high temperature superconductivity.
- H.J. Rosen, M.C. Krantz, and R.M. Macfarlane of IBM Almaden are collaborating with D.E. Morris on Raman scattering.
- The group of T. Venkatesan at Bellcore has provided high-quality thin-film samples for collaborative investigations with J. Clarke (flux noise), P. Richards (far-infrared spectroscopy), and G. Thomas (electron microscopy of defects). R. Ramesh of Bellcore also contributed to the electron microscopy research.

- Conductus, Inc. is collaborating with J. Clarke (SQUIDs) and with P. Richards (high-T_c bolometers). As a part of these collaborations, Conductus provides high-quality YBCO films.
- US, Inc., a manufacturer of sputtering equipment, is collaborating with M. Rubin on film deposition research.
- The Rocketdyne Division of Rockwell International is collaborating with R. Russo on pulsed laser deposition of high-T_c thin films.
- S. Johnson of SRI International is collaborating with J. Evans on electron microscopy studies of the tetragonal-orthorhombic phase transition in $YBa_2Cu_3O_{7-x}$.

Technology Transfer

- The YBCO/$SrTiO_3$/YBCO crossover technology is being patented and transferred to Conductus, Inc.
- The high-T_c superconducting microbolometer is being patented and transferred to Conductus, Inc.
- The long-laser-pulse method of producing superconducting thin films is being patented.
- A day of introductory reviews was presented at the Conference on the Science and Technology of Thin-Film Superconductors (Colorado Springs).
- LBL was active in the organization of the International Conference on Materials and Mechanisms of Superconductivity-HTSC (Stanford). This Conference drew 1200 participants who presented 1000 papers, most of which are now published in Physica C.

Industrial Fellow

- Mark Colclough of Conductus, Inc. works at LBL with J. Clarke's group on SQUID R&D.
- Scott Sachtien of Conductus, Inc. worked at LBL with P. Richard's group on bolometer research.

BIBLIOGRAPHY

Refereed Journal Articles

Balooch, M., D.R. Olander, and R.E. Russo, "Y-Ba-Cu-O Superconducting Films Produced by Long-Pulse Laser Vaporization," *Appl. Phys. Lett.*, vol. 55, p. 197, 1989.

Barbee, III, T.W., A. Garcia, and M. Cohen, "First-Principles Prediction of High-Temperature Superconductivity in Metallic Hydrogen," *Nature*, vol. 340, p. 369, 1989.

Burmester, C.P. and L.T. Wille, "Monte Carlo Study of Transient States of Order in $YBa_2Cu_3O_z$," *Phys. Rev. B*, vol. 40, p. 8795, 1989.

Clarke, J., "High T_c SQUIDs Show Enhanced Potential for Application," *ISTEC Journal*, vol. 2, p. 25, 1989.

Crommie, M.F., A.Y. Liu, A. Zettl, M.L. Cohen, P. Parilla, M.F. Hundley, W.N. Creager, S. Hoen, and M.S. Sherwin, "C-axis Stress Dependence of Normal and Superconducting State Properties of $YBa_2Cu_3O_7$," *Phys. Rev. B*, vol. 39, p. 4231, 1989.

de Fontaine, D., M.E. Mann, and G. Ceder, "States of Partial Order in $YBa_2Cu_3O_z$," *Phys. Rev. Lett.*, vol. 63, p. 1300, 1989.

Falicov, L.M., "Superconductivity, A Brief Introduction to its Phenomenolgy and Theories," *IEEE J. Quantum Electronics*, vol. 25, p. 2358, 1989.

Ferrari, M.J., M. Johnson, F.C. Wellstood, J. Clarke, A. Inam, X.D. Wu, L. Nazar, and T. Venkatesan, "Low Magnetic Flux Noise Observed in Laser-Deposited *in situ* Films of $YBa_2Cu_3O_{y-\delta}$ and Implications for High T_c SQUIDs," *Nature*, vol. 341, p. 723, 1989.

Ferrari, M.J., M. Johnson, F.C. Wellstood, J. Clarke, P.A. Rosenthal, R.H. Hammond, and M.R. Beasley, "Flux Noise and Flux Creep in YBCO Thin Films," *IEEE Trans. Magn.*, vol. 25, p. 806, 1989.

Green, S.M., Y. Mei, A.E. Manzi, and H.L. Luo, "Effects of Compositional Variations on the Properties of Superconducting $(Bi, Pb)_2\ Sr_2Ca_2Cu_3O_\delta$," *J. Appl. Phys.*, vol. 66, p. 728, 1989.

Ham, W.K., S.W. Keller, J.N. Michaels, A.M. Stacey, D. Krillov, D.T. Hodul, and R.H. Flemming, "Partial Substitution of ^{18}O in $YBa_2Cu_3O_7$: Investigations of Inhomogeneities and their Effect on T_c," *J. of Mat. Res.*, vol. 4, p. 504, 1989.

Hassenzahl, W., "Superconducting Magnetic Energy Storage," *IEEE Trans. Magn.*, vol. 25, p. 750, 1989.

Hazen, R.M., L.W. Finger, and D.E. Morris, "Crystal Structure of $Dy\ Ba_2\ Cu_4\ O_8$: A New Bulk Superconductor," *Appl. Phys. Lett.*, vol. 54, p. 1057, 1989.

Hillebrecht, F.U., J. Fraxedas, L. Ley, H.J. Tradahl, J. Zaanen, W. Braun, M. Mast, H. Petersen, M. Schaible, L.C. Bourne, P. Pinsukanjana, and A. Zettl, "Experimental Electronic Structure of $Bi_2CaSr_2O_{8+\delta}$," *Phys. Rev. B*, vol. 39, p. 236, 1989.

Hoen, S., W.N. Creager, L.C. Bourne, M.F. Crommie, T.W. Barbee III, M.L. Cohen, and A. Zettl, "Oxygen Isotope Study of $YBa_2Cu_3O_7$," *Phys. Rev. B*, vol. 39, p. 2269, 1989.

Hu, Q. and P.L. Richards, "Design Analysis of a High-T_c Superconducting Microbolometer," *Appl. Phys. Lett.*, vol. 55, p. 2444, 1989.

Imer, J.-M., F. Patthey, B. Dardel, W.-D. Schneider, Y. Baer, Y. Petroff, and A. Zettl, "Reply to Comment by Chang et al.," *Phys. Rev. Lett.*, vol. 63, p. 102, 1989.

Imer, J.-M., F. Patthey, B. Dardel, W.D. Schneider, Y. Baer, Y. Petroff, and A. Zettl, "High-Resolution Photoemission Study of the Low-Energy Excitations Reflecting the Superconducting State of Bi-Sr-Ca-Cu-O Single Crystals," *Phys. Rev. Lett.*, vol. 62, p. 336, 1989.

Jeffries, C.D., Q.H. Lam, Y. Kim, C.M. Kim, A. Zettl, and M.P. Klein, "Nonlinear Electrodynamics in the Granular Superconductor $YBa_2Cu_3O_7$: Experiments and Interpretation," *Phys. Rev. B*, vol. 39, p. 11526, 1989.

Jou, C.J. and J. Washburn, "Formation of Coherent Twins in $YBa_2Cu_3O_{7-\delta}$ Superconductors," *J. Mater. Res.*, vol. 4, p. 795, 1989.

Krantz, M.C., H.J. Rosen, J.Y.T. Wei, and D.E. Morris, "Raman Scattering from Superconducting Gap Excitations in $Tl_2Ca_2Ba_2Cu_3O_{10}$ Single Crystals," *Phys. Rev. B*, vol. 40, p. 2635, 1989.

Kresin, V.Z., G. Deutscher, and S.A. Wolf, "Properties of the New High-T_c Materials: An Analysis Based on Fermiology," *IEEE Trans. Magn.*, vol. 25, p. 2333, 1989.

Lam, Q.H. and C.D. Jeffries, "Harmonic Generation and Flux Quantization in Granular Superconductors," *Phys. Rev. B*, vol. 39, p. 4772, 1989.

Liu, M. and L.C. De Jonghe, "Effect of Geometry and Interfacial Resistance on Current Distribution and Energy Dissipation at Metal/Superconductor Junctions," *J. Mater. Res.*, vol. 4, p. 530, 1989.

Morris, D.E., N.G. Asmar, J.H. Nickel, J.Y.T. Wei, and J.E. Post, "Stability of 124, 123, and 247 Superconductors," *Physica C.*, vol. 159, p. 287, 1989.

Morris, D.E., N.S. Asmar, J.Y.T. Wei, J.H. Nickel, R.L. Sid, J.S. Scott, and J.E. Post, "Synthesis and Properties of the 2:4:7 Superconductors $R_2Ba_4Cu_7O_{15-x}$ (R=Y, Eu, Gd, Dy, Ho, Er)," *Phys. Rev. B*, vol. 40, p. 11406, 1989.

Morris, D.E., C.T. Hultgren, A.M. Markelz, J.Y.T. Wei, N.F. Asmar, and J.H. Nickel, "Concentration Effect on T_c of Bi-Ca-Sr-Cu-O Superconductor," *Phys. Rev. B*, vol. 39, p. 6612, 1989.

Morris, D.E., J.H. Nickel, J.Y.T. Wei, N.G. Asmar, J.S. Scott, U.M. Scheven, C.T. Hultgren, A.G. Markelz, J.E. Post, P.J. Heaney, D.R. Veblen, and R.M. Hazen, "Eight New High Temperature Superconductors with the 1:2:4 Structure," *Phys. Rev. B*, vol. 39, p. 7347, 1989.

Portis, A.M. and K.W. Blazey, "Microwave Studies of Granular Superconductivity," *IEEE Trans. Magn.*, vol. 25, p. 2390, 1989.

Ramesh, R., S.M. Green, C. Jiang, Y. Mei, H.L. Luo, and G. Thomas, "Bi-Ca-Sr-Cu-O Superconductors: The Connectivity Issue," *IEEE Trans. Magn.*, vol. 25, p. 2360, 1989.

Ramesh, R., G. Thomas, R.L. Meng, P.H. Hor, and C.W. Chu, "Electron Microscopy of a Gd-Ba-Cu-O Superconductor," *J. Mater. Res.*, vol. 4, p. 515, 1989.

Richards, P.L., J. Clarke, R. Leoni, Ph. Lerch, S. Verghese, M.R. Beasley, T.H. Geballe, R.H. Hammond, P. Rosenthal, and S.R. Speilman, "Feasibility of the High-T_c Superconducting Bolometer," *Appl. Phys. Lett.*, vol. 54, p. 283, 1989.

Richards, P.L., S. Verghese, T.H. Geballe, and S.R. Spielman, "The High-T_c Superconducting Bolometer," *IEEE Trans. Magn.*, vol. 25, p. 1335, 1989.

Rosenthal, P., R.H. Hammond, M.R. Beasly, R. Leoni, Ph. Lerch, and J. Clarke, "Low Frequency Resistance Fluctuations in Films of High Temperature Superconductors," *IEEE Trans. Magn.*, vol. 25, p. 973, 1989.

Rubin, M.I., G. Brown, E. Yin, and D. Wruck, "Ion Implantation of Sputtered Y-Ba-Cu-O Films," *J. Appl. Phys.*, vol. 66, p. 3940, 1989.

Svensmark, H. and L.M. Falicov, "Ginzburg-Landau Theory of Deformable Superconductors," *Phys. Rev. B*, vol. 40, p. 201, 1989.

Urbach, J.S., D.B. Mitzi, A. Kapitulnik, J.Y.T. Wei, and D.E. Morris, "Low-Temperature Specific Heat of Single Crystal $Bi_2CaSr_2Cu_2O_8$ and $Tl_2Ca_2Ba_2Cu_3O_{10}$," *Phys. Rev. B*, vol. 39, p. 12391, 1989.

Wille, L.T., "Mean-Field Theory of Oxygen-Vacancy Ordering in $YBa_2Cu_3O_{7-\delta}$" *Phys. Rev. B*, p. 6931, 1989.

Xiang, X.-D., M. Chung, J.W. Brill, S. Hoen, P. Pinsukanjana, and A. Zettl, "Elastic Properties of Single Crystal $Bi_2Sr_2CaCu_2O_8$," *Solid State Comm.*, vol. 69, p. 833, 1989 .

Refereed Refereed Conference Proceedings

Morris, Jr., J.W. and A.G. Khachaturyan, "The Structural Properties of $YBa_2Cu_3O_{6+\delta}$," *Proceedings of the 1989 Materials Research Society International Meeting on Advanced Materials*, vol. 6, p. 563, 1989.

Other Publications

Ramesh, R., S.M. Green, and G. Thomas, "Microstructure Property Relationships in the Bi (Pb) Sr-Ca-Cu-O Ceramic Superconductors," in *Studies of High Temperature Superconductors*, ed. A. Narlikar, vol. 4, Nova Science, 1989.

Zettl, A., A. Behrooz, G. Briceno, W.N. Creager, M.F. Crommie, S. Hoen, and P. Pinsukanjana, "Anisotropic Transport in Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O," in *Mechanisms of High-Temperature Superconductors*, ed. H. Kaminura, and A. Oshiyama, p. 249, Springer Verlag, 1989. (A. Behrooz, IBM Postdoctoral Fellow.)

LBL Reports (including journal articles submitted or in press)

Behrooz, A. and A. Zettl, *Normal State A.C. Conductivity of $YBa_2Cu_3O_{7-\delta}$.* (A. Behrooz, IBM Postdoctoral Fellow.)

Briceno, G. and A. Zettl, *Tunneling Spectroscopy in $Bi_2Sr_2CaCu_2O_8$: Is the Energy Gap Anisotropic?.*

Briceno, G. and A. Zettl, *Variable Hall Coeficient in $Bi_2Sr_2CaCu_2O_{8-x}$ Across the Insulator-Metal Transition.*

Ceder, G., M. Asta, W.C. Carter, M. Kraitchman, and D. de Fontaine, "Phase Diagram and Low Temperature Behavior of Oxygen Ordering in $YBa_2Cu_3O_z$ using ab initio Interactions," *Phys. Rev. B.* (Submitted.)

Ceder, G., M. Asta, and D. de Fontaine, "Oxygen Ordering in $YBa_2Cu_3O_z$ at Low Temperature," *Mat. Res. Soc. Symp. Proc.* (In press.)

Cohen, M.L., LBL 27615, "Theoretical Overview of Proposed Mechanisms for High-Temperature Superconductivity," *Proc. 9th International Conf. on Vac. Ultraviolet Radiation Physics.* (In press.)

Cohen, M.L., D.R. Penn, and T.W. Barbee III, LBL 27895, "Limitations on Electronic Mechanisms for High Temperature Superconducting Oxides," *Proc. 9th Int. Conf. on Vac. Ultraviolet Radiation Physics.* (In press.)

Crommie, M.F., G. Briceno, and A. Zettl, "Transport and Tunneling in $Bi_2Sr_2CaCu_2O_{8-x}$," *Physica C.* (In Press.)

Crommie, M.F., A.Y. Liu, M.L. Cohen, and A. Zettl, LBL-26985, "Universality of Transport Properties of High-T_c Superconductors," *Phys. Rev. Lett.* (Submitted.)

Ferrari, M.J., M. Johnson, F.C. Wellstood, J. Clarke, T.H. Geballe, A. Kapitulnik, and M.R. Beasley, "Distribution of Flux Pinning Energies in $YBa_2Cu_3O_{7-\delta}$ and $Bi_2Sr_2CaCu_2O_{8-\delta}$ from Flux Noise," *Phys. Rev. Lett.* (Submitted.)

Ferrari, M.J., M. Johnson, F.C. Wellstood, J. Clarke, D. Mitzi, P.A. Rosenthal, M.R. Beasley, A. Kapitulnik, and V.Y. Lee, "Flux Noise Mechanisms in Copper-Oxide Superconductors," *Physica C.* (Submitted.)

Fisher, R.A., J.E. Gordon, S. Kim, and N.E. Phillips, "Lattice and Electronic Specific Heat of $YBa_2Cu_3O_7$," *Physica C.* (Submitted.)

Fisher, R.A., S. Kim, Y. Wu, N.E. Phillips, H. Ledbetter, and K. Togano, "Specific Heat in the High-T_c Superconductor System (Bi, Pb)-Ca-Sr-Cu-O," *Physica C.* (Submitted.)

Gordon, J.E., M.L. Tan, R.A. Fisher, and N.E. Phillips, LBL-25845, "Specific Heat Data of High-T_c Superconductors: Lattice and Electronic Contributions," *Solid State Communications.* (Submitted.)

Kim, S., R.A. Fisher, N.E. Phillips, and J.E. Gordon, "Specific Heat of $YBa_2(Cu_{3-x}M_x)O_7$ with M=Cr or Zn," *Physica C.* (Submitted.)

Kingston, J.J., F.C. Wellstood, P. Lerch, A.H. Miklich, and J. Clarke, "Multilayer $YBa_2Cu_3O_x$ - $SrTiO_3$ $YBa_2Cu_3O_x$ Films for Insulating Crossovers," *Appl. Phys. Let.* (Submitted.)

Krantz, M.C., H.J. Rosen, R.M. Macfarlane, N.G. Asmar, and D.E. Morris, "Raman Study of Bulk $YBa_2Cu_4O_8$ High-T_c Superconductors," *Physica C.* (Submitted.)

Krantz, M.C., H.J. Rosen, J.Y.T. Wei, and D.E. Morris, "Raman Scattering from Superconducting Gap Excitations in $Tl_2Ca_2Ba_2Cu_3O_{10}$," *Physica C.* (Submitted.)

Kresin, V.Z., "High T_c Superconductor in an AC Field," *J. Superconductivity.* (Submitted.)

Kresin, V.Z. and H. Morawitz, "Normal and Superconducting Properties of the New High T_c Oxides and the Phonon-Plasmon Mechanism of Superconductivity," *High T_c Superconductivity.* (In press.)

Kresin, V.Z. and S.A. Wolf, "A Method for Evaluating the Electron-Phonon Coupling in Cuprates from Heat Capacity Measurements," *Physica C.* (In press.)

Morris, D.E., N.G. Asmar, J.Y.T. Wei, J.H. Nickel, and J.E. Post, "Stability and Interconversion Between the 124, 123, and 247 Superconducting Phases in the Y-Ba-Cu-O System," *Physica C.* (Submitted.)

Morris, D.E., P. Narwankar, A.P.B. Sinha, K. Takano, B. Fayn, and V.T. Shum, "Calcium Substituted Y-BA-Cu-O Superconductors with Enhanced T_c Synthesized at Elevated Oxygen Pressures," *Phys. Rev. B.* (In press.)

Morris, D.E., J.Y.T. Wei, N.G. Asmar, J.H. Nickel, and J.E. Post, "Rare Earth Substituted 124 and 247 Superconductors," *Physica C.* (Submitted.)

Portis, A.M., D.W. Cooke, and H. Piel, "Microwave Surface Impedance of Granular Superconductors," *Physica C.* (In press.)

Ramesh, R., S.M. Green, H.L. Luo, and G. Thomas, "Microstructure-Property Correlations in the Bi(Pb)-Sr-Ca-Cu-O Superconducting System," *Physica C.* (Submitted.)

Ramesh, R., D.M. Hwang, T. Venkatesan, T.S. Ravi, L. Nazar, A. Inam, X.D. Wu, B. Dutta, G. Thomas, A.F. Marshall, and T.H. Geballe, "Direct Observation of Structural Defects in Laser Deposited Superconducting Y-Ba-Cu-O Thin Films," *Science.* (In press.)

Talvacchio, J., LBL-26578, *Bibliography of High-T_c Superconductive Films,* January 1989. (J. Talvacchio, Westinghouse Electric Corporation.)

Yau, W.-F., A.M. Portis, E.R. Weber, Z.Z. Wang, and N.P. Ong, "Complex Microwave Susceptibility of Natural SQUID Structures," *Physica C.* (In press.)

Yau, W.-F., R. Ramesh, A.M. Portis, E.R. Weber, G. Thomas, S.M. Green, and H.L. Luo, "Magnetic-Field Modulated Microwave Absorption Study of Pb-Modified Bi-Ca-Sr-Cu-O," *Physica C.* (In press.)

Zandbergen, H.W., R. Gronsky, and G. van Tendeloo, LBL-26397, "Atomic Structure of Grain Boundaries and Surfaces in $YBa_2Cu_3O_{7-\delta}$," *Journal of Superconductivity.* (Submitted.)

Zettl, A., L.C. Bourne, W.N. Creager, M.F. Crommie, and S. Hoen, *Electron-Phonon Interactions in the High-Temperature Oxide Superconductors: Isotope Effects and Elasticity Studies.*

Invited Talks

Clarke, J., *High-T_c dc SQUIDS,* International Superconducting Technology Center, 1989.

Clarke, J., *SQUIDs, Present and Future,* Plenary Lecture, Annual Solid State Physics Conference of the Institute of Physics, Warwick, England, December 1989.

Clarke, J., *Flux Noise and Pinning Energies in High-T_c Superconductors,* Imperial College, London, November 1989.

Clarke, J., *Superconductors, SQUIDs and Brains,* Clare Hall, Cambridge, England, November 1989.

Clarke, J., *Technology of High-T_c SQUIDs*, Seminar, Interdisciplinary Research Center for Superconductivity, University of Cambridge, England, November 1989.

Clarke, J., *Macroscopic Quantum Tunneling*, Bristol University, England, October 1989.

Clarke, J., *Noise Characteristics of HTSC Thin Films*, SPIE Symposium on Processing of Tilms for High-T_c Superconductivity Electronics, Santa Clara, October 1989.

Clarke, J., *Macroscopic Quantum Tunneling in Josephson Junctions*, University of Trondheim, Norway, September 1989.

Clarke, J., *SQUIDs and the Impact of High-Temperature Superconductivity*, Superconductivity - Microjoule Applications, Cambridge, England, September 1989.

Clarke, J., *Superconducting QUantum Interference Devices*, Superconductivity - Microjoule Applications, Cambridge, England, September 1989.

Crommie, M.F., G. Briceno, and A. Zettl, *Transport and Tunneling in* $Bi_2Sr_2Cu_2O_{8-x}$, M^2S-HTSC Conference, Stanford, CA, July 1989. (To be published in the Proceedings.)

Ferrari, M.J., M. Johnson, F.C. Wellstood, J. Clarke, D. Mitzi, P.A. Rosenthal, C.B. Eom, T.H. Geballe, A. Kapitulnik, and M.R. Beasley, *Distribution of Pinning Energies in* $YBa_2Cu_3O_{7-\delta}$ *and* $Bi_2Sr_2CaCu_2O_{8-\delta}$ *from Flux Noise*, Materials and Mechanisms of Superconductivity Conference - High-Temperature Superconductors, Stanford, CA, July 1989.

Kresin, V.Z., *Proximity Effect and High T_c Superconductivity*, 2nd International Symposium on Superconductivity, Tsukuba City, Ibaraki, Japan, November 1989.

Richards, P.L, *High T_c Applications: Infrared and Millimeter Wave Sensors*, American Vacuum Society 36th National Symposium and Topical Conference, Boston, MA, October 1989.

Richards, P.L., *High T_c Superconducting Infrared Detectors*, Second Workshop on High-Temperature Superconducting Electron Devices, Hokkaido, Japan, June 1989.

Richards, P.L., *Progress in Superconducting Mixers and Detectors for Infrared and Millimeter Waves*, 1989 International Superconductivity Electronics Conference, ISEC '89, Tokyo, Japan, June 1989.

Richards, P.L., *Bolometric Infrared Sensors: Non-Superconducting and Superconducting*, 1989 Superconducting Electronics Workshop, St. Michaels, MD, October 1989.

Thomas, G., *High Resolution Electron Microscopy and Microanalysis of Ferrites and Cuprates*, ICF - 5 Conference, Bombay, India, January 1989.

Thomas, G., W.F. Yau, R. Ramesh, A.M. Portis, E.R. Weber, S.M. Green, and H.L. Luo, *Field-Modulated Microwave Absorption Study of Pb-Modified Bi-Ca-Sr-Cu-O*, Intl. M^2S-HTSC Conference, Stanford, CA, July 1989.

Contributed Talks

Kueper, T. and L.C. De Jonghe, *Electrodeposition of Silver and Aluminum in YBCO Superconductors*, Am. Ceram. Soc., Indianapolis, IN, April 1989.

Ramesh, R., E. Wang, J.M. Tarascon, and G. Thomas, *Structural Imaging of Polytypoids in High T_c Superconductors*, EMSA Meeting, San Antonio, TX, July 1989.

Richards, P.L and Q. Hu, *Progress in Superconducting Mixers and Detectors for Infrared and Millimeter Waves*, 1989 International Superconductivity Electronics Conference (ISEC '89), Tokyo, Japan, June 1989. (Published in the Proceedings, v. 77., 1989.)

Richardson, T.J. and L.C. De Jonghe, *Oxidation Kinetics and Microcracking in Superconducting YBCO*, 1989 TMS Annual Meeting and Exhibition, Las Vegas, Nevada, February 1989. (To be published in the proceedings.)

Polymers and Composites

Enzymatic Synthesis of Materials
Anisotropic Polymeric Materials
Polymer-Surface Interactions

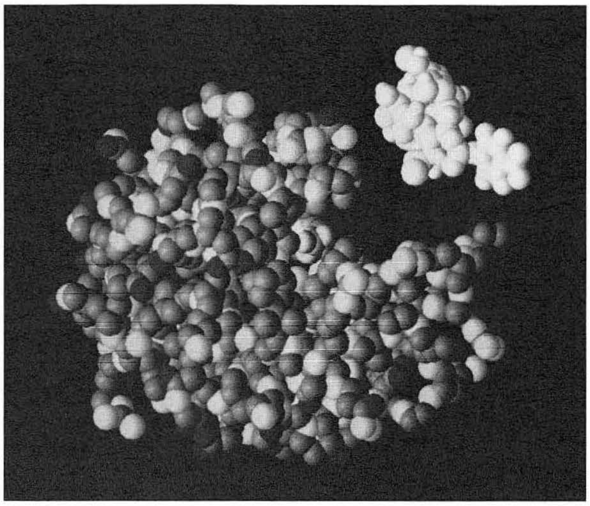
Polymers and Composites Program

The CAM Polymers and Composites Program is concerned with the prediction and control of structure development in high-performance polymers and the enzymatic synthesis of novel polymeric and related types of materials. The program focuses on three areas.

ENZYMATIC SYNTHESIS OF MATERIALS—Enzymes catalyze reactions in a manner that makes them ideally suited to the synthesis of materials. They produce highly uniform and regular products at low temperatures and pressures and leave no side products that might be toxic or wasteful. The CAM program on enzymatic synthesis of materials seeks to explore the application of recently developed techniques in molecular biology, biochemistry and bio-organic chemistry to the synthesis of materials and to understand and exploit the expected enhanced properties of these materials. Research is focused on using enzymes as they are found in nature, on engineering enzymes through genetic and chemical means, and on creating new enzymes—all for the purpose of allowing them to catalyze reactions with non-biological substrates and to produce materials with interesting and important properties. Target products include modified polyamides and polysaccharides, non-biological materials including those polymerized through carbon-carbon linkages, and metal or semiconductor surfaces modified for surface properties or for applications in devices such as sensors.

Significant highlights of the past year include:

- Synthesis of novel polymers through chemical polymerization of enzymatically modified monomers.
- Enzymatic synthesis and polymerization of fluorinated and thiolated carbohydrate monomers.
- Engineering of an enzyme for further enhanced thermal stability.
- Engineering of an enzyme for alteration of its substrate specificity.



ANISOTROPIC POLYMERIC MATERIALS are characterized by a "domain" structure in the melt— micron-scale regions of high local order, interconnected by submicron regions of rapid change in local orientation. The orientation and flow of the molecules in a given domain have a major effect on the macroscopic properties of the polymer product. During the past year:

- Rheological and NMR spectroscopy experiments established that the flow properties of liquid crystalline polymers are dominated by a three phase microstructure: the nematic liquid; small, high-melting crystallites of homopolymer; and a temperature-dependent non-periodic crystal phase with the stoichiometry of the bulk polymer.
- Differential scanning calorimetry experiments on processed, filled liquid crystalline polymer indicated that compounding at temperatures below the normal melt processing temperature induces structural changes that can be annealed out at processing temperatures.

POLYMER-SURFACE INTERACTIONS play a significant role in the development of bulk structure during processing and of the mechanical properties of the manufactured object, failure and fatigue of composite materials, the properties of thin films for microelectronics and food packaging applications, and in performance areas such as tribology and biomedical applications such as implant wear. During the past year:

- A Molecular Mechanics simulation of thin films of a glassy polymer sandwiched between smooth solid surfaces was completed.
- Density functional theory calculations were used to study details of interfacial bonding at the interfaces of oxygen- and nitrogen-containing oligomers with aluminum.
- The theory of adhesive failure between non-crystalline polymers and a non-polymeric surface was used as a framework for the analysis of processing instabilities in melts at high stress levels.

Above: The enzyme lysozyme binds its substrate and then synthesizes its product. (XBC 890-9744)

ENZYMATIC SYNTHESIS OF MATERIALS*

The concept of using purified enzymes in the synthesis of materials is a relatively new one. Its validity rests on the demonstration that recent advances in molecular biology and biochemisty allow the manipulation of the substrate and reaction specificity of enzymes. Considerable research remains to be done, however, before these advances can be routinely applied to the synthesis of useful materials. In support of this goal, the CAM program has focused on:

- understanding the fundamental properties of enzymes and enzyme-catalyzed reactions that could be involved in the synthesis of materials.
- engineering enzyme structure, activity and reaction conditions to allow the synthesis of materials from novel substrates.
- determining the structure/function relationships of enzyme-synthesized materials, predicting properties from structure, and designing structures to achieve target properties.

ENZYMATIC SYNTHESIS OF POLYSACCHARIDES

M. Bednarski, H. Blanch, D. Clark, J. F. Kirsch, M. Corey, S. Edwards,
C. Hobbs, A. Michiels, L. Oehler, A. Wong

Polysaccharides perform a wide range of functions and there is therefore a great deal of interest in the properties of unusual derivatives that might be produced enzymatically. Fluorinated polysaccharides may, for example, find commercial use as lubricants, adhesives or plastic additives. One of the most important obstacles to be overcome in using enzymes in the synthesis of polysaccharides lies in the fact that in many cases, degradative hydrolysis rather than synthesis is thermodynamically favored. Phosphorylases are enzymes that catalyze the reversible cleavage of the polymer glycogen to form glucose-1-phospate (Figure 1) (MB, LO). In this case, synthesis of polymer can be driven through the coupling of this reaction with others that involve the consumption of the phosphate formed as a byproduct. In an attempt to force the enzyme to make novel polymers using nonnatural monomers, a variety of glucose derivatives were synthesized, including those with fluorines in the 2, 3 and 6 position, thiols in the 3 and 5 position, azide in the 6 and amines in the 2, 3 and 6 position. To date, fluorinated (6 position) and thiolated derivatives (3 and 5 position) have been shown to be substrates for the enzyme and likely to

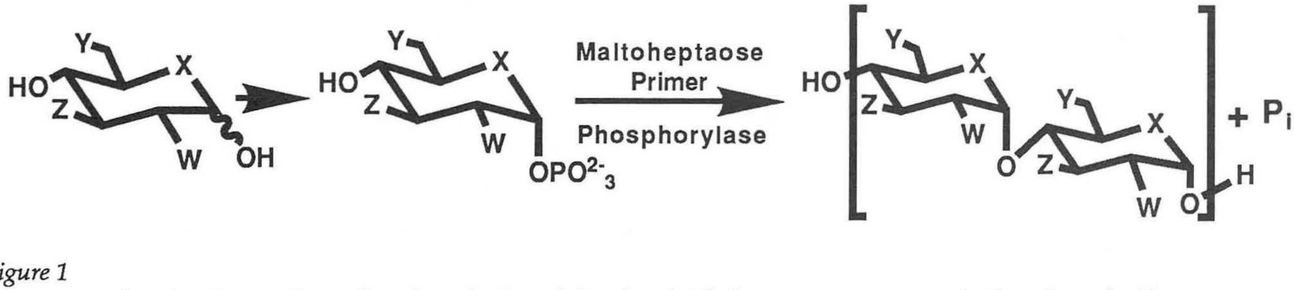


Figure 1
The enzyme phosphorylase catalyzes the polymerization of phosphorylated glucose monomers to make the polysaccharide glycogen. Inorganic phosphate is released in the process and removed enzymatically to pull the reaction towards synthesis. (XBL 901-262)

---

* Additional support from the Division of Energy Biosciences, U.S. Department of Energy.

	SUBSTITUTION			
POSITION	NH_3	F	S(H)	N_3
W	✓	✓		
X			✓✓	
Y	✓	✓✓		✓
Z	✓	✓	✓✓	

Table 1
Glucose phosphate monomers have been synthesized with the indicated substitutions (✓). Positions W, Y, and Z, as shown in figure 1, are normally OH, X is O in the ring form, OH in the straight chain form. Monomers with substitutions (✓✓) were shown to be active substrates of the enzyme phosphorylase, with actual polymerization demonstrated for 6-flouro derivative.

be polymerizable into unnatural polysaccharides (Table 1). The polymer with flourine in the 6 position has been made. Scale-up of these syntheses is progressing as is the modeling of the fit of these substrates in the active site to determine how controlled alterations of the enzyme active site through mutagenesis might allow it to polymerize others.

Another solution pursued for the problem of synthesis rather than degradation involves the modification of the enzyme so that its solubility in organic solvents is increased. Reactions run in those solvents, which, of course, have a significantly reduced concentration of water, would have their equilibrium shifted substantially to the synthetic direction. In one such study, the enzyme lysozyme was modified by treating it with cyanuric chloride-activated polyethylene glycol (JFK, SE). The modified protein was shown to be as active as native lysozyme in aqueous solution. Its activity in organic solvents is now being determined.

A third solution is being pursued through mutagenesis of the enzyme and custom design of a new substrate (JFK, MB, CH, MC). Based upon the known crystal structure and mechanism of action of lysozyme, substitutions of individual active site amino acids were designed to prevent a key enzyme-polymer interaction that is necessary for activity. New oligomer substrates were designed so that the the mutant enzyme could react with them to allow synthesis. The product polymer would be the same as that made with "normal" oligomers and thus resistant to degradation. Construction of the mutant enzyme has been achieved. One substrate has been synthesized and synthesis of the others are in progress.

Another enzyme whose catalytic ability has been explored for polymer synthesis is dextransucrase (HB, DC, AW). This enzyme is different from the others studied in that it naturally acts in the synthetic mode converting sucrose into $\alpha(1\rightarrow6)$ "polyglucose" and fructose. Since glucose-1-fluoride is a known substrate of dextransucrase, a number of derivatives were synthesized (MB, LO, AM) and assayed (HB, DC, AM, AW) as substrates, including the 2- and 3-fluoro, and the 3- and 5-thio-. Surprisingly none led to polymer synthesis. All the fluorides were, however, found to be competitive inhibitors, suggesting that although they could bind to the enzyme, their added fluorines interfered with the polymerization reaction.

The fluoronated derivatives were also tested as substrates for the enzymes cyclodextrin glucosyl transferase and α-amylase. Although both enzymes have transfer activity with underivatized glucose polymers, neither exhibited transferase activity with the derivatized glucose substrates.

These results, combined with the work of others on glycosidases, polymerases and transferases, suggest that these enzymes are far more specific in binding their substrates than the degradative enzymes such as phosphorylase. Site-directed mutagenesis should, however, allow modification of their active sites, permitting them to accept new substrates. Since these enzymes are, by their nature, synthetic enzymes, they might be easier to use than those whose reactions favor degradation.

ENZYMATIC SYNTHESIS OF POLYAMIDES

J. F. Kirsch, C. H. Wong, J. A. Bibbs, J. Petithory

Polypeptides with well defined secondary structure have potential for the development of novel materials. Structures such as helices, sheets, and turns exist in many proteins and are involved in the formation of higher-order protein structures and biological activities. Polypeptides which mimic these regular structures may thus have properties useful for a number of applications. Incorporation of functional groups into such regular polypeptides will create a new class of molecules which could find use in materials science, biology, and chemistry.

Chemical synthesis of polypeptides has traditionally been dependent on the anhydride method using phosgene. The need for the milder, stereoselective, racemization-free, catalytic procedure achievable through the use of enzymes is timely and important. Work in this area is currently focused in two areas: the cloning and expression of one such enzyme, papain; and the modification of another such enzyme, subtilisin, and of its reaction conditions.

The extended amino acid recognition site of papain should facilitate its use in the synthesis of rationally designed polymers. Considerable success has been achieved over the last year in that the DNA coding region for this protein has been successfully cloned from the genome of the papaya plant and its nucleotide sequence has been confirmed (JFK, JP). The last remaining hurdle is to express this cloned gene (i.e., to synthesize the protein in an easily manipulated host organism such as E. coli).

Monomers	Degree of Polymerization	Yield (%)
1. *Single Amino Acids*		
Met-OMe·HCl	40	10 -15
Homo-Phe-OEt·HCl	ND	ND
Gly-OEt·HCl	20	3
2. *Dipeptides*		
Gly-Gly-OEt·HCl	9.5	20
Glu(Bzl)-Glu(Bzl)-OBzl·TFA	ND*	2
Leu-Met-OMe·TFA	ND*	10
Ala-Met-OET·TFA	11	15
Phe-Met-OMe-TFA	3	10
Ala-Tyr-OBzl·TFA	ND*	ND
3. *Tripeptides*		
Ala-Tyr-Met-OEt·TFA	ND*	10
Ala-Val-Phe-OMe·TFA	8	22

ND*: Insoluble precipitate is formed. The degree of polymerization was not determined due to the insolubility of the product.

Table 2
Synthesis of polyamides using the enzyme subtilisin in a mixture of 50% dimethylformamide/water. Substrates are amino acid esters or the esters of di- or tri-peptides.

Enzymatic procedures using proteases have been developed for the synthesis of small peptides. Again, however, proteases tend to cleave peptide (amide) bonds once they are formed. Work in this project (JAB, CHW)* is focused on two strategies to overcome this problem, both using the enzyme subtilisin.

The first method uses water-miscible organic solvents to selectively inhibit the amide cleavage activities of the enzyme yet to retain significant ester cleavage activity, which can form the basis for synthesis. The enzyme does catalyze the polymerization of several amino acid and peptide esters to make polyamides in 50% DMF/H_2O (Table 2).

The second method involves selective methylation of the active-site histidine residue of subtilisin to alter its activity. A new reagent, methyl (β-cinnamoyl) sulfonate, has been developed which is structurally similar to phenylalanine methyl ester, a natural substrate for subtilisin. This structural similarity allows the reagent to specifically bind to the enzyme active site where it transfers the reactive -CH_3 group to the histidine, which has been shown to play a major role in the catalytic process. The methylated enzyme is severely damaged with regard to its ability to break amide bonds, although it still binds to the normal substrates and has esterase activity, which should allow it to catalyze the condensation of amino acid or peptide esters to form polypeptides (Figure 2).

These results and those with phosphorylase in the synthesis of polysaccharides demonstrate that the concept of protein engineering to force normally degradative enzymes to become synthetic enzymes is a valid one and that this is a viable route to the synthesis of polymeric materials. Detailed knowledge of the structure and function of enzymes (for instance, of the reactive amino acids and the shape of the active site) can allow the rational design of reagents to alter the active site and thereby alter the functioning of the enzyme. Successful engineering of subtilisin, papain, phosphorylase and lysozyme will be followed by the controlled synthesis and the characterization of interesting polyamides and polysaccharides.

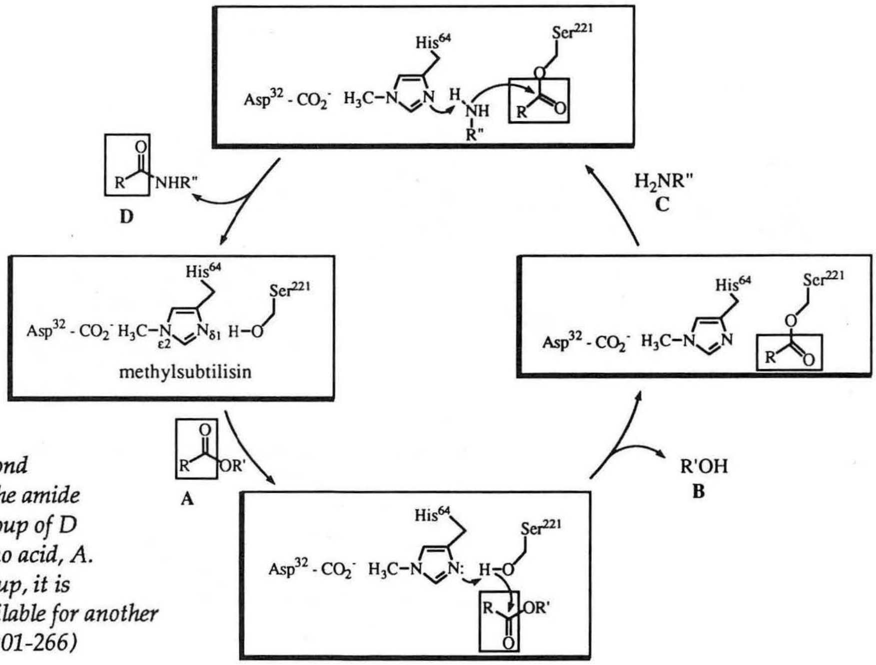


Figure 2
The enzyme subtilisin contains three amino acids, aspartate (asp), histidine (his) and serine (ser), in its active site that are directly involved in the making or breaking of amide bonds. When the active site histidine is methylated, as shown here, conditions can be found to limit amide bond degradation yet allow synthesis. Starting at left and proceeding counterclockwise, the serine of the enzyme binds an amino acid ester, A, splitting off the alcohol group B. A second amino acid ester is brought in, C, and the amide bond is made, D, between the amino group of D and the carbonyl group of the first amino acid, A. Since the R" in D includes an ester group, it is structurally analogous to A, and is available for another round of amide bond synthesis. (XBL 901-266)

---

*Research in this CAM Project is performed at the Research Institute of Scripps Clinic (RISC), La Jolla, CA, where C.H. Wong is a professor in the Department of Chemistry. J.A. Bibbs is a CAM postdoctoral fellow working with Wong at RISC.

ENZYMATIC SYNTHESIS OF "NONBIOLOGICAL" POLYMERS

M. Bednarski, H. Blanch, M. Callstrom*, D. Clark, P. Schultz, A. Braisted, A. Wong

Traditional views of materials synthesized enzymatically restrict the products to polyamides, polysaccharides, polyesters, polynucleotides and the like. Two projects in the program are focused on expanding the applicability of enzymes to the synthesis of polymeric materials that are not "biological" in nature. The goal here is the use of enzyme to make "classical" polymers with properties that are enhanced by the nature of the control of structure or the low temperature synthesis achieved only through the use of enzymes.

Enzymatic Synthesis of Monomers with Chemical Polymerization

M. Bednarski, M. Callstrom*, H. Blanch, D. Clark, A. Wong

One approach involves the "coating" of chemically polymerized materials with enzymatically synthesized derivatives that would have significant influence on the properties of the material as a whole. The scheme involves the enzymatic synthesis of surface active groups attached to a polymerizable monomer. A focus of effort in this area has been the use of the enzyme hexokinase in the synthesis of phosphorylated polymers (MB, MC) (Figure 3)†. The primary physiological role of hexokinase is to catalyze the phosphorylation of glucose to give glucose-1-phosphate. This enzyme, however, has been shown to accept a variety of other substrates including aminosugars. It has been used here to synthesize derivatives of glucosamine-1-phosphate. The phosphorylated glucosamine is then converted to its acrylamide derivative and the compound polymerized using ammonium persulfate as a catalyst. Using this methodology a variety of unnatural carbohydrate-based polymers have been synthesized. Preliminary characterization suggests that these polyanionic materials exhibit interesting rheological properties and are very soluble in water.

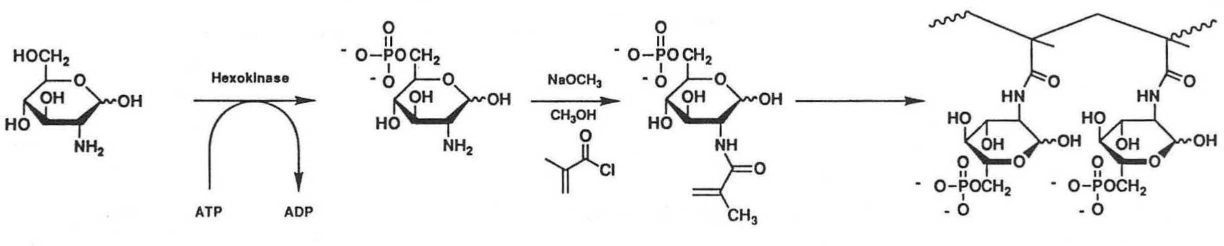


Figure 3
The enzyme hexokinase can specifically attach a phosphate group to the 6-position of the glucose ring. Chemical or enzymatic atttachment to form methacrylate or acrylamide derivatives produces a polymerizable monomer with, in this case, polyanionic character. The degree of charge on the polymer can be controlled through the copolymerization of unphosphorylated monomers. Use of enzymes insures absolute control of the degree and position of the derivatization of the sugar residue. (XBL 901-263)

---

* Department of Chemistry, The Ohio State University.

† This work was supported through a contract with the Cargill Corporation.

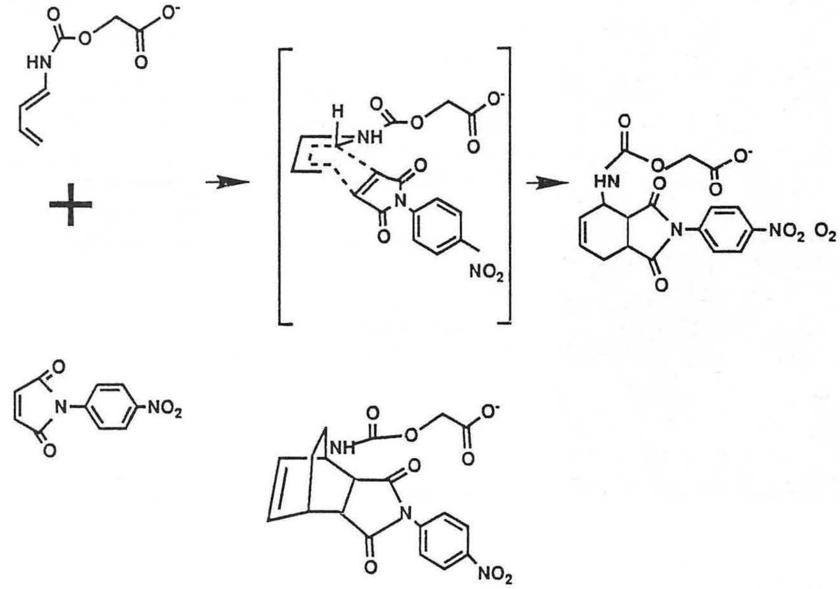


Figure 4
The Diels-Alder reaction involves the making of carbon-carbon bonds between a diene (above left) and a dienophile (below left). The reaction has been determined to proceed through the very short-lived transition state shown in the brackets. Synthesis of a stable transition-state analog (shown below the transition state) allows for the preparation of antibodies to the transition state These antibodies can act as catalysts for the reaction, thus producing "nonbiological" molecules through biological processes. (XBL 901-264)

A twist in this procedure involves the successful use of the transferase activity of glycosidases such as β-galactosidase to enzymatically link the carbohydrate residue to the polymerizable backbone, in this case hydroxy-ethyl methacrylate (HEMA) (HB, DC, AW). This material has applications, for example, as contact lenses, in part because it is a very low protein adsorbing biopolymer. Since this property would be enhanced by attachment of sugars, these modified poly-HEMA's might become an important class of biocompatible materials.

Catalytic Antibodies

P. SCHULTZ, A. BRAISTED

With the advent of technologies to produce monoclonal antibodies, it has become possible to generate proteins that selectively recognize virtually any given target substrate. Research described here last year demonstrated the ability of certain of these antibodies to catalyze reactions. Thus it now is reasonable to expect that catalytic antibodies can be created even for those reactions that involve substrates that are not "biological" in nature. These antibodies could then be used in an almost unlimited range of reactions leading to the synthesis of the full breadth of organic materials.

Work is progressing on the development of catalytic antibodies for polymer synthesis involving sequential Diels-Alder reactions for the making of carbon-carbon bonds. Chemical synthesis of analogs of the transition state for the linkage reaction has been achieved (Figure 4) and this material has been coupled to a carrier protein for antibody production. Purification of the first group of antibodies is in progress.[§]

[§] Note added in proof: Antibodies with this catalytic activity have been produced.

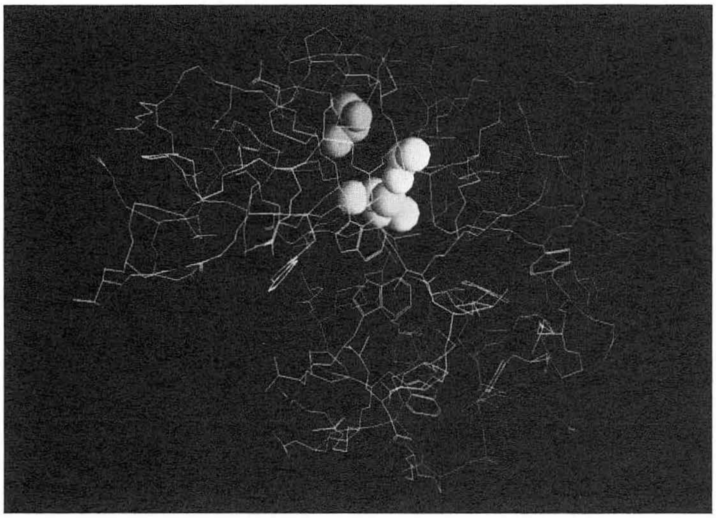


Figure 5
Three dimensional structure of the carbon chain backbone of the enzyme lysozyme shows the position of the active site cleft at top right. Three amino acids at the base of the active site, at positions 40, 55, and 91, are shown in space-filling form. They have been replaced by other, larger amino acids, leading to a 7°C increase in the thermal stability of the enzyme as measured by T_m. Mutations at positions 68, 101 have also made the enzyme more stable at higher temperatures, and mutants with all these changes are being made to examine the additivity of the effects. (BBC 8911-10248)

ENZYME ENGINEERING

Thermostability of Enzymes

J. F. Kirsch, B. Malcolm, P. Shih

Reaction rates approximately double with a 10°C increase in temperature. Thus, the stabilization of enzymes so that they can function effectively at elevated temperatures will be an important advantage in bioreactors. Site-directed mutagenesis technology coupled with x-ray crystallographic structure analysis offers the opportunity to deal with this problem by explicit protein design, even though much remains to be learned about the relationship between protein structure and thermostability.

As discussed here last year, a collaboration with evolutionary biochemist Allan Wilson at Berkeley led to the identification of a set of three amino acids at the base of the active site of the enzyme lysozyme (positions 40, 55, 91) (Figure 5) which, when replaced by other amino acids, led to a 7°C increase in the thermostability of the enzyme. This stabilization corresponds to an almost 3-fold increase in enzyme lifetime at 37°C. During the past year, the x-ray structural analysis of the wild-type and mutant proteins has been completed in collaboration with Brian Matthews and his student Keith Wilson at the University of Oregon. Their work has demonstrated that the large changes in thermostability induced by the genetic engineering of these modest perturbations in structure, i.e., the addition of a single methylene (-CH_2) group, can be clearly attributed to hydrophobic packing. The simple conclusion is that increases in hydrophobic packing brought about without concomitant introduction of strain in the rest of the molecule can lead to greater thermostability. This finding has far reaching implications for the design of enzymes for use in reactors.

In view of this, further investigations have been undertaken in order to define rigorously the conditions leading to enhanced thermostability of proteins. By substituting phenylalanine for the naturally occurring isoleucine at position 55, a large increase in the mass of this position was introduced. The x-ray structure suggested that such a large change cannot be accommodated without seriously perturbing the structure. Indeed, a significantly lower melting point was found (67°C vs 74°C) for wild-type enzyme. Substitution of alanine for serine in position 91, however, removes the β-hydroxyl group, but increases the hydrophobicity of the amino acid, giving an increase in stability from 74° to 76°C. This raises further possibilities for tinkering for greater thermostability, i.e., by the replacement of hydrophilic with hydrophobic amino acids of smaller size. Also in accord with prediction, is the observation that substitution of alanine, a smaller hydrophobic amino acid, for isoleucine, a larger one in position 55 reduces the T_m from 74° to 70°.

Further, almost every substitution introduced for aspartic acid at the 101 position has yielded an enzyme of greater thermostability than wild-type. It thus appears that the wild-type enzyme is selectively destabilized at position 101. Since this residue is involved in substrate binding, this destabilization might have evolved for reasons having to do with efficient catalysis. The mutants, however, are all active. Yet another locus for mutations giving enhanced thermostability has been tentatively identified at position 68. Experiments are now underway to see if mutations at remote positions are additive.

Engineering of the Substrate Specificity of Enzymes

J. F. Kirsch, P. Cioni

Enzymes of living organisms evolved to bind and catalyze reactions with naturally occurring substrates of use to those organisms. They cannot, then, usually bind nonnatural substrates that might react to produce interesting materials. Synthesis of catalytic antibodies is one route to an enzyme for these substrates. Another route is synthesis of specifically engineered enzymes. To study whether this rational redesign is possible, a model system, involving the enzyme aspartate amino transferase, has been investigated. Earlier success, reported here last year, on converting this enzyme (through site-directed mutagenesis) from one that preferentially catalyzes the transamination of negatively charged substrate amino acids to one that transaminates a positively charged substrate (i.e., the complete reversal of substrate charge specificity) encouraged efforts to attempt to find second generation mutants where the catalysis of the new substrate was enhanced further (Figure 6). Crystallographic investigations by collaborators at MIT (Dagmar Ringe) implicated asparagine 142 as a possible target for further mutagenesis studies because it had the potential to hydrogen bond with asp 192 and, therefore, weaken the density of charge around the carboxyl group of that substrate-binding aspartate. Accordingly, asparagine 142 was mutated to alanine. Catalytic

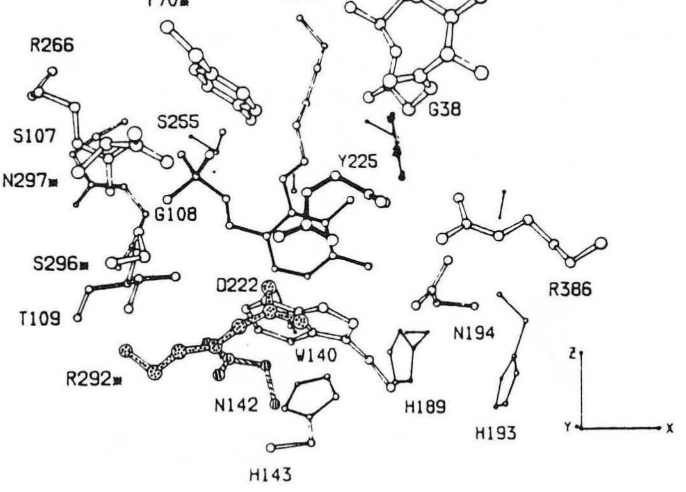


Figure 6
Structure of the active site of the enzyme aspartate aminotransferase. The figure shows 20 amino acids that make contact with the substrate or with another amino acid that makes contact with the substrate. Selective substitutions of these amino acids should produce a new enzyme that can catalyze reactions with a new selected substrate. A substrate analog is shown with filled circles. Substitution of arginine by aspartate in position 292 (stippled) gave a 10^5 fold reduction in activity on the original substrate and a 15 fold increase in activity on the new one. Substitution of asparagine 142 by alanine (partially shown, hatched) increased the activity on the new substrate to 50 fold over that of the original enzyme. Additional substitutions should further enhance the desired selectivity. (XBL 888-3008)

activity was enhanced an additional three-fold giving a total of 50 fold increase with the two mutations. This second success in amino acid substitution for a defined purpose is encouraging. Eleven amino acids make some contact with the substrate, and many more contact those residues and can affect their action. In continuing work more mutations surrounding the active site of the enzyme are being made to enhance activity on the new substrate. This is one of the few successful model systems in which a significant change in substrate specificity has been achieved, and it augurs well for the the long range goal of this work: the achievement of sufficient understanding of protein structure so that site directed mutagenesis can be used in such a way that substrate specificity can be treated as an easily maneuverable experimental parameter.

Semi-Synthetic Enzymes

P. Schultz, C. Noren

Site-directed mutagenesis, although promising in its potential to help redesign enzymes, is restricted to the use of the 20 naturally occurring amino acids, thus limiting the fine tuning of geometry and functionality. As reported last year, this problem has been overcome by the development of a technique that allows the site-specific substitution of virtually any alpha-amino acid that can be synthesized in the laboratory. Technical aspects of the process have been significantly improved during the past year. The first system developed used a chemically modified and acylated tRNA to carry the unnatural amino acid. A far simpler technique for tRNA preparation has now been developed, involving the synthesis of a synthetic tRNA gene redesigned for this process, and its use in a transcription system to produce the tRNA. Further, the amino-acylation step has been improved through the direct synthesis of the terminal nucleotides of the tRNA linked to the unnatural amino acid. This group can then be enzymatically linked to the rest of the tRNA. This new tool clearly provides a vastly increased potential for specific modification of enzymes to tailor their activities for desired reactions. It is now being pursued with enzymes of interest in materials synthesis, including T4 lysozyme.

CHEMICAL AND ENZYMATIC SYNTHESIS OF BIOELECTRONIC AND OPTICAL DEVICES

M. Bednarski

As reported last year, methods have been developed to chemically and enzymatically modify silicon oxide surfaces. The goal in this area of research is to develop materials for new bioelectronic and optical devices to be used as molecular sensors. The combination of chemical and enzymatic methods has allowed derivatization of silicon chips with carbohydrate molecules with specifical binding properties, in this case, for certain pathogenic bacteria. The nonspecific adhesion of bacteria that might be similar to the target can be prevented by the use of specifically designed

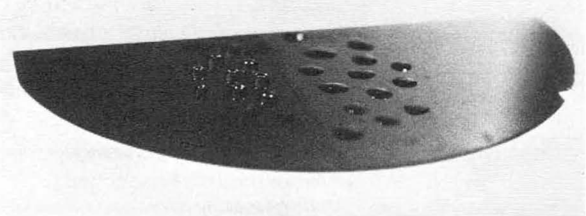


Figure 7
Attachment of hydrocarbon chains to a silicon wafer can change its surface properties from hydrophilic to hydrophobic. Untreated silicon surface (right) is wet by water. Water beads on treated surface. (XBB 8910-9344)

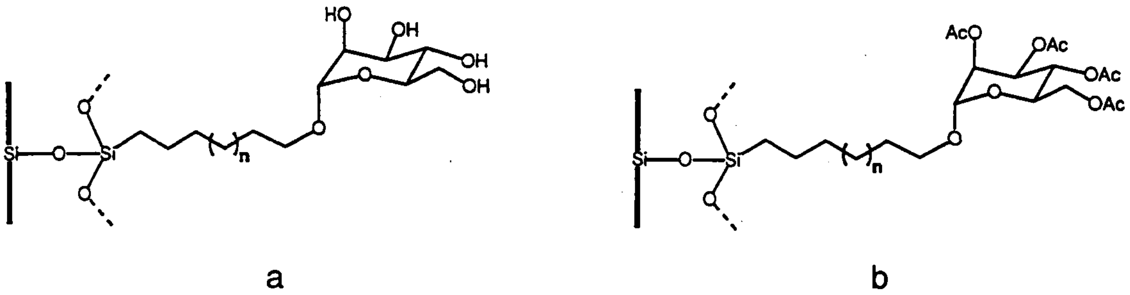
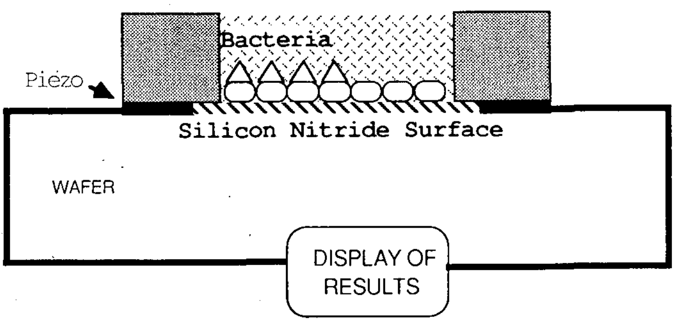


Figure 8
Enzymatic attachment of specific sugars to the end of the hydrocarbon chain can control the binding of selected agents, here bacterial cells, to the surface. Mannose residues act as specific receptors, allowing binding (a). Acetlyation of the mannose prevents binding (b). (XBL 901-267)

mixed monolayers. Hydrophobic groups, for example, prevent the non-specific adhesion of bacteria such as Salmonella. The altered character of the surface can be seen in the change of the shape of water droplets on the surface (Figure 7). Attachment of specific carbohydrate derivatives such as mannose to the ends of hydrophobic groups allows receptor mediated adhesion of the bacteria to occur (Figure 8a). Modification of the mannose can eliminate that binding (Figure 8b).

These coatings have been transferred on to a surface acoustic wave sensor device (Figure 9) to allow detection of the presence of the target structure through its binding to the synthetic surface. This device relies on the generation and modification of an acoustic wave by a piezoelectric material on a silicon nitride membrane. The binding of the receptor molecules to the device can cause a shift in the resonance frequency of the wave, leading to an assay of the binding event. The feasibility has been demonstrated using Salmonella and E. coli, and these devices are currently being refined for sensitivity and versatility. Further applications include the detection of small molecules. The process of chemical and enzymatic surface modification will also be used to synthesize polymers on the surface of the custom designed electro-optical materials.

Figure 9
Mounting of a self assembling hydrocarbon chain/sugar derivatized structure on a silicon nitride surface through which a standing acoustic wave has been generated can form the basis for a sensing device. Binding of bacterial cells to the receptors alters the from of the wave in a manner detectable by the attached electronics.
(XBL 901-265)



ANISOTROPIC POLYMERIC MATERIALS

The processing of liquids which are anisotropic at rest is common in the manufacture of advanced polymeric materials. The anisotropy might be a consequence of the presence of fibers, as in fiber-filled composite materials, or of the molecular structure of a liquid crystalline polymer. Prediction and control of orientation development of anisotropic liquids during processing remains a major outstanding technical problem.

Liquid crystalline polymers contain rigid elements in the backbone which cause them to exist in a highly oriented ("mesophase") state in the melt. Melt-processible nematic liquid crystalline polymers are currently molded for use as interconnects in electronics applications; the low resistance to flow enables easy filling of small, complex shapes. The rigid polymer backbone, which causes the high degree of local order in the liquid state, is also the cause of other properties of these materials that are considered to be exploitable in high-performance applications: high melting point, high modulus and strength, small in-plane coefficient of thermal expansion, and excellent resistance to chemical solvents. The high degree of local order has stood in the way of the development of shaping processes (other than fiber formation, which is well-established commercially) which can exploit these other desirable properties, however, because it leads to poor transverse physical properties and poor adhesion (and self adhesion).

We have studied the properties of several melt-processible liquid crystalline polymers using rheology and nuclear magnetic resonance spectroscopy as complementary tools. We find that the unusual flow behavior of these materials, and the sensitivity to prior thermal history, are a consequence of the presence of as many as two crystal-like phases at normal processing temperatures: one phase consists of small crystallites of homopolymer, while the other is a non-periodic structure with a stoichiometry very close to that of the bulk melt. Possible transesterification reactions at compounding temperatures may account for some of the unusual properties of filled materials. During the past year we have initiated work on solution-processed (lyotropic) liquid crystalline polymers.

As part of our continuing work on the simulation of structure development in anisotropic liquids, we have extended our computational work on hyperbolic methods to include the theory of fiber suspensions. We have simulated some recent experiments reported in the literature on the flow of fiber suspensions with reasonable success.

THERMOTROPIC LIQUID CRYSTALLINE POLYMERS

J.A. Reimer, M.M. Denn, K. Amundson, D. Giles, D. Kalika

As described last year, we have obtained complementary data using three rheometers and high-temperature NMR on the wholly nematic copolymer of 80 mol % p-hydroxybenzoic acid and 20 mol % poly(ethylene terephthalate) manufactured by Tennessee Eastman. The viscosity data are inconsistent with any available theory for anisotropic liquids. The NMR data indicate the presence of a small fraction of crystallites of poly(hydroxybenzoic acid), which will have a melting point that is higher than the normal processing temperatures. The NMR data at melt temperatures also indicate a slowly decaying component of the proton spin relaxation spectrum with a stoichiometry that is very close to that of the bulk polymer. We have now identified this structure, which comprises a fraction greater than 10%, as likely to be "non-periodic crystals" as discussed by Windle and co-workers. This crystal-like structure is undoubtedly associated with the thermal history-dependent transients observed in rheological experiments; the structure induced during these transients can be melted out reversibly by brief excursions to higher temperatures.

The picture that emerges has considerable significance for processing, since the multiphase nature of the system clearly needs to be taken into account in any analysis. The small crystallites undoubtedly act as tie elements to produce a structure whose rheological properties are reminiscent of those commonly associated with suspensions of submicron particles like carbon black, rather than the properties normally associated with classical nematic liquids.

FILLED LIQUID CRYSTALLINE POLYMERS

M.M. Denn, L. Nuel

Thermotropic (melt-processible) liquid crystalline polymers are often used with particulate fillers, in part because the fillers appear to improve the isotropy of properties in molded parts. We reported last year that the compounding in a twin-screw extruder appears to induce a gap-dependence of the viscosity that is much greater than that observed in the unprocessed polymer, and that the polymer shows an apparent viscosity decrease in a small capillary but not in a larger one upon addition of small amounts of carbon black.

We have carried out differential scanning calorimetry (DSC) experiments on filled and unfilled polymers, the latter with and without compounding. DSC traces at the compounding temperature show marked differences between compounded and uncompounded polymers, with the compounded polymer showing an apparent phase transition that does not exist in the uncompounded material. Annealing at processing temperatures for a sufficiently long time removes the second peak, however. It is likely that the difference between compounded and uncompounded material observed rheologically is affected by the residence time in the rheometer, and the thermal history associated with individual data points is again shown to be a relevant parameter. The changed DSC behavior of the compounded material may be associated with transesterification reactions that have been reported for these polymers.

FLOW SIMULATION OF FIBER-FILLED LIQUIDS

R. Keunings, M.M. Denn, J. Rosenberg

Some years ago we developed a procedure for simulating the flow of fiber-filled liquids in converging geometries at low fiber loadings.

Excellent agreement was obtained between our theoretical predictions and experiments on flow through a 4:1 contraction, where the presence of the fibers effected a major change in the flow structure; this work demonstrated that predictions of fiber orientation distributions based on flow fields ignoring the presence of the fiber could be grossly in error.

That work was limited, in that it required certain characteristics of the flow field to insure that an approximation roughly equivalent to assuming that the fiber orients with the flow could be utilized. We have extended our algorithms for hyperbolic viscoelastic constitutive equations, described last year, to include the theory of fiber suspensions in a Newtonian fluid, and we have simulated several flows. The simulations include a series of experiments carried out by a group at the Los Alamos and Sandia National Laboratories on falling-sphere rheometry in a tube containing

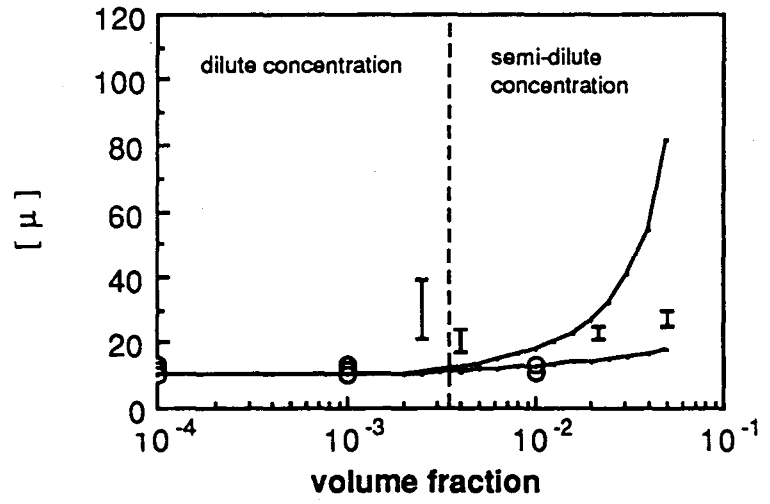


Figure 10
Intrinsic viscosity (i. e., fractional contribution per unit volume of fibers to the suspension viscosity) as a function of volume fraction for a sphere falling in a tube filled with the suspension. The data, indicated by error bars, are from experiments by Milliken and co-workers for randomly distributed fibers. Experiments by the same group on fibers initially aligned with the tube axis show an intrinsic viscosity of about 10. The circles are computed points for random and aligned orientations. The two lines in the semi-dilute range reflect the fact that the theory is ambiguous here, with the value of crucial coefficients depending on the bulk orientation of the fibers. Overall, the theory captures the large intrinsic viscosity observed experimentally, but it does not agree quantitatively with some of the data. The difference is probably due to the fact that the spheres used in the experiments were comparable in size to the fiber length, while the theory assumes that the fibers are much smaller in all dimensions than the sphere. (XBL 901-119)

fiber suspensions. We found that in the case of this confined flow, the velocity field is approximately that of an unfilled system, although the stress distribution is quite different. The apparent viscosity of the suspension can be computed and expressed as an intrinsic viscosity; the intrinsic viscosity, when multiplied by the fiber volume fraction, gives the fractional correction to the suspension viscosity.

The computed and experimentally measured intrinsic viscosities are shown in Figure 10 for the case of a random initial distribution of fibers. The theory predicts that the intrinsic viscosity is insensitive to the initial fiber orientation distribution, but the experiments showed a large effect.

The difference is probably a consequence of the fact that the theory assumes that the fibers are small relative to the size of the sphere, while the experiments were carried out with spheres of a size comparable to the fibers. Theoretical calculations are in good agreement with an asymptotic solution of the model equations.

POLYMER/SURFACE INTERACTIONS

The physical or chemical interactions between polymer segments and a non-polymeric surface results in conformational changes of the polymer in the neighborhood of the interface, making it different from that in the bulk.

Interaction during melt processing between the melt and the metal shaping surface is known to affect adhesion and the onset of flow instabilities, and hence the throughput and bulk material properties. The properties of polymer composites are determined by the nature of the interaction between the matrix and the particulate or fiber filler; the interaction affects not only interface adhesion, but such properties as failure and fatigue as well. The interactions of thin polymer films with metal and metal oxide interfaces are of importance in a variety of applications in the microelectronics industry; in polymer/metal interactions only certain functional groups of the organic polymer may interact chemically with the substrate. The interaction of a polymer with a non-polymeric surface is also of significance in other areas, including tribology and such biomedical applications as implant wear.

Because of the industrial significance of polymer/surface interactions, we initiated research in this area in 1987. We have made significant progress in identifying the apparent interfacial basis of certain processing instabilities. Our theoretical work has been successful in moving towards the goal of predicting macroscopic thermodynamic and mechanical behavior at interfaces from the chemical constitution of chains and solid surfaces. Experimental studies using nuclear magnetic resonance spectroscopy and attenuated total reflectance Fourier transform infrared spectroscopy are currently underway and should produce useful results during the coming year.

MOLECULAR MODELING

D. THEODOROU, K. MANSFIELD

This work aims at the development of statistical-mechanics-based simulation methods for the prediction of polymer interfacial properties from chemical constitution. The motivation is to provide a foundation for the rational, "molecular engineering" design of multiphase materials containing polymers, such as composites, adhesives, and coatings.

Recently, we designed an efficient Molecular Mechanics simulation approach for glassy amorphous polymers. During this year we applied this approach to thin films of a glassy polymer (atactic polypropylene) sandwiched between smooth solid substrates (graphite basal planes). The film thickness was chosen large enough so that each half of the sandwich is representative of a single bulk polymer/solid interface. Our objective was to understand the organization of macromolecules in the interfacial region, and to test our ability to predict interfacial thermodynamic properties from first principles.

Our model "composite" system is represented as an ensemble of atomistically detailed microstates, each in mechanical equilibrium. To create a microstate, polymer chains are first grown between the confining

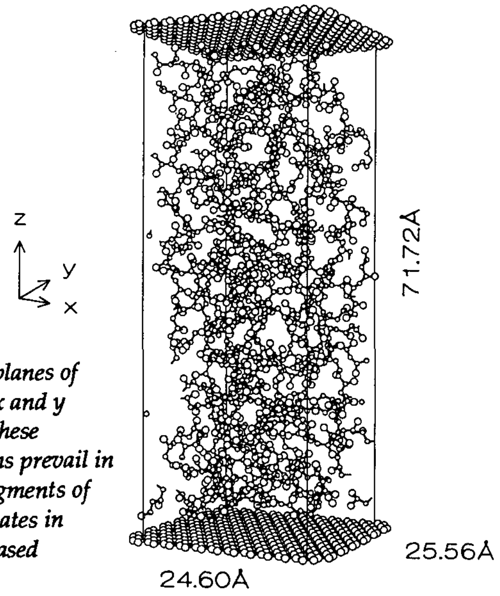


Figure 11
Model microstate of glassy atactic polypropylene sandwiched between two basal planes of graphite. The microstate is characterized by periodic boundary conditions in the x and y directions; it can thus be considered as part of a film which extends infinitely in these directions. The film thickness has been chosen large enough so that bulk conditions prevail in the middle, yet small enough to keep computations tractable. The box contains segments of seven polymer chains, each of molecular weight 3,214. Ensembles of such microstates in detailed mechanical equilibrium are useful in providing quantitative molecular-based information on the properties of composite interfaces. (XBL 901-114)

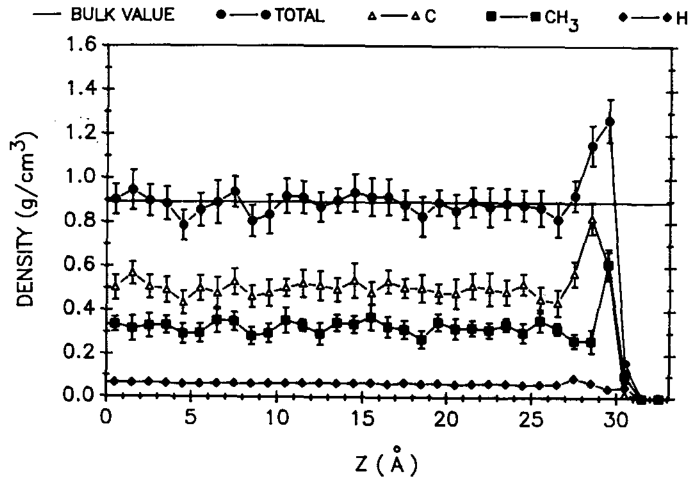


Figure 12
Local mass density distribution at a glassy polypropylene/graphite interface. The centers of carbon atoms of the graphite surface are located at z=33.1Å. The region at small z values is representative of unperturbed bulk polymer. The solid line indicates the experimentally observed macroscopic density at the simulation temperature (20°C below T_g). Individual contributions to the mass density profile from carbon, hydrogen, and methyl groups are also shown. The local density displays a strong maximum next to the highly attractive graphite surface. Chains adsorb on the surface through their pendant methyl and hydrogen groups. (XBL 8910-3660)

solid surfaces through a Monte Carlo procedure that resembles polymerization. The microstate is subsequently relaxed through an energy minimization technique on a Cray X-MP supercomputer. Potential parameters are based on recommendations of Flory and Steele, and are not adjusted in the simulation. A model microstate is illustrated in Figure 11.

From the microstates we have generated so far, we were able to obtain an estimate for the work of adhesion between glassy polypropylene and graphite which is within 4% of available experimental values. In addition, we have elucidated details of chain organization and conformation at the interface. Local segment density is enhanced, and bond orientation deviates from isotropy over a 10Å-thick region near the graphite. Chains adsorb on the graphite through their pendant methyl and hydrogen groups (Figure 12). There is a distinct tendency for adsorbed hydrogens to locate themselves preferentially over the centers of hexagons in the graphite surface honeycomb. The segment clouds of individual chains orient with their longest principal axes parallel to the solid substrate. Local structure assumes its bulk characteristics at distances larger than two radii of gyration from each graphite surface.

NEAR-SURFACE STRUCTURE OF POLYMER-METAL/METAL OXIDE INTERFACES

A. Chakraborty, J.S. Shaffer

This work focuses on the use of quantum and statistical mechanical methods to study the details of interfacial bonding and chain conformations at the interfaces of oxygen- and nitrogen-containing polymers with aluminum, nickel, and their oxides. We have made significant progress in studying the segment-level interactions of polymethyl methacrylate (PMMA) oligomers and 4-4'-n-propylcyclohexyl cyanocyclohexane with aluminum surfaces. We use two models to represent the surface; one is the so-called jellium model, and the other is one wherein the surface is represented as a finite cluster of metal atoms.

Density functional theory has been our method of choice to study the interfacial interactions under consideration. We have calculated both the energetics and the changes in the electronic properties of the surface as the oligomers approach the metal surface. In our calculations with the jellium representation of the aluminum surface, we use linear response theory, and we construct the exchange-correlation energy functional by using the local density approximation and the Perdew-Zunger expression for the

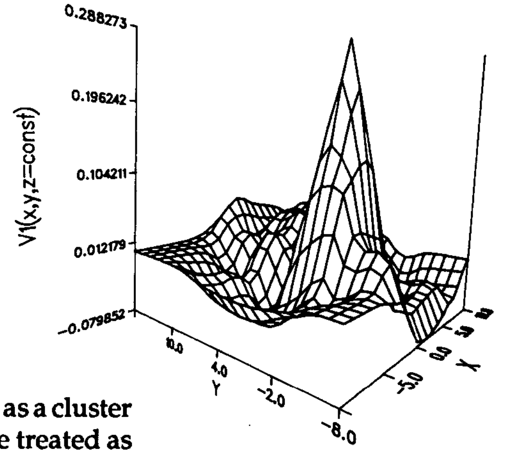


Figure 13
Spatially variant potential induced on a "jellium" representation of the aluminum surface due to a PMMA dimer unit approaching the surface (the closest carbonyl group is 4.0 bohr from the surface). The X-Y plane is the metal surface. The spatial variation is directly related to the electronic and stereochemical properties of the organic oligomer. This induced potential can be related to STM currents for adsorbed oligomers. Furthermore, calculating this potential is crucial for calculating the energetics of oligomer-metal surface interactions. Our calculated energetics using these induced potentials reflect the strength and specificity of chemical interactions at the interface. (XBL 901-115)

exchange-correlation energy. When the surface is represented as a cluster of metal atoms, the organic oligomer and the metal cluster are treated as one supermolecule and the full Kohn-Sham equations are solved. Pseudopotentials are used to represent the metal core electrons in the cluster calculations, and again, we use the local density approximation.

We find that the potential induced on the surface as a consequence of interacting with the organic oligomers is spatially variant (Figure 13). Furthermore, the spatial variation of the induced potential is directly related to differences in the electron density distribution around various functional groups of the organic molecule. This spatial variation of the induced potential has been related to recent scanning tunnelling microscope studies of adsorbed layers of 4-4'-n-propylcyclohexyl cyanocyclohexane by Spong and co-workers at IBM. We have also calculated the energy hypersurface of PMMA oligomers interacting with aluminum surfaces. The energy hypersurface calculated in this way reflects the strength and specificity of the interfacial interactions, and cannot be represented by a simple potential.

ADHESION AND MELT FRACTURE

D. HILL, T. HASEGAWA, M.M. DENN

There is evidence that the onset of melt flow instabilities at high stress levels ("melt fracture") is affected by interactions between the polymer

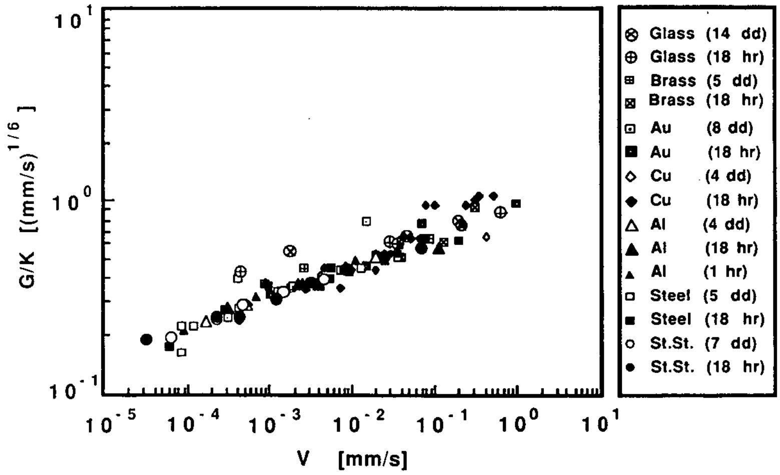


Figure 14
Normalized peeling force plotted versus the speed of propagation of the interface for cast films of linear low density polyethylene on a variety of substrates. The times in parentheses indicate the aging of the film between sample preparation and testing. The best fit through the data is a line with slope of 1/6 on logarithmic coordinates. (XBL 901-117)

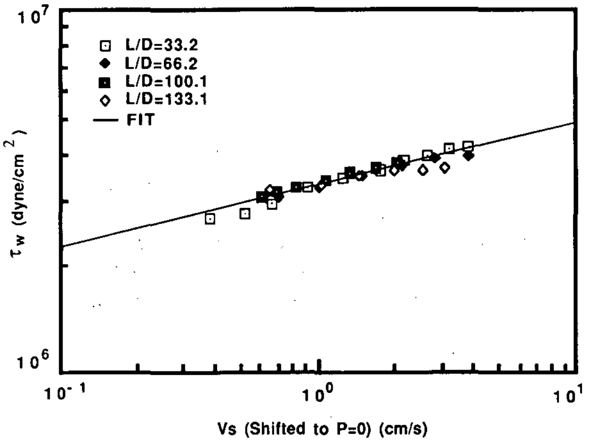


Figure 15
Wall stress versus inferred wall slip velocity data of Kalika and Denn for the same linear low density polyethylene used in the peel experiments, adjusted to atmospheric pressure using the pressure dependence derived from the bulk rheological properties. According to the adhesion theory the slope of these data should be the same as the data in Fig. 14, and this is the case. The theory predicts the magnitude of the data to within about 40% without any adjustable parameters. (XBL 901-118)

and the metal surface of the extrusion die. We have used the theory of adhesive failure between non-crystalline polymers and a non-polymeric surface to provide a framework for the analysis of melt fracture. Data from adhesion "peel" experiments of cast films of linear low-density polyethylene on a variety of metal and metal-oxide substrates, which were mentioned in a previous report, were shown to superimpose on a master curve of strain energy release rate versus the velocity of the interface, as shown in Figure 14, with a slope on logarithmic coordinates of 1/6. The theory predicts that inferred slip velocities for melt flow of this polymer at high stress levels should show the same functional dependence between the wall stress and the slip velocity after adjustment for high-pressure free-volume effects. Data of Kalika and Denn are shown in Figure 15; the best-fit line through the data has a slope of 0.17, as predicted by the theory. The theory predicts the magnitude of the stress corresponding to a given slip velocity to within 40%.

The results of this study are by no means conclusive, but they do make a strong case for the fact that melt fracture is a consequence of an adhesive failure between the melt and the metal or oxide surface of the die. It is particularly striking that both the onset of extrudate surface distortions and the functional form and magnitude of the melt slip velocity can be obtained solely from peel tests on the polymer below the melt processing temperature and a knowledge of the temperature and pressure dependence of the bulk rheological properties.

STAFF

Program Leader
Morton Denn

Project Leaders
Mark Alper—Enzymatic Synthesis of Materials
Morton Denn—Anisotropic Polymeric Materials
Doros Theodorou—Polymer/Surface Interactions

Investigators
Mark Bednarski
Alexis Bell
Harvey Blanch
Arup Chakraborty
Douglas Clark
Roland Keunings
Jack Kirsch
Bruce Novak
Clayton Radke
Jeffrey Reimer
Peter Schultz
Paul Smith
(University of California, Santa Barbara)
David Soane
Chi-Huey Wong
(Research Institute of Scripps Clinic, La Jolla, CA)

Postdoctoral Fellows
Jeffrey Bibbs
Patricia Cioni
Benoit Ernst
Davide Hill
Christopher Hobbs
Joanne Petithory

Graduate Students
Spencer Anthony-Cahill
Claudia Bachmann
Andrew Braisted
Michael Corey
Douglas Devens, Jr.
Laura Dietsche
Mirtha Fernandez
David Giles
Veronica Lim
Bruce Malcolm
Kevin Mansfield
Alan Michiels
Steven Musarra
Christopher Noren
Joseph Rosenberg
Michael Schonberg
James Shaffer
Robert Shipman
Rebecca Taylor
Ward Tegrotenhuis
Albert Wang

Technical Support
Whitney Carrico
Sydney Edwards
Lynn Oehler

AWARDS

- Peter Schultz received the ACS Award in Pure Chemistry and the ACS Arthur C. Cope Scholar Award.
- Joanne Petithory received an NIH postdoctoral fellowship.
- Claudia Bachmann was awarded a U.C. Berkeley fellowhsip.
- Laura Dietsche was awarded an NSF predoctoral fellowship.
- Mark Mastandrea was awarded an NSF predoctoral fellowship.

INDUSTRY INTERACTIONS

Advisory Board

J. D. Moseley (Chairman)	Dow Chemical Company
W. A. Fraser	Union Carbide Corporation
Michael Jaffe	Hoechst Celanese Research Division
Manuel Paner	E.I. du Pont de Nemours & Company
Isaac Sanchez	University of Texas at Austin
C. Grant Wilson	IBM Almaden Research Division

Industrial Collaborations

- Dr. Patrick Gruber of the Cargill Corporation is working with the Enzymatic Synthesis of Materials project on the development of a new class of carbohydrate-based polymers derived for monosaccharides or oliosaccharides functionalized with polymerizable side groups.

- Dr. Steven Rosenberg of Chiron Corporation is continuing his work on cloning and gene expression with the Enzymatic Synthesis of Materials project.

- Dr. Hans Ribi, Biocircuits, Inc., is collaborating with the Enzymatic Synthesis of Materials project on the use of enzymes in the fabrication of sensors.

- Affymax Inc. is collaborating with the Enzymatic Synthesis of Materials group in the production of catalytic antibodies.

- Dr. A.E. Zachariades, IBM Almaden Research Center, worked with the Anisotropic Polymeric Materials project on the mechanisms by which structure develops in liquid crystalline polymers.

- Dr. Peter Pierini, Dow Chemical Company, is collaborating with the Anisotropic Polymeric Materials project on a study of structure development in lyotropic liquid crystalline polymers.

- Dr. Mohammud Zaidi, Alcoa, is collaborating with the Anisotropic Polymeric Materials Project on a study of the rheology (deformation characteristics) of liquid crystalline polymers at temperatures where the material can be deformed and shaped in the solid phase.

Gifts

- Gifts from Alcoa, E.I. du Pont de Nemours & Company, and Raychem supported general studies in the Anisotropic Polymeric Materials project and the Polymer-Surface Interactions project.

- Gifts from BP America, Cray, Exxon, Shell, and Union Carbide supported studies in the Polymer-Surface Interactions Project.

- A gift from Dow Chemical Company supported studies in the Anisotropic Polymeric Materials project.

Contracts

- The Cargill Corporation is working with the Enzymatic Synthesis of Materials project on the study of new carbohydrate-based polymers.

- IBM Almaden is working with the Polymer-Surface Interactions project on polymer-surface interactions.

Technology Transfer

- Biocircuits, Inc. is using techniques developed in the Enzymatic Synthesis group in the fabrication of sensing devices.

- Affymax, Inc. is using techniques developed by the Enzymatic Synthesis group in the production of catalytic antibodies.

BIBLIOGRAPHY

Polymers Project

Refereed Journal Articles

Denn, M.M., D.S. Kalika, and L. Nuel, "Gap-Dependence of the Viscosity of a Thermotropic Liquid Crystalline Polymer," *J. Rheology*, vol. 33, p. 1059, 1989.

Denn, M.M. and A.D. Rey, "Analysis of Transient Periodic Textures in Nematic Polymers," ***Liquid Crystals***, vol. 4, p. 409, 1989.

Denn, M.M. and A.D. Rey, "Converging Flow of Tumbling Nematic Liquid Crystals," ***Liquid Crystals***, vol. 4, p. 253, 1989.

Denn, M.M., W.E. Tegrotenhuis, and C.J. Radke, "Self-Diffusion in Electrostatically Stabilized Colloidal Suspensions Using Brownian Dynamics," ***Molecular Simulation***, vol. 2, p. 3, 1989.

Denn, M.M. and Renee van de Griend, "Co-Current Axisymmetric Flow in Complex Geometries: Experiments," *J. Non-Newtonian Fluid Mechanics*, vol. 32, p. 229, 1989.

Hill, D.A. and D.S. Soane, "Rotational Diffusivity of Rodlike Molecules in Amorphous Polymeric Matrices," *J. Polym. Sci.*, vol. 27, p. 261, 1989.

Mansfield, K.F. and D.N. Theodorou, "Interfacial Structure and Dynamics of Macromolecular Liquids: A Monte Carlo Simulation Approach," *Macromolecules*, vol. 22, p. 3143, 1989.

Musarra, S. and R. Keunings, "Co-Current Axisymmetric Flow in Complex Geometries: Numerical Simulation," *J. Non-Newtonian Fluid Mechanics*, vol. 32, p. 253, 1989.

Theses

Amundson, K.A., *Investigation of the Morphology of Liquid Crystalline Polymers using Nuclear Magnetic Resonance Spectroscopy.* (Ph.D. Thesis, Department of Chemical Engineering, U.C. Berkeley. Advisors: J.A. Reimer and M.M. Denn.)

Hill, D.A., *Rheology of Mixtures of Amorphous Polymers and Rigid Rod-like Macromolecules.* (Ph.D. thesis, Department of Chemical Engineering, University of California, Berkeley. Advisor: D.S. Soane.)

LBL Reports (including journal articles submitted or in press)

Denn, M.M., B.D. Freeman, and D.S. Soane, "Effect of Hydrostatic Pressure on Polystyrene Diffusivity in Toluene," *Macromolecules.* (In press.)

Denn, M.M. and D.W. Giles, "Strain-Measurement Error in a Constant-Stress Rheometer," *J. Rheology.* (In press.)

Denn, M.M., D.A. Hill, and T. Hasegawa, LBL 27793, "On the Apparent Relation Between Adhesive Failure and Melt Fracture," *J. Rheology.* (In press.)

Denn, M.M., D.S. Kalika, and D.W. Giles, "Shear and Time-Dependent Rheology of a Fully-Nematic Thermotropic Liquid Crystalline Copolymer," *Rheology.* (In press.)

Denn, M.M., D.S. Kalika, M.-R. Shen, X.-M. Yu, N. Masciocchi, D.Y. Yoon, and W. Parrish, LBL-27647, "Rheological and Dielectric Properties of a Thermotropic Polyester Displaying Smectic, Nematic, and Isotropic Phases," *Macromolecules.* (Submitted.) (N. Masciocchi, D.Y. Yoon and W. Parrish, IBM Almaden Research Center.)

Theodorou, D.N., LBL-27168, "Variable Density Model of Polymer Melt/Solid Interfaces: Structure, Adhesion Tension, and Surface Forces," *Macromolecules.* (In press.)

Theodorou, D.N., LBL-27167, "Variable Density Model of Polymer Melt Surfaces: Structure and Surface Tension," *Macromolecules.* (In press.)

Invited Talks

Chakraborty, A.K., *Fundamental Studies of Polymer-Metal Interfaces*, Presented at Raychem Corporation, Menlo Park, CA, May 1989; and IBM Almaden Research Center, San Jose, CA, April 1989.

Chakraborty, A.K., *Organic Oligomers at Jellium Surfaces: A Density Functional Study*, Department of Chem. Eng. and Mat. Sci., University of Minnesota, August 1989.

Chakraborty, A.K., *Theoretical Studies of Polymer-Metal Interfaces*, Monsanto Chemical Company, Springfield, MA, January 1989.

Denn, M.M., *Flow Instabilities in Polymer Melt Processing*, Stanley Katz Lecture, City College, CUNY, New York, NY, April 1989.

Denn, M.M., *Reflections on Asymptotic Analyses for Fibers and Films*, 5th Annual Meeting of the Polymer Processing Society, Keynote Lecture, Kyoto, Japan, April 1989.

Denn, M.M., *Mechanics of Anisotropic Fluids*, Tenth Australian Fluid Mechanics Conference, Keynote Lecture, Melbourne, Australia, December 1989.

Denn, M.M., *Rheology of Thermotropic Liquid Crystalline Polymers*, Macromolecular Science Department, Case Western Reserve University, March 1989.

Denn, M.M., *Flow of Anisotropic Fluids*, Aris 60th Birthday Symposium, University of Minnesota, October 1989.

Denn, M.M., *Rheology and Flow in Anisotropic Polymers*, Department of Chemical Engineering, Illinois Institute of Technology, October 1989.

Denn, M.M., *Flow-Induced Orientation in Anisotropic Liquids*, Symposium on Liquid Crystalline Polymers, Ann Arbor, MI, September 1989.

Denn, M.M., *Rheology and Microstructure of Thermotropic Liquid Crystalline Polymers*, Symposium on Liquid Crystalline Polymers, Ann Arbor, MI, September 1989.

Denn, M.M., *Speculations on the Mechanism of Melt Extrusion Instabilities*, Department of Chemical Engineering, University of Kyoto, September 1989.

Denn, M.M., *Structure Development in Thermotropic Liquid Crystalline Polymers*, Japanese Society of Materials Science, Kyoto, September 1989.

Mansfield, K.F. and D.N. Theodorou, *Molecular Modeling of Polymers at Interfaces*, Presented at the Annual Meeting of the American Chemical Society, Miami Beach, Florida, September 1989; Department of Chemical Engineering, California Institute of Technology, Pasadena, California, February 1989.

Novak, B., *Inorganic-Organic Liquid Crystal Composites*, IBM Almaden Research Center, San Jose, CA, November 1989.

Reimer, J.A., *On the Application of Solid State NMR to the Study of Polymers*, Annual Meeting of the American Institute of Chemical Engineers, San Francisco, CA, November 1989.

Spontak, R.J. and M.C. Williams, *Novel Factors Influencing Microphase Separation in SB/SBS Block Copolymers*, NATO/ASI Meeting, Phase Transitions in Soft-Condensed Matter, Geilo, Norway, April 1989. (To be printed in the Proceedings.)

Theodorou, D.N., *Molecular Modeling of Polymers at Interfaces*, Department of Chemical Engineering, MIT, Cambridge, MA, March 1989; and Air Products and Chemicals, Inc., Allentown, PA, May 1989.

Theodorou, D.N., *Surface and Interfacial Properties of Polymers: A Molecular Modeling Approach*, Process Technologies Laboratory, 3M Corporate Research, St. Paul, Minnesota, May 1989.

Theodorou, D.N., *Data and Knowledge for Material Design*, Alcoa Laboratories Technical Symposium on Opportunities for Computer Science to Advance Material Science, Nemacolin, PA, October 1989.

Contributed Talks

Chakraborty, A.K., M. Tirrell, H.T. Davis, and J.L. Martins, *Density Functional Theory of PMMA Adsorption on Aluminum Surfaces*, March Meeting of the APS, St. Louis, MO, March 1989.

Chakraborty, A.K., M. Tirrell, H.T. Davis, and J.L. Martins, *The Acrylic Polymer-Metal Interface: A Density Functional Study*, Annual Meeting of the A.I.Ch.E., San Francisco, CA, November 1989.

Hill, D. and M.M. Denn, *Speculations on the Relation between Adhesive Failure and Melt Fracture*, 61st Annual Meeting of the Soc. of Rheology, Montreal, Canada, October 1989.

Kalika, D.S., N. Masciocchi, D.Y. Yoon, W. Parrish, and M.M. Denn, *Structure and Dynamics of a Thermotropic Liquid Crystalline Polymer*, Annual Meeting of the American Institute of Chemical Engineers, San Francisco, CA, November 1989.

Konstandinidis, K., J. Evans, M. Tirrell, and A.K. Chakraborty, *A Solid State NMR Study of the PMMA-Al_2O_3 Interface*, Annual Meeting of the A.I.Ch.E., San Francisco, CA, November 1989.

Mansfield, K.F. and D.N. Theodorou, *Molecular Simulation of Glassy Polymer/Graphite Interfaces*, Annual Meeting of the American Institute of Chemical Engineers, San Francisco, CA, November 1989.

Nuel, L. and M.M. Denn, *Viscosity of Processed and Filled Vectra A-950*, 60th Annual Meeting of the Society of Rheology, Gainesville, Florida, February 1989.

Rosenberg, J. and R. Keunings, *On the Numerical Integration of Viscoelastic Flow Equations,* Seventh International Conference on Finite Element Methods in Flow Problems, Huntsville, Alabama, April 1989. (To be published in the proceedings.)

Shaffer, J.S. and A.K. Chakraborty, *Interactions of Acrylic Polymers with Aluminum Surfaces,* Fall Meeting of the MRS, Boston, MA, November 1989.

Shaffer, J.S. and A.K. Chakraborty, *Interactions of Polymers with Jellium Surfaces,* Annual Meeting of the A.I.Ch.E., San Francisco, CA, November 1989.

Shipman, R., M.M. Denn, and R. Keunings, *Simulation of Extensional Rheometers,* International Conference on Extensional Flow, Combloux, France, March 1989x.

Spontak, R.J. and M.C. Williams, *Effect of Polydispersity on the Microstructure of Microphase-Separated Block Copolymers,* Annual Meeting of the Norwegian Physical Society, Kvam, Norway, September 1989.

Enzymatic Synthesis of Materials Project

Refereed Journal Articles

Anthony-Cahill, S.J., M.C. Griffith, C.J. Noren, D.J. Suich, and P.G. Schultz, "Site-Specific Mutagenesis with Unnatural Amino Acids," *Trends in Biochemical Sciences,* vol. 14, p. 400, 1989.

Malcolm, B.A., 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," *Proc. Natl. Acad. Sci.*, vol. 86, p. 133, 1989. (S. Rosenberg, J.S. Allen, Chiron Corporation.)

Noren, C., S.J. Anthony-Cahill, M.C. Griffith, and P.G. Schultz, "A General Method for Site-Specific Incorporation of Unnatural Amino Acids into Proteins," *Science,* vol. 244, p. 182, 1989.

Robertson, S.A., C.J. Noren, S.J. Anthony-Cahill, M.C. Griffith, and P.G. Schultz, "The Use of 5'-phospho-2'-deoxyribocytidylylriboadenosine as a Facile Route to Chemical Aminoacylation of tRNA," *Nucleic Acids Research,* vol. 17, p. 9649, 1989.

Weitz, D. and M.D. Bednarski, "Synthesis of Acyclic Sugar Aldehydes by the Ozonolysis of Oximes," *J. Org. Chem.*, vol. 18, p. 83, 1989.

Other Publications

Kirsch, J.F., B.A. Malcolm, M.F, M.J. Corey, L. Zhang, and A.C. Wilson, "Mechanistic and Evolutionary Studies on Genetically Engineered Chicken Lysozyme," in *The Immune Response to Structurally Defined Proteins: The Lysozyme Model,* ed. S. Smith-Gill, E. Sercarz, p. 59, Adenine Press, 1989.

LBL Reports (including journal articles submitted or in press)

Bibbs, J.A. and C.-H. Wong, "Active-Site Directed Modification of Subtilisin with Methyl (β-Cinnamoyl) Sulfonate: Mechanism and Synthetic Applications," *J. Am. Chem. Soc.* (In press.)

Chen, S.T., J.A. Bibbs, W.J. Hemmen, Y.F. Wang, J. Liu, M.W. Pantoliano, M. Whitlow, P.N. Bryan, and C.-H. Wong, "Enzymes in Organic Synthesis: Use of Subtilisin and a Highly Stable Mutant Derived from Mutations," *J. Am. Chem. Soc.* (In press.)

Edwards, S.G., LBL 28397, "Polyethylene Glycol-Modified Chicken Lysozyme," *Journal of Polymers for Advanced Technologies.* (Submitted.)

Malcolm, B.A., K.P. Wilson, B.W. Matthews, J.F. Kirsch, and A.C. Wilson, "Ancestral Lysozymes Reconstructed, Neutrality Tested, and Thermostability Linked to Hydrocarbon Packing," *Nature.* (In press.)

Mastandrea, M., T. Wilson, and M.D. Bednarski, LBL-27701, "Sugar Coated Semiconductors: Model Surfaces to Study Biological Adhesion," *J. Am. Chem. Soc.* (Submitted.)

Michiels, A.G., A. Wang, D.S. Clark, and H.W. Blanch, "Inhibition of Dextransucrase by Fluoro- and Thioderivatives of α-D-Glucosyl Fluoride Modified at C2, C3 and C5," *Carbohydrate Research.* (Submitted.)

Noren, C.J., S.J. Anthony-Cahill, D.J. Suich, K.A. Noren, M.C. Griffith, and P.G. Schultz, "*In Vitro* Suppression of an Amber Mutation by a Chemically Aminoacylated Transfer RNA Prepared by Runoff Transcription," *Nucleic Acids Res.* (In press.)

Invited Talks

Alper, M.D., *Enzymes and Polymer Synthesis,* Gordon Conference, Polymers for Biomedical and Agricultural Applications, Ventura, California, February 1989.

Bibbs, J.A., Z. Zhong, and C.-H. Wong, *Modification of Proteases for Peptide Synthesis,* Mat. Res. Society Fall Meeting on Materials Synthesis Utilizing Biological Process, November 1989. Boston, MA

Contributed Talks

Oehler, L., C. Hobbs, M. Mastandrea, and M. Bednarski, *The Use of Proteins in the Synthesis of Polymers and the Modification of Silicon Surfaces,* Biologically Engineered Polymers 1989, Cambridge, UK, July 1989.

Structural Materials

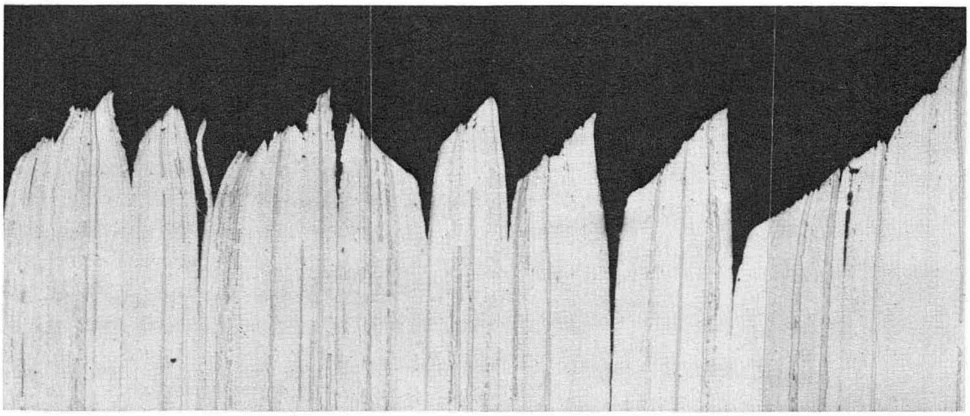
Structural Metals and Alloys
Mechanical Behavior of Materials
Ceramic Processing

Structural Materials

The CAM program on Structural Materials is intended to further develop the fundamental materials science of metals, alloys, and ceramics to the solution of basic structural problems that affect U.S. industry. Research is carried out in three areas:

The ***STRUCTURAL METALS AND ALLOYS*** project develops and applies fundamental research in the materials science of metal alloys to the solution of generic problems that affect American industry. It includes projects in light alloys, high resolution characterization of structures, formability, methods for high-field superconducting magnets, and alloy theory. The research is conducted in close collaboration with other national laboratory groups and with industry—the potential users of the research. Research on light alloys is done in collaboration with several aluminum and aerospace companies and has received support from Alcoa, Lockheed, Northrop, Allied Chemical and NASA. Research on sheet metal forming is conducted with and receives support from Ford Motor Company, Rouge Steel and LTV steel. Research highlights of the past year include:

- The successful casting and processing of Al-Li-Sc alloys, which may offer an outstanding combination of superplastic forming characteristics and cryogenic mechanical properties.
- Confirmation of the decompositional theory for spinodal ordering by high resolution imaging.
- Demonstration of high ductility in Al-Li base alloys in the coherently ordered spinodal condition.
- Demonstration that thin, as-solidified solder contacts may deform superplastically when loaded in shear at moderate temperature.
- Demonstration that the creep and thermal fatigue resistance of eutectic solder contacts is improved by Cd and In additions.
- Direct observation of the microstructural mechanism of electromigration failure in Al-Cu thin film conducting lines.
- Clarification of the relation between austenite stability and fracture toughness when metastable austenitic steels are fractured in high magnetic fields.
- Semi-quantitative model for the rate of fatigue crack growth in metastable austenitic steels.
- New method for determining the instantaneous free energy of systems that are far from equilibrium.



The aim of the *MECHANICAL BEHAVIOR OF MATERIALS* project is to develop a fundamental mechanistic understanding of fracture processes in order to provide guidelines for improved life prediction and the design of superior fracture-critical materials. It provides direct support to other CAM projects studying materials with important and interesting fracture properties. Work during the past year includes:

- Modelling of mechanisms associated with fatigue-crack propagation and cryogenic fracture-toughness properties of advanced aluminum-lithium alloys in plate vs. sheet and I/M vs. P/M product forms.
- Characterization of cyclic fatigue-crack propagation along glass/Cu and Al_2O_3/Al-alloy ceramic-metal interfaces (in collaboration with R.M. Cannon of the CAM Electronic Materials Program), with specific emphasis on microelectronic packaging applications.
- Characterization of cyclic fatigue in structural ceramics, including measurement of stress/life (SN) curves and the role of microstructurally small cracks on crack-propagation behavior.

The *CERAMIC PROCESSING* project develops a fundamental, predictive description of the micro-processes that determine the microstructural evolution of a range of ceramic systems, including particulate microcomposites. It exploits the potential benefits that can derive from the use of coated powders to produce such microcomposites with a highly homogeneous structure. It examines the role of a number of parameters of practical processing methods, such as heating rate and compaction stress in determining the microstructure of final ceramic bodies. Recent results include:

- The determination of the effects of initial compaction stress on the densification behavior of SiC/ZnO matrix particulate composites.
- Demonstration of the agreement between the densification behavior of a uniform glass powder and the theory of glass densification kinetics.
- Determination of the temperature dependence of the densification and creep viscosity.
- Examination of the relationship between pore size, grain growth, and sintering stress.
- Preparation of dense compacts of silicon carbide whiskers in an alumina matrix from coated whiskers.

Above: Through-thickness delamination cracking during low temperature fracture of commercial aluminum-lithium alloys. 1cm = 200μm. (XBB 892-1272)

STRUCTURAL METALS AND ALLOYS

LIGHT ALLOYS

Research on light alloys is currently focused on low density aluminum alloys. The main emphasis is on lithium-containing aluminum (Al-Li) alloys that can reduce aircraft or spacecraft weight by providing lower densities and higher elastic stiffnesses than competing aluminum alloys with similar combinations of mechanical properties. Although the development of these alloys was primarily aimed at the commercial aircraft market, their advantages over conventional alloys are even greater for spacecraft. Our investigations are organized primarily around the requirements of a specialized application, cryogenic fuel tankage for space vehicles, and it focuses on three main research areas: *cryogenics and weldability; structural studies; and fatigue and fracture.* Much of the work is advised, performed jointly with, or funded by industrial partners.

Cryogenic Studies

J. Glazer, S. Verzasconi, A.J. Sunwoo, D. Chu, J.W. Morris, Jr.

Three of the barrier problems to the application of Al-Li alloys in cryogenic tankage are addressed in the current research program: the strength-toughness relation of aluminum-lithium alloys at cryogenic temperatures, the weldability of Al-Li alloys for cryogenic use, and the formability of advanced Al-Li alloys. Research on strength-toughness relations and weldability has concentrated on the commercial Al-Li-Cu alloys 2090 and 2091 in plate form. Research in formability has focused on superplastic modifications of 2090 and on the development of Al-Li-Sc alloys that may combine exceptional superplastic forming properties with excellent fracture toughness properties at 4 K. This work was supplemented by research on the hydrogen sensitivity of Al-Li alloys, and by the completion of a laboratory melting furnace that gives us the capability to cast and fabricate light alloys, including Al-Li and Al-Sc alloys.

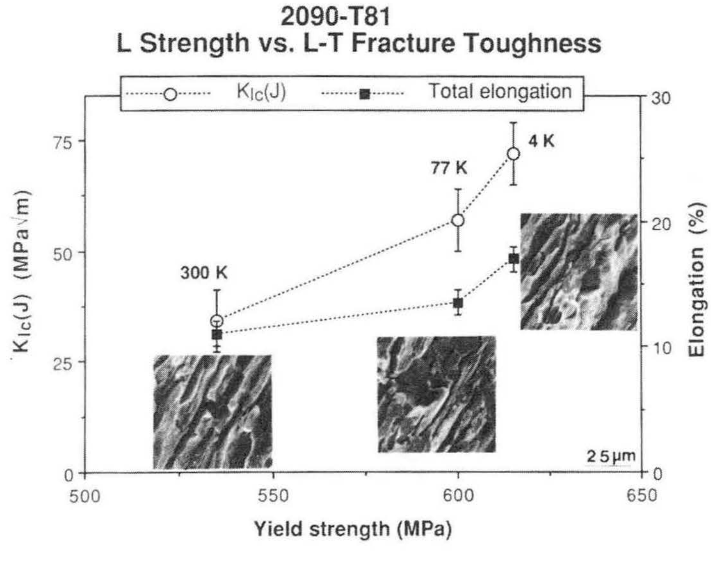


Figure 1
Summary of 2090-T81 L strength and L–T toughness combination as a function of temperature. Tensile data were obtained at T/2. Error bars represent scatter in data. Insets are scanning electron micrographs of fracture surfaces of J_{Ic} specimens used to determine fracture toughness. (XBB 894-3137)

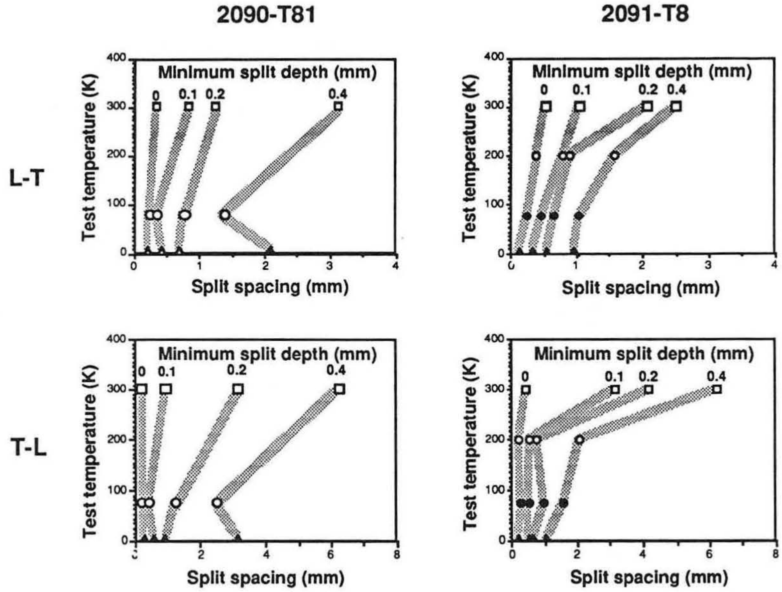


Figure 2
Variation in mean split spacing with test temperature and minimum split depth for 2090-T81 and 2091-T8 J_{Ic} specimens in the L-T and T-L orientations. Note the change in the horizontal scale for L-T and T-L orientations. (XBL 902-435)

—Metallurgical Sources of Mechanical Behavior at Cryogenic Temperature

J. Glazer, D. Chu, J.W. Morris, Jr.

In previous work we established the attractive cryogenic mechanical properties of the Al-Li alloy, 2090, in the T81 condition. The strength, elongation and fracture toughness of the alloy increase significantly and monotonically as the temperature drops from room temperature to 4 K. It is important to know the metallurgical sources of this phenomenon to guide the development and use of cryogenic modifications of the alloys. Previous work showed that the increase in tensile elongation is associated with an increase in work hardening rate as the temperature decreases. The metallurgical source of increased work hardening is still under investigation. Two sources have been suggested for the improvement in toughness: the improvement in tensile properties as temperature decreases, and the observed delamination of the alloy transverse to the fracture surface.

The systematic measurement of the cryogenic mechanical properties of alloys 2090 and 2091 from room temperature to 4 K was completed during 1989. The results demonstrate that two factors largely govern toughness: the tensile ductility and the fracture mode. In 2090-T81 plate the fracture mode is unchanged, and the toughness scales with the ductility, as measured by the total elongation (Figure 1). The toughness of the 2091 plate tested was influenced by a fascinating change in fracture mode. The alloy undergoes an *inverse ductile-brittle transition,* in which cleavage-like fracture at room temperature disappears into a ductile fracture mode at lower temperature. Where the fracture mode is constant the toughness of this alloy also scales with its ductility.

The influence of transverse delamination was investigated by stereological studies of delamination during fracture from room temperature to 4 K. The results show that there is no consistent correlation between the extent or spacing of delaminations and the fracture toughness (Figure 2). In fact, the extent of delamination decreases significantly between 77 K and 4 K, where the fracture toughness shows its most dramatic increase. This result is consistent with prior work on fracture in steels, which shows that the intrusion of delamination often causes a loss of toughness. The

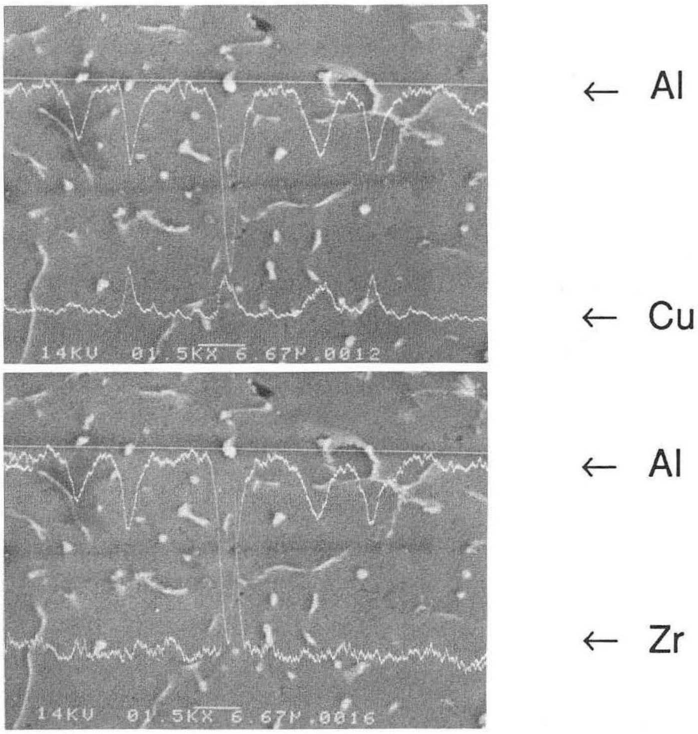


Figure 3
Energy dispersive X-ray line scans of the gas tungsten are fusion zone: (a) concentration profiles of Al and Cu, (b) concentration profiles of Al and Zr. (XBB 883-2252)

result is surprising, since delamination divides the plate into thin sheets, and toughness ordinarily increases as thickness decreases. The reason is under investigation, but is probably due to the fact that, in contrast to machining, natural delamination creates irregular, flawed sheets with inherently low toughness. The results leave open the question of whether delamination is needed to suppress a change to a brittle fracture mode.

—Welding

A.J. SUNWOO, J.W. MORRIS, JR.

While aluminum alloy components in aerospace vehicles are usually joined with fasteners, cryogenic tankage must be welded. Hence the weldability of Al-Li alloys is important for this application. The weldability of alloy 2090 has been investigated using gas tungsten arc and electron beam welding techniques, in both the autogenous condition and with filler metal additions, and the welded plates studied in both the as-welded condition and after post-weld heat treatments. The results show that the weld metal is invariably lower in strength than the base metal, and has different aging characteristics. These are associated with the chemical heterogeneities within the weld (Figure 3). The best filler additions of those studied to date are rich in Cu, which substantially improves elongation.

The heat-affected zone (HAZ) of the weldment is of particular concern. If the plate is welded in the aged condition, the aging distribution in the HAZ is disturbed, leading to a loss of strength and embrittlement at low temperature. The HAZ properties of plates aged after welding were studied and correlated with precipitation reactions in the microstructually disturbed HAZ (Figure 4). The results show that the best ductility is obtained when the alloy is welded in the unaged condition and given appropriate post-welding heat treatments.

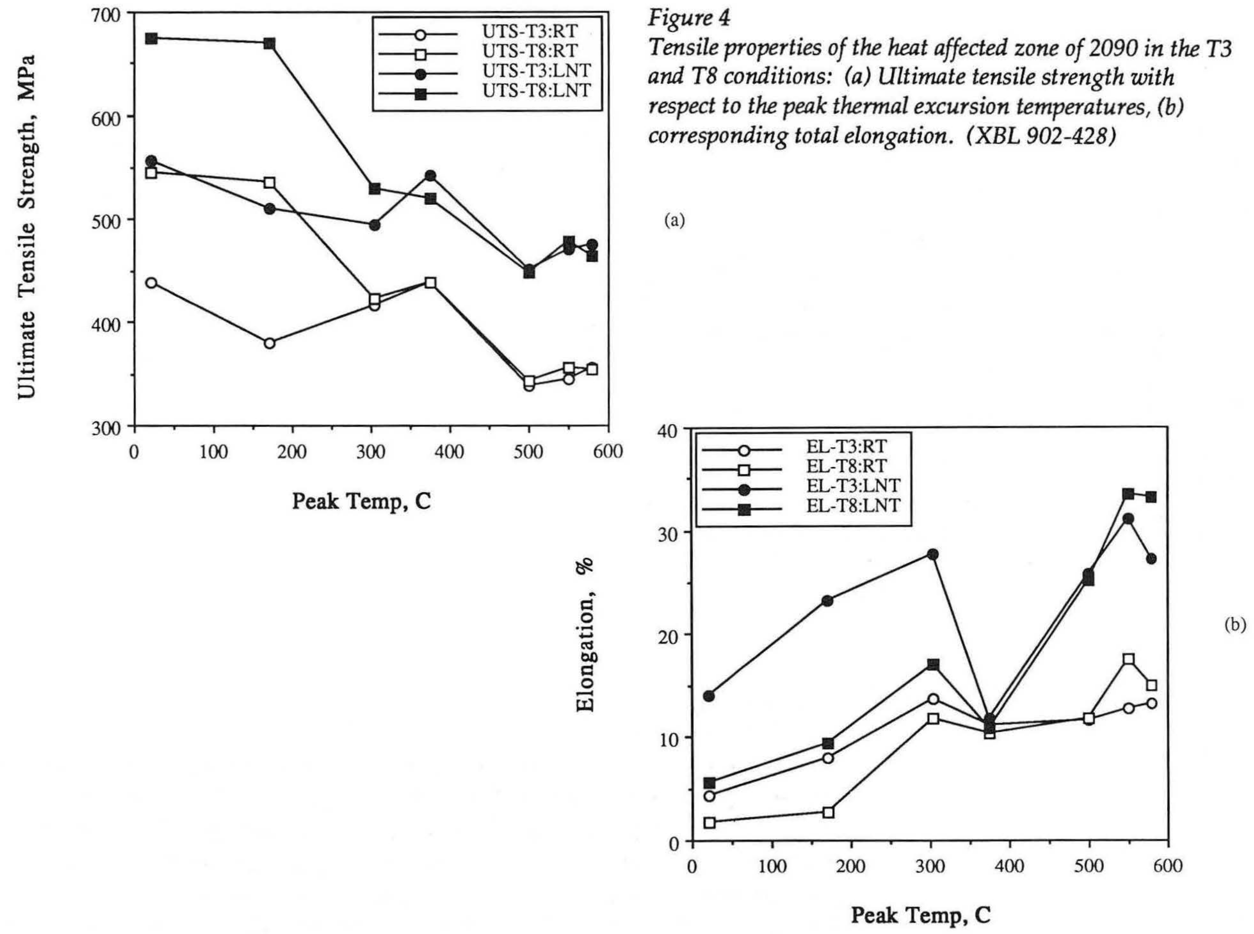


Figure 4

Tensile properties of the heat affected zone of 2090 in the T3 and T8 conditions: (a) Ultimate tensile strength with respect to the peak thermal excursion temperatures, (b) corresponding total elongation. (XBL 902-428)

—*Superplastic Al-Li Alloys*

S. Verzasconi, E. Bradley, J. W. Morris, Jr.

There is interest in the use of superplastic modifications of Al-Li and other light alloys to construct cryogenic tankage, since superplastic forming may reduce manufacturing costs and minimize required welding. The alloy used must combine superplasticity with good cryogenic mechanical properties. In previous work done in collaboration with Lockheed, a superplastic modification of alloy 2090 was shown to have increased ductility at 4 K. However, the eventual fracture mode changed from ductile to brittle intergranular, suggesting that the toughness might decrease. Research done in collaboration with NASA-Langley and Northrop during the past year tested the cryogenic mechanical properties of In-doped 2090 in a superplastic condition, and research done in collaboration with Alcoa tested the mechanical properties of a series of Al-Mg-Sc superplastic alloys. Since all alloys were in thin sheet form, the Kahn tear test was used as a measure of toughness.

Studies of superplastic 2090 and In-doped 2090 suggest that both have low toughness in the superplastic condition at 4 K. While the strength and ductility increase, the toughness decreases, in part because of a change to an intergranular fracture mode in the fine-grained, equiaxed alloys. Superplastic Al-Mg-Sc alloys, on the other hand, have outstanding combinations of strength and toughness at 77 K (Figure 5), which suggests the further development of these alloys for possible cryogenic use.

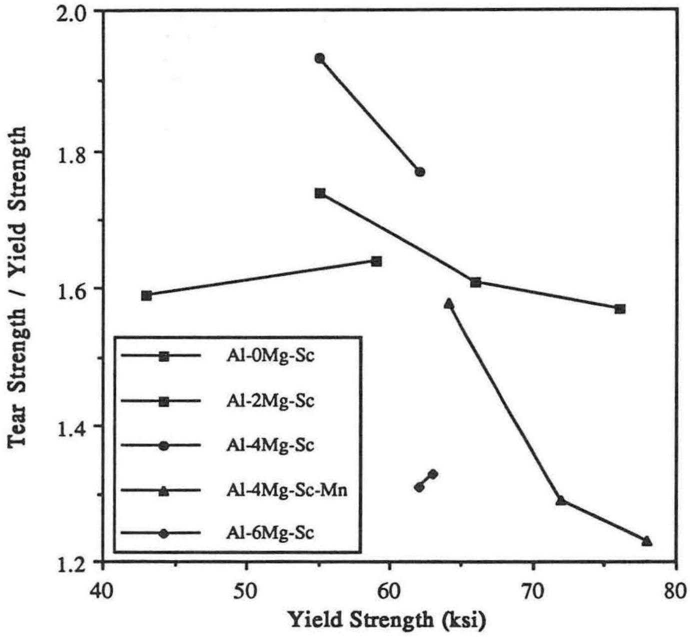


Figure 5
Yield strength versus tear-yield for SPF Al-Sc alloys. (XBL 902-429)

—*Exploratory Research on Al-Li-Sc Alloys*

R. Emigh, S. Verzasconi, E. Bradley, J.W. Morris, Jr.

A program of exploratory alloy development of Al-Li-Sc alloys has been undertaken in collaboration with Alcoa, with the intent of combining the excellent superplastic and cryogenic mechanical properties of Al-Sc alloys with the lower density that can be attained with Li additions. Previous work at Alcoa has documented exceptional superplasticity, and the recent CAM research reported above has shown good cryogenic toughness. To conduct this research a light alloy melting facility was constructed at LBL that permits the melting and rapid casting of Al alloys under inert atmosphere. This facility was used to cast alloys of composition Al-2.2Li-0.5Sc and Al-2.0Li-2.0Mg-0.5Sc (wt. %). Research is underway to identify processing sequences that maximize strength and superplastic properties. A yield strength of 55 ksi has been obtained in the Al-Li-Sc alloy in the solution-treated and aged condition, which compares favorably with the strength of Al-Li-Zr alloys (Figure 6). Transmission

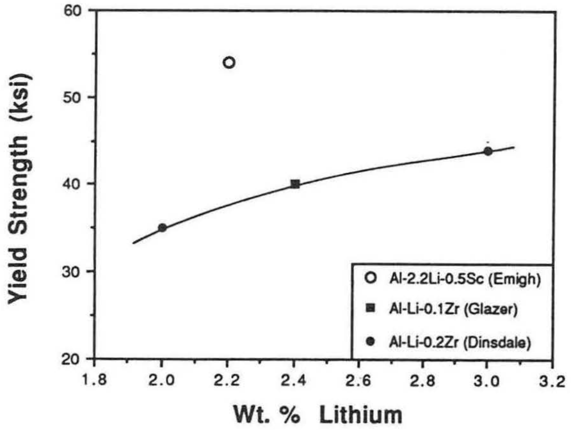


Figure 6
Yield strength comparison between Al-Li-Sc and Al-Li-Zr alloys. (XBL 902-430)

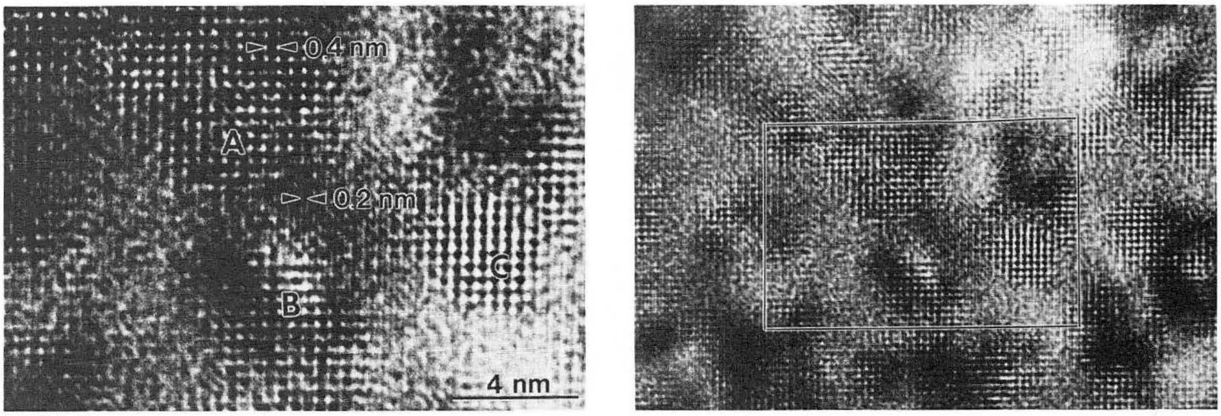


Figure 7
HREM image of Al-Li alloy after quenching and room temperature aging for 24 hours. The modulated order/disorder structure is shown in (a). Antiphase domains, A and B, are shown in (b), a high magnification image of (a). The disordered aluminum matrix may be considered an antiphase domain boundary. (XBB 893-1742)

electron microscopic studies done in collaboration with S. Miyasato and G. Thomas have demonstrated that fine, equiaxed subgrain structures are obtained. Measurements of superplastic deformation are now underway.

Structural Studies

G. THOMAS

The basic emphasis of the research on Al-Li base alloys is to utilize electron microscopy, especially high resolution imaging and microanalytical techniques, including the critical voltage effect, to characterize and understand the mechanisms of precipitation so that eventually the most appropriate processing routes can be established to control the microstructure and morphology of precipitation so as to improve the uniformity of the mechanical properties.

A second part of the program is to explore composites of Al alloys such as silicide-ceramics and to develop new composites utilizing submicron diameter whiskers of mullite in Al and Al-alloy matrices. Research in the former group is being partially supported by Allied Signal. Support for the mullite whiskers project is being sought.

—Microstructural Evolution in an Al-2.6 Li-1Cu-0.5 Mg Alloy

S. MIYASATO AND G. THOMAS

Since the subsequent microstructure and properties depend upon the initial decomposition process, and hence, processing route, the early development of precipitation in a binary Al-Li and a quaternary Al-Li-Cu-Mg alloy was investigated by high resolution transmission electron microscopy. The as-quenched microstructure was found to consist of small ordered domains which were unaffected by the presence of Cu and Mg alloying addition, δ' (Al_3Zr) dispersoids and grain boundaries, and are interpreted as forming by spinodal decomposition from a homogeneously ordered lattice. The ordered domains, ~4 nm in diameter, were often observed in antiphase with each other and were separated by regions of disordered matrix (Figure 7). The metallographic details are consistent with the theory of Khatchaturyan et al.

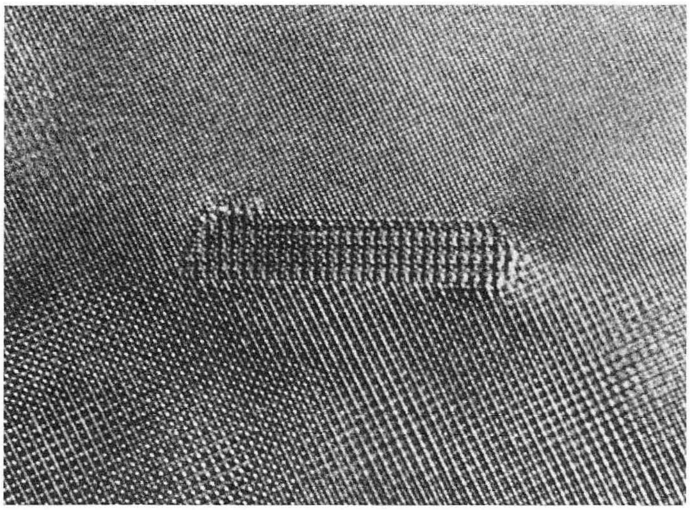


Figure 8
S′ precipitate at δ′/Al matrix interface in Al-Li-Cu-Mg alloys; orientation is [001] Al. Note also the superstructure along <102> similar to ordered phases in Ni-Mo found by Das and Thomas. (XBB 888-7750)

—Nucleation and Growth of Al_2CuMg (S′) in Al-Li-Cu-Mg and Al-Cu Mg Alloys

V. Radmilovic, G. Thomas, G.J. Shiflet,* E.A. Starke, Jr.*

Since the mechanical properties of Al alloys depend critically on the microstructure and its heterogeneities, research to understand precipitation mechanisms in these alloys is very important.

The alloys which were studied were Al/2Cu/1Mg/0.14Zr/0.08Fe and Al/1.3Cu/1Mg/2.5Li/0.9Zr with attention being devoted to formation of the so called S′ phase of (ideal) composition (Al_2CuMg).

In the non-Li alloy S′ principally nucleates preferentially at quenching defects following clustering of Mg and Cu. In Li bearing alloys S′ forms mainly at δ′/matrix interfaces (Figure 8) and on dislocations. In both cases growth occurs by ledge migration and ordered periodicities along develop $<102>_m$.

Fatigue and Fracture

Low density lithium containing aluminum alloys are currently of considerable interest to the aerospace industry owing to cost benefits from potential weight and fuel savings. Despite early limitations of poor ductility and toughness properties, recent developments in alloying and thermomechanical processing of such alloys have resulted in optimized chemistries and microstructures; the result is a series of commercial alloys that show strength-toughness combinations comparable, and in many instances superior, to traditional high strength Al-Cu and Al-Zn-Mg alloys, particularly at cryogenic temperatures.

Commercial Al-Li alloys are presently available in various product forms, i.e., sheets, plates, extrusions, and forgings, and have been designed specifically for five primary categories: high strength; damage tolerance; stress corrosion cracking resistance; minimum density; and superplasticity. Prominent among these alloys are the IM (ingot metallurgy) Al-Li-Cu-Zr and Al-Li-Cu-Mg-Zr systems commercially registered as 2090, 8090, 8091 and 2091; alloys 2090 and 8091 are planned as high strength replacements for series 7000 alloys, whereas 8090 and 2091 are planned for medium strength and damage tolerant applications replacing series 2000 alloys.

Although the role of microstructure in influencing the strength, toughness and fatigue-crack growth properties of experimental Al-Li alloys has

---

* Supported by U.S. Army Res. Office grant DAAL03-86-K0128.

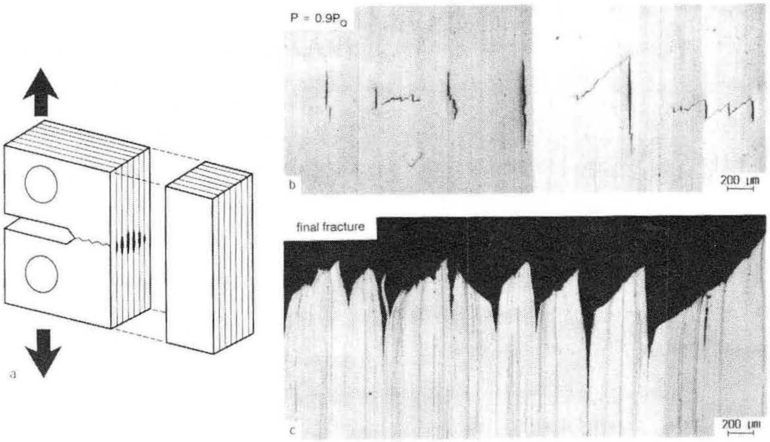


Figure 9
a) Schematic illustration of crack-divider delamination toughening via through-thickness splitting, and sections taken through the specimen thickness ahead of the fatigued-precrack tip, b) at a load corresponding to 0.9 P_Q, where P_Q is load at crack initiation, and c) following fast fracture. Optical micrographs obtained from near peak-aged 2090-T81 plate tested a 77 K. (XBB 8912-10553)

been widely reported, there is a paucity of data on the performance of commercial alloys. Accordingly, the CAM program over the past year has focused on examining the toughness and cyclic crack-growth properties of these alloys, with specific emphasis on elucidating the micromechanisms underlying their mechanical behavior.

—Fracture-Toughness Properties: Cryogenic Behavior

R.O. RITCHIE AND K.T. VENKATESWARA RAO

Cryogenic strength-toughness relationships for advanced aluminum-lithium alloys 2090, 8090, 8091 and 2091 were examined as a function of microstructure, plate orientation and wrought-product form (plate vs. sheet), with specific emphasis on the underlying micromechanisms associated with crack advance. It was found that, with decrease in temperature from 298 K to 77 and 4 K, strength, tensile elongation and strain-hardening exponent are increased for all alloy chemistries, microstructures and product forms; however, the longitudinal (L-T, T-L) fracture toughness may increase or decrease depending upon the prevailing microscopic mechanism (microvoid coalescence vs. transgranular shear) and macroscopic mode (plane strain vs. plane stress) of fracture. In general, alloy microstructures that exhibit changes in either the fracture mechanism or mode at low temperatures show a decrease in L-T toughness. Conversely, when the fracture mechanism is unchanged between ambient and 4 K, observed variations in toughness with temperature are a strong function of the degree of local stress-triaxiality that develops at the crack tip. In very thin sheets, where the fracture mode remains one of plane stress ("stant" fracture), the elevation in toughness at low temperatures is associated with the concurrent increase in tensile strength and ductility; conversely, in thick plate, the increased occurrence of through-thickness delaminations (due to the weak short-transverse properties) at low temperatures locally promotes plane-stress conditions, thereby enhancing toughness by relaxing triaxial constraint (Figure 9). In sheets of intermediate

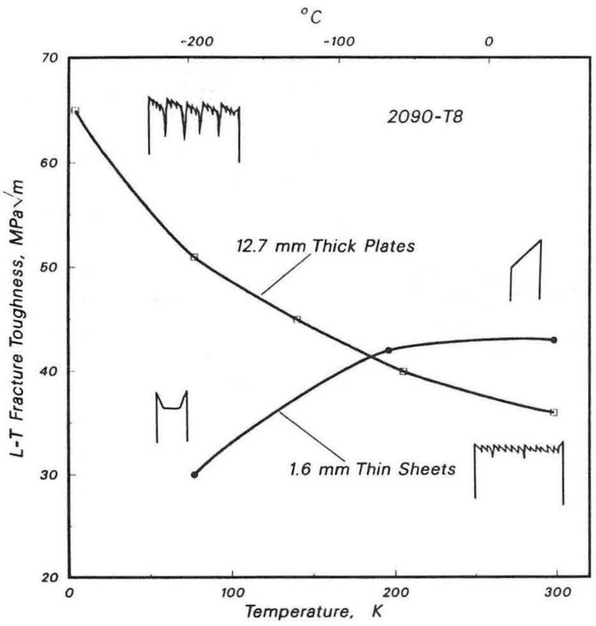


Figure 10
Variation in the fracture toughness (L-T orientation) with test temperature for 1.6-mm-thin (T83) sheet and 12.7-mm-thick (T81) plate of near peak-aged 2090- T8 aluminum-lithium alloy. Note that with decreasing temperature the toughness of the T83 sheet decreases whereas that of the T81 plate increases. (XBL 892- 623)

thickness, however, the absence of such through-thickness delaminations permits the expected transition from plane-stress to plane-strain conditions, with the result that the toughness now decreases with reduction in temperature (Figure 10).

—Fatigue-Crack Propagation: Role of Microstructure

R.O. Ritchie, K.T. Venkateswara Rao

Mechanisms influencing the ambient-temperature fatigue-crack propagation properties of commercial aluminum-lithium alloys 2090, 2091, 8090 and 8091 were examined, with specific emphasis on the role of microstructure. Results on fatigue-crack propagation behavior were obtained, for both "long" (≤ 5 mm) and "microstructurally small" (~1 to 1000 μm) cracks, and compared with behavior in traditional high-strength aluminum alloys. In general, it was found that the growth rates of long fatigue cracks in Al-Li alloys are up to two to three orders of magnitude slower than in traditional 7000 and 2000 series alloys, when compared at an equivalent stress-intensity range (ΔK). Corresponding growth rates of microstructurally small fatigue cracks, conversely, were up to two to three orders of magnitude faster than the long-crack results. Such observations are attributed to the prominent role of crack-tip shielding in aluminum-lithium alloys, resulting from the tortuous and deflected nature of the crack paths which leads to a reduced crack-tip "driving force" from crack deflection and, more importantly, from the consequent crack closure induced by the wedging of fracture-surface asperities (Figure 11). As microstructurally small cracks are unable to develop the same degree of shielding from crack closure by virtue of their limited wake, small-crack growth rates are significantly accelerated. Unlike fracture-toughness behavior, artificial aging of commercial Al-Li alloys to peak strength has a mixed influence on the (long-crack) fatigue resistance. Although behavior at high growth rates is relatively unaffected, in 2091 nominal threshold ΔK_{TH} values are increased by ~17%, whereas in 8090 and 8091 they are decreased by 16-17%. All alloys, however, showed reduced effective fatigue thresholds at peak strength after correcting for crack closure.

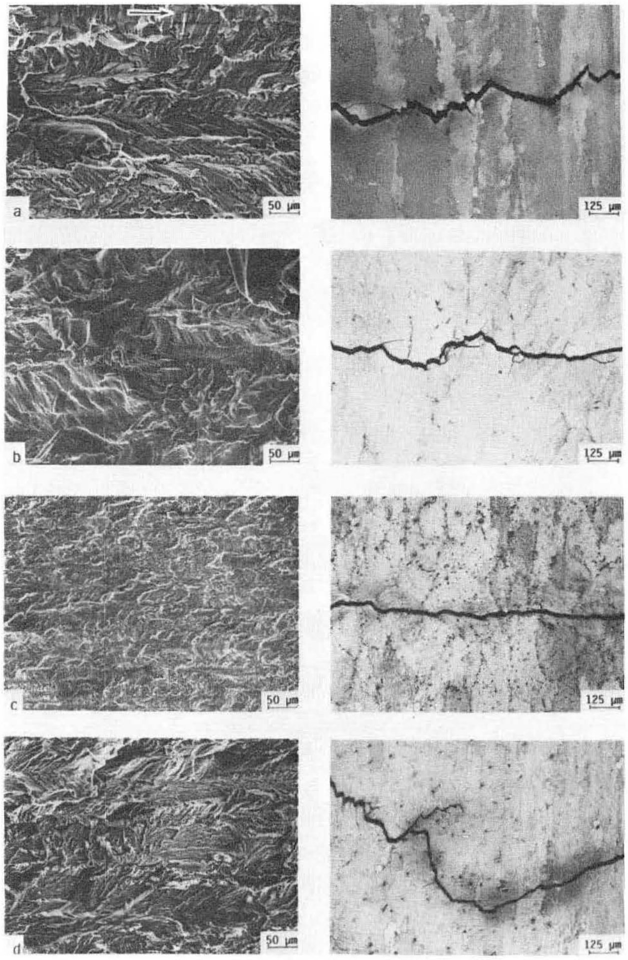


Figure 11
Fatigue fracture surfaces (SEM) and corresponding crack path morphologies (optical) of various commercial Al-Li alloys; highly deflected crack paths in 2090, 2091, and 8090 alloys, compared with relatively linear crack path in 8091 alloy, should be noted. a) 2090-T8E41; b) 8090-T8x; c) 8091-T8X; d) 2091-T8X. Arrow indicates general direction of crack growth. (XBB 883-2387)

—*Fatigue-Crack Propagation: Sheet vs. Plate Material*

R.O. Ritchie, K.T. Venkateswara Rao

Micromechanisms influencing the propagation of long (>10 mm) fatigue cracks in aluminum-lithium alloys were examined by specifically comparing crack-growth kinetics in a peak-aged Al-Li-Cu-Zr alloy 2090, processed as 1.6-mm thin (T83) sheet and 12.7-mm thick (T81) plate. It was found that in general crack-growth rates are significantly faster in the sheet material at equivalent stress-intensity levels, due to differences in the role of crack-tip shielding, resulting from crack deflection and consequent crack closure from wedging of fracture-surface asperities (Figure 12). Microstructurally, such differences were related to the role of microstructure in inducing various mechanisms of crack-tip shielding. In plate material, where microstructures are unrecrystallized and show coarse elongated grains with strong deformation texture, fatigue-crack paths were unusually tortuous with significant crack deflection; such a morphology promotes marked (roughness-induced) crack closure, concomitant with reduced crack-growth rates. In sheet material, conversely, microstructures were recrystallized with a finer and essentially equiaxed grain size; crack paths were correspondingly highly linear with the result that crack-closure levels were significantly reduced.

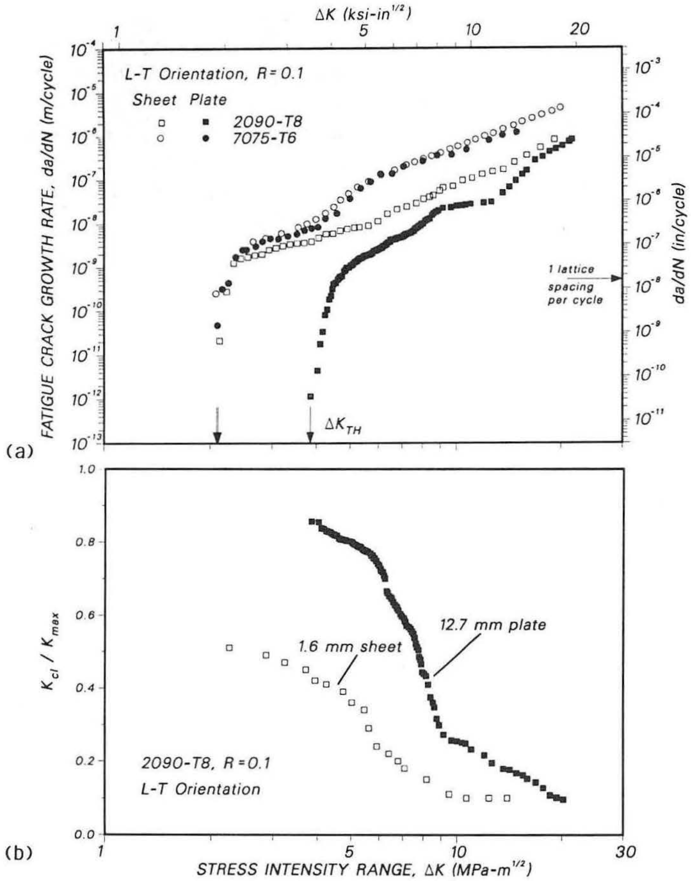


Figure 12

a) Fatigue-crack growth and b) crack-closure (K_{cl}/K_{max}) behavior in 2090-T8 sheet and plate at $R = 0.1$, as a function of the nominal stress-intensity range ΔK. Growth-rate data are compared with corresponding results on 7075-T6. T81 plate data obtained on 6.4 mm thick specimens (T/2 location). (XBL 8912-4416)

—Fatigue-Crack Propagation and Cryogenic Toughness: Powder Metallurgy Alloys

R.O. Ritchie, K.T. Venkateswara Rao

Fatigue-crack propagation and cryogenic fracture-toughness properties of powder-metallurgy (P/M) aluminum-lithium alloys were examined in mechanically alloyed (MA) Al-4.0Mg-1.5Li-1.1C-0.8O_2 (Inco 905-XL) and rapid-solidification-processed (RSP) Al-2.6Li-1.0Cu-0.5Mg-0.5Zr (Allied 644-B) extrusions, and were compared with previous data on equivalent high-strength aluminum alloys fabricated by both ingot-metallurgy (I/M) and P/M methods. It was found that the fatigue-crack propagation resistance of the RSP Al-Li alloy is superior to traditional RSP aluminum alloys without Li, and even comparable to I/M Al-Li alloys, particularly at near-threshold and intermediate stress-intensity levels. In contrast, crack-growth rates in mechanically alloyed 905-XL P/M extrusions were nearly three orders of magnitude faster. Growth-rate behavior in the RSP 644-B alloy, however, is highly anisotropic; for example, crack-growth rates were up to three orders of magnitude faster in the T-L, compared to L-T, orientation. With respect to toughness, plane-strain K_{Ic} values in the RSP alloy were observed to increase with decrease in temperature from 298 to 77 K. Such results were interpreted in terms of the micromechanisms of fatigue and fracture behavior in P/M Al-Li alloys, specifically involving the microstructural role of hardening mechanism, slip mode, grain structure and texture on the development of crack-tip shielding (crack-path deflection and crack closure) and short-transverse delamination cracking.

The forming of sheet metal is integral to many manufacturing operations. Problems associated with metal forming have particular economic significance in the automobile industry, where much of the research is concentrated. Formability is controlled by two primary factors: (1) the response of the base metal to large plastic deformations, and (2) the friction of the metal or its surface coating against the tool piece. Neither of these factors is well understood scientifically. Large-scale plastic deformation and the effective friction of coated metal surfaces under heavy loads are two of the least understood areas of mechanical behavior. Parallel research efforts in these two areas are under way.

Metal Plasticity

P. Johnson, A. Philip*, C. Tseng, J.-H. Schmitt*, J.W. Morris, Jr.

The practical goal of fundamental research in sheet metal plasticity is the development of metallurgically sound constitutive relations that describe deformation and failure. This is a difficult task. Deformation is ultimately governed by dislocation motion and interactions within grains, but is also affected by the transmission of deformation from grain to grain, which depends strongly on the crystallographic texture of the material. As an alternative to constructing microstructural models at this level, one can try to incorporate the effects of the microstructure by incorporating appropriate variables directly into a macroscopic constitutive equation, and seeking their appropriate forms. Both approaches are taken in this research, which is done in collaboration with the University of Grenoble.

Macroscopic tensile tests on drawing-quality steel showed that tensile deformation at moderate strain rate below room temperature can be described with a consitutive equation that contains a single microstructural variable, whose value is measured by the instantaneous flow stress at given temperature. Further test are under way at Grenoble to determine the applicability of this constitutive equation in multiaxial stress situations. To gain insight into the nature of the microstructural parameter, *in situ* observations of dislocation motions during deformation were made with high voltage electron microscopy. Computer simulation studies are also in progress.

Formability of Electrogalvanized Steel

S. Shaffer, W. Nojima, P. Skarpelos, C. Tseng, J.W. Morris, Jr.

The recent commitment to the use of corrosion resistant sheet steel in the automobile industry has given rise to a variety of new coating methods and types, and has resulted in some difficulty with the substitution of coated steels for their bare steel predecessors. The predominant material used in this country is unalloyed zinc electrogalvanized steel.

Research of the formability of electrogalvanized (EG) steel is done in collaboration with the Ford Motor Company, Rouge Steel, and LTV. The research is currently focused on determining which features, among several microstructural and morphological, control the effective friction of EG steel during forming. The problem is made difficult by the simultaneous variation of several microstructural factors from sample to sample of commercial steel. The variables are separated by analyzing specimens coated in a laboratory simulator at LTV Steel. Specialized characterization techniques have been developed to study the microstruc-

---

* University of Grenoble, France.

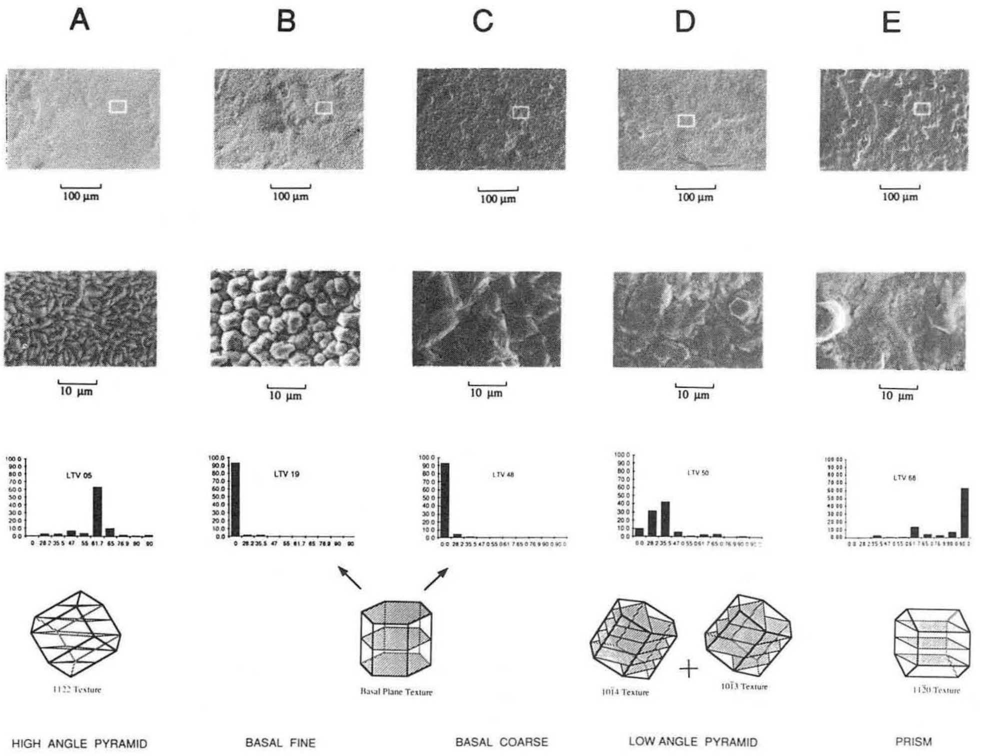


Figure 13
Five samples of laboratory produced electrogalvanized steel displaying different microroughnesses and textures (preferred crystallographic orientation). A model incorporating the effect of texture on the resistance to deformation of the surface is the basis of selection of these samples for friction testing. (XBB 901-238)

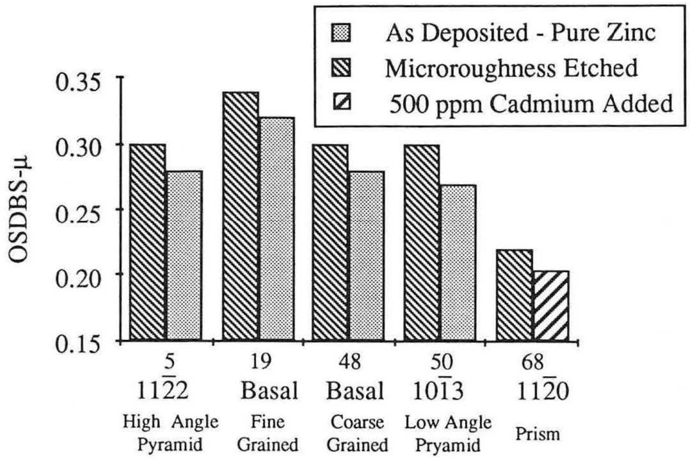
ture of the layer. Initial studies have focused on the influence of crystallographic texture and hardness on the mechanical response of the zinc layer. Surface roughness measurement and description techniques are being developed for these materials.

Figure 13 shows five of a series of 74 laboratory-produced control samples with their predominant textures. Results of tests on these samples (Figure 14) indicate that the coefficient of friction is lowered by the presence of a prism texture ($\{11\bar{2}0\}$ planes in the zinc coating parallel to the steel sheet surface) and is raised by the presence of a fine grained, basal texture ({0001} planes parallel to the sheet). Current studies are aimed at resolving the reasons for the difference in friction between fine grained and coarse grained basal texture, as well as the possible role of cadmium in lowering the friction of the prism texture samples.

STRUCTURAL MATERIALS FOR HIGH FIELD SUPERCONDUCTING MAGNETS

Structural materials in high field superconducting magnets operate under extreme conditions of stress, temperature and magnetic field. The influence of the magnet environment on mechanical properties must be understood to prevent structural failure and guide the development of new materials with exceptional properties. Many of the alloys that are used or proposed for high field magnet structures are metastable austenitic steels whose cryogenic mechanical properties are affected by strain-induced martensitic transformations. The extent and consequences of these transformations are not well understood. They are studied in this program, which is funded by the Office of Magnetic Fusion Energy of DOE.

Figure 14
Results of friction testing with a drawbead simulation (DBS) machine shows that the electrogalvanized sheet with the fine grained basal texture deposit has the highest coefficient of friction, while the prism texture deposit has the lowest. The mechanisms responsible for these results are currently under investigation.
(XBL 902-431)



The Influence of High Magnetic Fields on Fracture Toughness

J.W. Chan, J.W. Morris, Jr.

Prior research in this laboratory has documented the influence of high magnetic fields on the strength, ductility and fracture toughness of metastable austentic alloys. The most pronounced effect is on fracture toughness; prior research showed that the fracture toughness of alloy 304 at 4 K is increased by approximately 30% in an 8.0 Tesla field. This result disagreed with parallel work in Japan, which found a 25-30% decrease in toughness under comparable conditions.

To address this discrepency, AISI 304 and the less stable alloy 304L were tested at 4.2 K with and without an applied 8 T magnetic field (Figure 15). While the fracture toughness of 304 increased, that of the less stable 304L was lower in the magnetic field. Both metallographic analysis and theoretical studies show that there are two factors that influence the fracture toughness: the transformation strain, which promotes toughness, and the brittleness of the fresh martensite, which tends to lower toughness. The transformation strain dominates in 304, the fresh martensite in 304L. The results are consistent with the Japanese data since the alloy tested there, while indentified as 304, in fact has a composition and stability equivalent to 304L in U.S. designations.

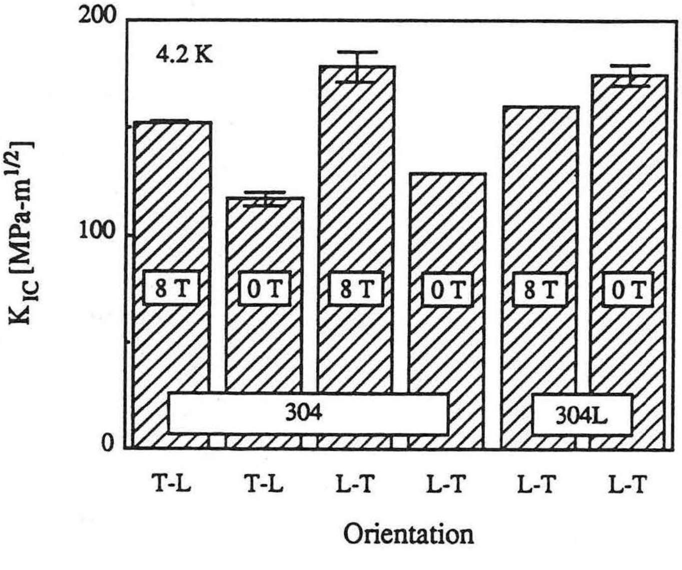


Figure 15
4.2 K AISA 304 and AISI 304L austenitic stainless steel $K_{IC}(J)$ as a function of specimen orientation and applied magnetic fields.
(XBL 902-432)

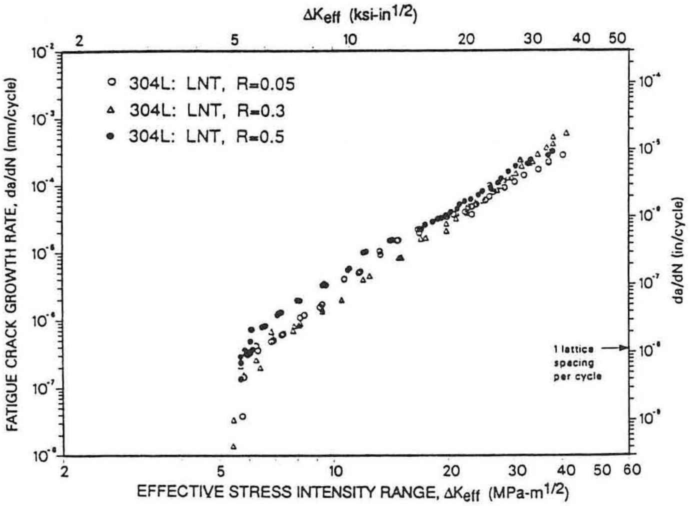


Figure 16

Crack growth rates vs. effective stress intensity factor range, $\Delta K_{eff} = K_{max} - \max\{K_{min}, K_{cl}, [K_{tran}]\}$*, for 304L austenitic stainless steel tested at 77 K with three load ratios.* K_{cl} *is the closure stress intensity,* K_{tran} *is the martensite-induced stress intensity reduction calculated from the measured transformation zone size. (XBL 902-434)*

Fatigue Crack Growth in Metastable Austenitic Steel

Z. Mei, S. Takaki*, J.W. Morris, Jr.

Research on fatigue crack growth in metastable austenitic steels at cryogenic temperature examined the alloys AISI 304L, 304LN, and 310 (a stable alloy studied for comparison). The extent of the transformation was varied through composition changes (304L compared with the more stable 304LN), test temperature (298 K, 77 K, and 4.2 K), and load ratio (mean stress). It was found that decreasing the mechanical stability of the austenite by changing composition or lowering temperature reduces the fatigue crack growth rate and increases the threshold stress intensity for crack growth. However, this beneficial effect diminishes as the load ratio increases, even though increasing the load ratio increases the extent of martensite transformation. Several mechanisms may be operative, including the perturbation of the crack-tip stress field, crack deflection, and the work hardening characteristics and relative brittleness of the transformed material. The perturbation of the stress fields appear to be the dominant effect. A theoretical model was developed to account for the influence of the martensite transformation on the stress field, and it provides a reasonably quantitative interpretation of the experimental results (Figure 16).

Crack growth rates for AISI 310 were measured at 298 K, 77 K, and 4.2 K. As temperature decreased, the fatigue crack growth rate decreased while the threshold stress intensity increased. At all three temperatures the fatigue crack propagated in a quasi-cleavage mode along a zigzag path. The propagating crack branched to an extent that increased as the temperature decreased. Since no martensite was detected on the crack surfaces and the crack surfaces were smoother at lower temperatures, neither transformation toughening nor roughness-induced crack closure can account for the temperature dependance of the crack growth rate. It is likely that in the threshold region, crack growth rate is controlled by a thermally activated process while in the Paris region, fracture due to static load operates in parallel with thermally activated processes.

THEORY OF STRUCTURE AND MICROSTRUCTURE

The science of materials processing is based on an understanding of the structures and structural transformations that create microstructure. Modern materials employ intermetallic and compound phases with

---

* Kyusu Univ., Japan.

complex structures, often as precipitate phases whose distribution in the microstructure is strongly affected by transformation strain. To help understand these phenomena, theoretical research is underway on the structures of multi-component intermetallic and oxide phases and on the microstructures of precipitates that interact elastically with one another.

Structures of Crystalline Compounds

T. LINDSEY, M. MCCORMACK, P. XU, A.G. KHACHATURYAN*, J.W. MORRIS, JR.

Many of the most important of the structures of ordered crystalline compounds are *Lifshitz structures*, which can be described as superpositions of ordering waves whose wave vectors reach the high-symmetry Lifshitz points of reciprocal space. A systematic analysis of these structures is underway which identifies their characteristics on the fcc, bcc, and hcp lattices and develops procedures for identifying these structures from the symmetry of diffraction patterns.

To understand the evolution of structure during phase transformations, it is useful to have a way of measuring the local equilibrium values of the free energies of systems that are evolving well away from equilibrium. The rate of evolution depends on two factors: the derivative of the free energy in the direction of change and a kinetic coefficient that governs the rate of change. By manipulating the general form of the kinetic equation, a method was developed to determine the free energy of the evolving state by integration.

Computer simulation techniques were used to study the evolution of a distribution of precipitates that interact elastically during growth. Using Fourier transform techniques to solve for the elastic interaction at every increment of growth, the evolution of the precipitate distribution was calculated. The results show the elastic splitting and inverse coarsening phenomena that have recently been seen experimentally.

MECHANICAL BEHAVIOR OF MATERIALS

This project has three major foci—fatigue and fracture of aluminum-lithium alloys, mechanical properties of ceramic-metal interfaces, and the newly discovered but potentially critical effect of cyclic fatigue in ceramics. The Al-Li work is described above (pages 92-96) with other CAM work on these alloys. The interface work is described on page 22 with other CAM work on interfaces.

CYCLIC FATIGUE IN CERAMICS

It has long been recognized that the vast majority of in-service structural failures in metallic components can be attributed to (cyclic) fatigue, involving the slow, subcritical growth of incipient cracks to catastrophic failure under cyclically varying loads. In contrast, it has been the perception that ceramic materials do not suffer marked degradation by cyclic fatigue. This refuted existence of true cyclic crack-propagation effects in monolithic and composites ceramics has been based primarily on the very limited crack-tip plasticity apparent in brittle solids at ambient temperatures. However, with the recent emphasis on the toughening of ceramics, e.g., by phase transformations, reinforcement, etc., to produce materials with credible structural integrity, evidence of inelastic deformation in ceramic materials, arising from transformation "plasticity," microcrack-

---

* Department of Mechanics and Materials Science, College of Engineering, Rutgers University

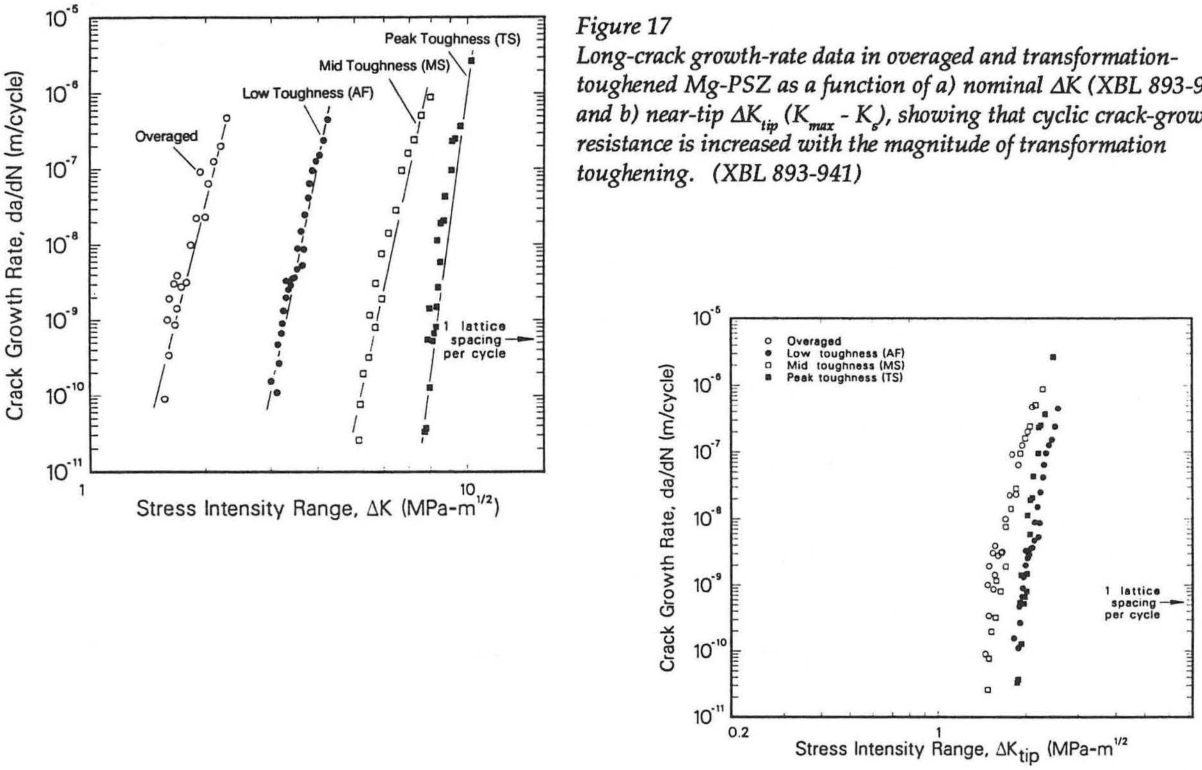


Figure 17

Long-crack growth-rate data in overaged and transformation-toughened Mg-PSZ as a function of a) nominal ΔK (XBL 893-931) and b) near-tip ΔK_{tip} (K_{max} - K_s), showing that cyclic crack-growth resistance is increased with the magnitude of transformation toughening. (XBL 893-941)

ing phenomena, ductile phase plasticity, or matrix-reinforcement interfacial displacements, has become apparent. Where such mechanisms of inelasticity prevail, even locally, the notion of "ceramic fatigue" clearly becomes feasible. Since most of the more significant applications for advanced ceramics will entail exposure to cyclic loading, e.g., in gas turbine and reciprocating heat engines, the existence of "ceramic fatigue" would pose a serious problem which has not been widely recognized and which would have severe implications on design and life prediction. Accordingly, the primary objectives of this study were to obtain evidence of true cyclic fatigue in ceramics, to characterize cyclic crack-growth rate behavior using fracture-mechanics methodology, and to provide credible models for the microstructural damage mechanisms associated with such crack advance.

Cyclic Fatigue-Crack Propagation in Mg-PSZ Ceramics

R.H. Dauskardt, R.O. Ritchie, A.A. Steffen, D.K. Veirs

The subcritical growth of long (>3 mm) fatigue cracks under (tension-tension) cyclic loading was demonstrated for ceramic materials, based on experiments using compact C(T) specimens of a MgO-partially stabilized zirconia (Mg-PSZ), heat treated to vary the fracture toughness K_c from ~3 MPa√m to 16 MPa√m and tested in inert and moist environments. Analogous to behavior in metals, cyclic fatigue-crack rates (over the range 10^{-11} to 10^{-5} m/cycle) were found to be a function of the stress-intensity range, environment, fracture toughness and load ratio, and to show evidence of fatigue crack closure. Unlike toughness behavior, growth rates were not dependent on through-thickness constraint. Under variable-amplitude cyclic loading, crack-growth rates showed transient accelerations following low-high block overloads and transient retardations following high-low block overloads or single tensile overloads, again analogous to behavior commonly observed in ductile metals. Cyclic crack-growth rates were observed at stress intensities as low as 50% of K_c, and are typically some 7 orders of magnitude faster than corresponding stress-corrosion crack-growth rates under sustained-loading conditions. Results in the four microstructures with varying toughness show that with increasing degrees of crack-tip shielding from transformation toughening, resistance to cyclic fatigue-crack propagation in Mg-PSZ is increased. By accounting for such shielding from both (roughness-induced) crack closure and phase transformation in the computation of an effective near-tip "driving force", $\Delta K_{tip} = K_{max} - K_s$, such crack-growth data could be normalized into a single relationship for the ceramic (Figure 17).

Fatigue-Crack Propagation in Ceramics: Role of Small Cracks

R.H. DAUSKARDT, R.O. RITCHIE, A.A. STEFFEN, D.K. VEIRS

The cyclic fatigue behavior of ceramics was examined in overaged and transformation-toughened magnesia-partially stabilized zirconia, with reference to the role of crack size. Specifically, stress/life (S/N) and cyclic fatigue-crack growth properties were studied in Nicra Mg-PSZ, subeutectoid aged to vary the fracture toughness K_c from ~3 MPa√m (overaged) to 16 MPa√m (TS-grade). S/N data, derived from unnotched cantilever-beam specimens, were seen to show markedly lower lives under tension-compression compared to tension-tension loading: "fatigue limits" (at 10^8 cycles) for the former case approach 50% of the tensile strength (Figure 18). When crack-growth behavior was examined under tension-tension loading in compact-tension specimens containing "long" pre-existing, through-thickness cracks of a length exceeding ~3 mm, cyclic crack-growth rates were found to be power-law dependent on the stress-intensity range ΔK (with an exponent between 20 and 40), and to show evidence of a fatigue threshold, ΔK_{TH}, of order 50% K_c. Conversely, for naturally occurring "small" (1 to 100 μm) surface cracks in the cantilever-beam specimens, crack growth was seen to occur at K levels some 2 to 3 times smaller than the long-crack threshold, to show a non-unique negative dependence on the stress-intensity range, and further to be sensitive to the level of applied stress (Figure 19), similar to the behavior in metallic materials.

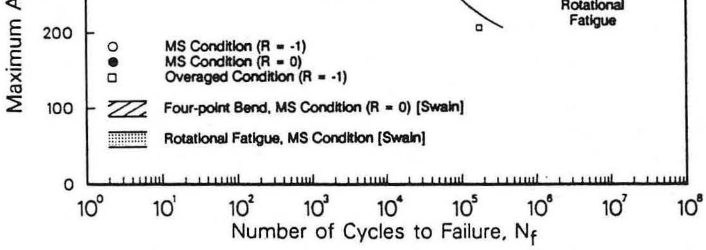
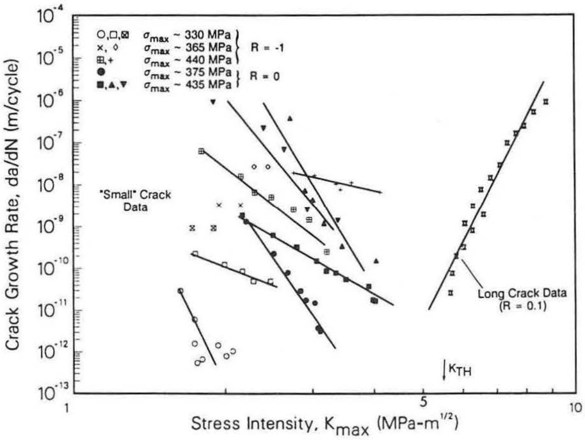


Figure 18

S/N fatigue curves for overaged and transformation-toughened (MS-grade) Mg-PSZ at $R(K_{min}/K_{max}) = 0$ (tension-tension) and = $^-1$ (tension-compression). Data from Swain et al. are shown for comparison. (XBL 8912-4414A)

Figure 19
Small-crack growth-rate data in MS-grade Mg-PSZ as a function of K_{max}, showing crack growth well below the long-crack fatigue threshold. (XBL 8912- 4415)



CERAMIC PROCESSING

An essential barrier to the use of ceramics in challenging environments is that their potentially advantageous properties, such as low specific density, high-temperature stability, and chemical resistance, cannot be exploited reliably and reproducibly (i.e., with a Weibull modulus significantly over 20), or with cost efficiency. Structural ceramics intended for use at high temperature require not only a high strength (ideally in excess of 50 kgf/mm^2) and a fracture toughness exceeding 10 MPm$^{1/2}$ but also often must withstand fluctuating loads over extended periods of use. Chemical stability in the operating environment, and creep resistance as well as fatigue resistance are all essential requirements. For example, materials such as the silicon nitrides have good fracture toughness with improving creep resistance but have suffered slow deterioration in oxidizing environments under static or dynamic loading. Indeed, problems with the fatigue resistance of the structural ceramics have emerged as an area of serious concern, as found by R.O. Ritchie at LBL-CAM and abroad, e.g., at NGK-Insulators and at GIRI-Nagoya, Japan.

Many of the important mechanical properties of ceramics depend critically on their homogeneity. Homogeneous, fine grain size at high density for single phase ceramics or spatially homogeneous distributions of dispersed phases for particulate composites can be expected to improve all forms of mechanical performance. However, the required homogeneity, especially for the particulate ceramic matrix composites, is not readily achieved. Processing methods must be devised that improve or assure homogeneity of the finished ceramic bodies. For single phase ceramics it has been found in our program that modifying the heating schedule during densification can lead to significant improvements in the performance of technical powders, while some microcomposites have been fabricated using coated ceramic powders prepared by a novel slurry method in this laboratory. These two findings are further pursued in the Ceramics Project and applied to single phase materials such as ZnO, and to alumina/silicon carbide composites, as well as to metal and polymer matrix composites with SiC powder as the dispersed phase.

A further important aspect of ceramic powder processing is that it often involves reactive sintering. In reactive sintering, powders of different chemical composition are mixed in the appropriate proportions and fired to yield the desired compound. When powder mixes are used for the initial compacts, reaction and densification, may occur at the same time. In some instances, it may be possible or advantageous to attempt to channel the reaction energy into densification or to exploit the reaction to form desirable microstructures. In this regard, the simultaneous use of steep temperature gradients, as in zone-sintering, may lead to formation of preferred textures that can impart interesting properties to the ceramic. The exploration of the fundamental aspects of reaction sintering is therefore a natural and important evolution of this project.

SINTERING OF SPHERICAL GLASS POWDER UNDER A UNIAXIAL STRESS

M.N. Rahaman*, L.C. De Jonghe

The sintering of spherical borosilicate glass powder (particle size 5-10 µm) under a uniaxial stress was studied at 800°C. The experiments allowed the measurement of the kinetics of densification and creep, the viscosities for creep and bulk deformation, and the sintering stress, which was found to increase with density. The data show excellent agreement with Scherer's theory of viscous sintering (Figure 20). They are compared with earlier observations for a crushed soda-lime glass powder.

NOVEL PROCESSING METHOD FOR ALUMINA-SiC WHISKER COMPOSITE

D. Kapolnek, L.C. De Jonghe

A method was developed for coating SiC whiskers with thick layers of a polycrystalline alumina precursor. The resulting composite powders are used to produce alumina/SiC composites for use in applications such as ceramic cutting tools.

The SiC whisker content in currently available alumina silicon carbide

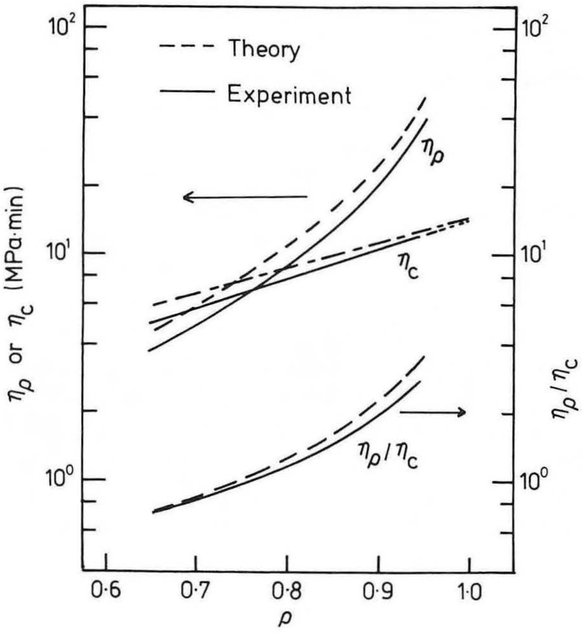


Figure 20
Comparison of the experimental data for the creep viscosity, bulk viscosity, and the ratio of bulk over creep viscosity with theoretical predictions. (XBL 892-429)

---

* Department of Materials Science and Engineering, University of Missouri, Rolla

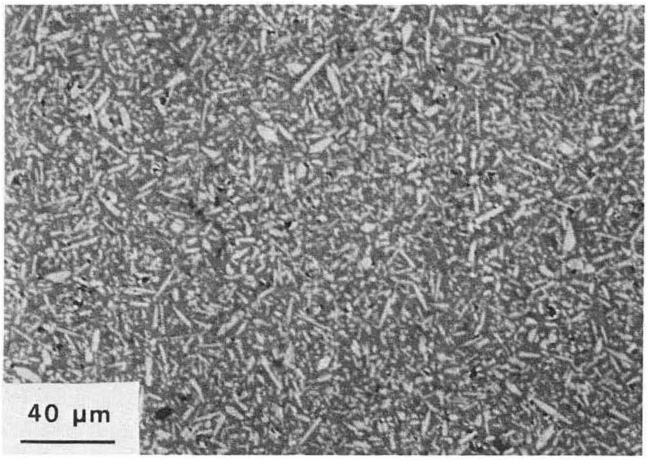


Figure 21
Polished surface of hot-pressed alumina-coated SiC whiskers showing uniform distribution of SiC whiskers (light grey phase). This surface is perpendicular to the hot pressing direction. (XBB 890-7086)

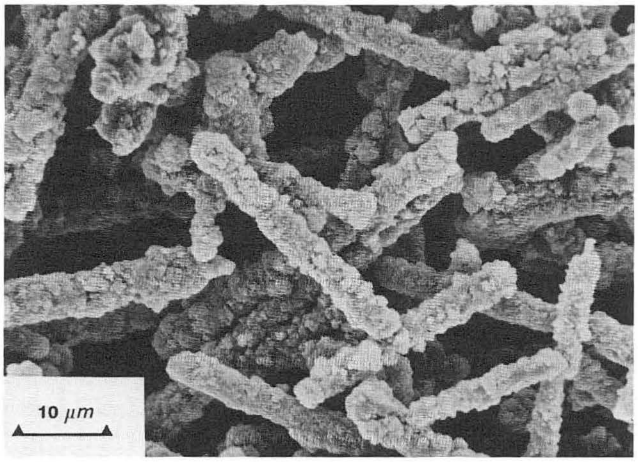


Figure 22
Alumina-coated SiC whiskers. These whiskers, originally with diameters ranging from 0.25 to 3 µm, have been fully coated, preventing direct whisker contacts in the green body. This enhances densification and provides a more uniform distribution of the whiskers in the composite. (XBB 894-3077)

ceramic composites is limited to about 15 vol %. Further, these composites tend to contain whisker clusters, resulting from the difficulties inherent in mechanical mixing of powder and whiskers. These clusters degrade the mechanical properties of the composites greatly. The method developed here has produced dense composites with over 40 vol % of SiC, and whisker clustering is completely eliminated. Composites of high uniformity, and high volume fraction of whiskers can be obtained. An optical micrograph of a composite produced in this manner is shown in Figure 21.

The process involves the use of a slurry in which SiC whiskers, suspended in water, are coated in a controlled precipitation reaction depositing aluminum sulfate on the whisker surfaces only. The resulting composite powder is dried and calcined, and then hot pressed around 1600°C to full density. A micrograph of some coated whiskers is shown in Figure 22. A key element in the process is the use of an appropriate polymeric dispersant and the careful control of the precipitation reaction.

Continuing research is focused on the extension of this slurry coating method to produce barrier coatings on the whiskers, and on the role of various particle shapes and process variables in determining the mechanical properties of the dense composites.

EFFECT OF TEMPERATURE ON DENSIFICATION/CREEP VISCOSITY DURING SINTERING

M.-Y. Chu, L.C. De Jonghe, M.N. Rahaman*

The densification and creep rates of polycrystalline zinc oxide and of alumina powder compacts have been measured simultaneously in a loading dilatometer, under constant heating rate and constant temperature conditions. The data show that the ratio of the densification to the creep rate is remarkably constant within a wide temperature range for densification, from the earliest stages of densification to at least the onset of the final stage. As a consequence, the ratio of the densification to the creep viscosity is nearly independent of temperature or sintered density. The analysis leads to a simple method for determining the simultaneous densification over the creep rate ratio.

PORE SIZE DISTRIBUTION, GRAIN GROWTH, AND SINTERING STRESS

L.C. De Jonghe, M.-Y. Chu, M.K.-F. Lin

The effects of a pore size distribution and of the pore coordination number on the sintering stress is examined using a simple model. The sintering stress is found to be proportional to the mean of the pore sizes weighted according to the Voronoi cell pertaining to each pore, rather than to the simple pore size average. Large heteropores are shown to have little effect on the sintering stress. Decreases in pore coordination number of such pores, resulting from grain growth, are found to affect the sintering stress little, but can significantly increase the stress intensification factor. The near-constancy of the sintering stress, observed experimentally for many powders over a wide range of sintered densities, does not directly follow from the simple model. It is argued that this constancy results from pore shrinkage, due to densification, which is compensated by pore growth due to coarsening.

DENSIFICATION OF PARTICULATE CERAMIC COMPOSITES: THE ROLE OF HETEROGENEITIES

L.C. De Jonghe , M.N. Rahaman*

Inert particulate inclusions in ceramic powder compacts can obstruct densification behavior significantly. The factors causing this decrease in the sinterability have been reviewed. It was concluded that the origin of the sintering difficulty resides in defects that processes such as die compaction introduce during the initial forming of the composite powder compact. Alternative processing methods have been suggested that should minimize the negative effects of the dispersed inclusion phase on densification.

---

* Department of Materials Science and Engineering, University of Missouri, Rolla

STAFF

Program Leader
J.W. Morris, Jr.

Project Leaders
Lutgard De Jonghe—Ceramic Processing
J.W. Morris, Jr.—Structural Metals and Alloys
Robert O. Ritchie—Mechanical Behavior of Materials

Investigators
Thomas Devine
A.G. Khatchaturyan
Gareth Thomas

Visiting Scientists
Richard Brook, Max-Planck Institute, Stuttgart
Armelle Philip, University of Grenoble, France
Mohammed N. Rahaman, University of Missouri, Rolla
Jean-Hubert Schmitt, University of Grenoble, France
V. Radmilovic, University of Belgrade, Yugoslavia

Postdoctoral Fellows
Reiner Dauskardt
K.T. Venkateswara Rao

Graduate Students
Yves P. Boiteux
Edwin L. Bradley, III
Gillian L. Brown
Thea K. Buchanan
Jin W. Chan
Jin-Syung Chen
S. Chi
David Chu
May-Ying Chu
Roger A. Emigh
Massimiliano Ghirlanda
Judith Glazer
Won-Shick Hong
Craig P. Jacobson
Patricia B. Johnson
David J. Kapolnek
Anthony G. Keslinke
Choong-un Kim
Pamela A. Kramer
Timothy W. Kueper
Christophe S. Dumai
Timothy Lindsey
Mark T. McCormack
Leslie T. McKnelly, Jr.
Zequn Mei
Shelly Miyasato
Tyrone D. Mitchell, Jr.
Kevin G. Mon
John Sanchez, Jr.
Steven Shaffer
Chi H. Sheu
Tammy S.E. Summers
Anne J. Sunwoo
Dana Tribula
Stephanie Verzasconi
Sheun Wu
Ping Xu

Administrative Support
Jane Fortado
Madeleine Penton
Linda Kelly

AWARDS

- Lutgard C. De Jonghe received the Alexander von Humboldt award (West Germany) for U.S. Senior Scientists.
- J.W. Morris, Jr. received the AT&T Foundation Award for the Pacific Southwest Section of the American Society for Engineering Educators.

- Robert O. Ritchie was elected Honorary Fellow, International Congress on Fracture.

- Robert O. Ritchie and Reiner H. Dauskardt were awarded the Department of Energy's Most Outstanding Scientific Accomplishment Award in Metallurgy and Ceramics for work on cyclic fatigue in ceramics.

- Robert O. Ritchie was awarded a Doctor of Science degree at Cambridge University, England, for "distinction in original contributions to the advancement of science."

INDUSTRY INTERACTIONS

Gifts

- Ford, LTV and Rouge Steel presented a gift as a group (their second such gift to the program) for fundamental and application-oriented research on formabiliy of sheet steels.

Contracts

- Electric Power Research Institute provided support for research on improved superconducting ceramics for high current applications.

- Naval Air Development provided partial support for a program on the mechanisms of corrosion fatigue in commercial aluminum-lithium alloys.

- Northrop provided support for a joint program on cyrogenic testing and analysis of advanced structural aluminum alloys for advanced superplasticity and for an experimental evaluation of the high-temperature fatigue properties of aluminum-lithium alloys.

- Materials Research Corporation provided funding and samples for research on electromigration of thin-film Al alloy lines.

Industrial Collaborations

- D.B. Marshall of Rockwell International collaborated with the Mechanical Behavior group on the fatigue of zirconia ceramics.

- N.J. Kim of Allied-Signal collaborated with the Mechanical Behavior group on the fatigue of P/M aluminum-lithium alloys.

- T.W. Duerig of Raychem collaborated with the Mechanical Behavior of Materials group on the fatigue of TiNi shape-memory materials.

BIBLIOGRAPHY

Metals for Advanced Applications Project

Refereed Journal Articles

Fox, A.G., V. Radmilovic, and G. Thomas, "Spinodal Decomposition of Al-Li Alloys," *Acta Met.*, vol. 37, p. 2385, 1989.

Frear, D.R., J.B. Posthill, and J.W. Morris Jr., "The Microstructural Details of β-Sn Precipitation in a 5Sn-95Pb Solder Alloy," *Met. Trans. A*, vol. 20, p. 1325, 1989.

Kumai, C., J. Kusinski, G. Thomas, and T.M. Devine, "Influence of Aging at 200°C on the Corrosion Resistance of Al-Li and Al-Li-Cu Alloys," *J. of Science and Engineering Corrosion*, vol. 45, p. 294, 1989.

Morris, Jr., J.W., D. Grivas, D. Tribula, T.S.E. Summers, and D. Frear, "Research on the Mechanism of Thermal Fatigue in Near-Eutectic Pb-Sn Solders," *Soldering and Surface Mount Technology*, vol. 3, p. 4, 1989.

Radmilovic, V., A.G. Fox, R.M. Fisher, and G. Thomas, "Lithium Depletion in Precipitate Free Zones (PFZ's) in Al-Li Base Alloys," *Scr. Met.*, vol. 23, p. 75, 1989.

Radmilovic, V., G. Thomas, G.J. Shiflet, and E.A. Starke, Jr., "On the Nucleation and Growth of Al_2CuMg (s') in Al-Li-Cu-Mg and Al-Cu Mg Alloys," *Scripta Met.*, vol. 23, p. 1141, 1989.

Tribula, D., D. Grivas, D.R. Frear, and J.W. Morris, Jr., "Microstructural Observations of Thermomechanically Deformed Solder Joints," *Welding Research Supplement*, p. 404s, 1989.

Refereed Conference Proceedings

Glazer, J. and J.W. Morris, Jr., "The Strength-Toughness Relationship at Cryogenic Temperatures in Aluminum-Lithium Alloy Plate," in *Aluminum-Lithium Alloys V, Proceedings of the Fifth International Aluminum Lithium Conference*, ed. T.H. Sanders, E.A. Starke, vol. 3, p. 1471, 1989.

Kusinski, J. and G. Thomas, "Microstructure of the Deformed Al-Li-Cu-Zr Alloy," *Proc. VIII Konferencja Mikroskopii Elektronowej Ciala Stalego, Krakow, Poland*, p. 286, Krakow, Poland, 1989.

Miyasato, S. and G. Thomas, "Microstructural Evolution in Al-Li and Al-Li-Cu-Mg Alloys," *Proc. Fifth Int. Al-Li Alloy Conf.*, p. 633, 1989.

Radmilovic, V., S. Miyasato, and G. Thomas, "Subgrain Boundary Structure in Al-Li-Cu-Zr Alloy," *Proc. III Balkan Congress on Electron Microscopy*, p. 473, 1989.

Sunwoo, A.J. and J.W. Morris, Jr., "Cryogenic Tensile Properties of AA 2090 Weldments," in *Aluminum-Lithium Alloys V, Proceedings of the Fifth International Aluminum-Lithium Conference*, ed. T.H. Sanders, Jr., E.A. Starke, Jr., vol. 3, p. 1481, 1989.

Sunwoo, A.J. and J.W. Morris, Jr., "Microstructure and Properties of AA 2090 Weldments," *Welding Journal, Research Supplement*, vol. 65, p. 262, 1989.

Verzasconi, S.L. and J.W. Morris, Jr., "Microstructures and Properties of Al-Li-Cu-Zr Alloy at Cryogenic Temperature," in *Aluminum-Lithium Alloys V, Proceedings of the Fifth International Aluminum-Lithium Conference*, ed. T.H. Sanders, Jr., E.A. Starke, Jr., vol. 3, p. 1533, 1989.

Verzasconi, S.L. and J.W. Morris, Jr., "Cryogenic Mechanical Properties of Low Density Superplastic Al-Mg-Sc Alloys," *Proc. Int. Cryogenic Mat. Conf.*, vol. 3, p. 1533, 1989.

Theses

Glazer, J., *The Strength-Toughness Combination of the Aluminum-Lithium Alloys 2090 and 2091 at Cryogenic Temperatures.* (Ph.D. Thesis, Department of Materials Science and Mineral Engineering, U.C. Berkeley. Advisor: J.W. Morris, Jr.)

Mei, Z., *Fatigue Crack Propagation in Austenitic Stainless Steels at Cryogenic Temperatures.* (Ph.D. Thesis, Department of Materials Science and Mineral Engineering, U.C. Berkeley. Advisor: J.W. Morris, Jr.)

Verzasconi, S.L., *Cryogenic Mechanical Properties of Low Density Superplastic Aluminum Alloys*, May 1989. (M.S. Thesis, Department of Materials Science and Mineral Engineering, U.C. Berkeley. Advisor: J.W. Morris, Jr.)

LBL Reports (including journal articles submitted or in press)

Chan, J.W., J. Glazer, Z. Mei, and J.W. Morris, Jr., "4.2K Fracture Toughness of 304 Stainless Steel in a Magnetic Field," *Proc. Int. Cryogenic Mat. Conf.* (In press.)

Chang, J.W., J. Glazer, Z. Mei, P.A. Kramer, and J.W. Morris, Jr., "Fracture Toughness of 304 Stainless Steel in an 8 Tesla Field," *Acta Met.* (In press.)

Chu, D. and J.W. Morris, Jr., "The Effect of Hydrogen Charging on the Mechanical properties of Aluminum-Lithium Alloys 2090," *Proc. Int. Cryogenic Mat. Conf.* (In press.)

Khachaturyan, A.G. and J.W. Morris, Jr., "A Possibility of Experimental Determination of a Nonequilibrium Free Energy of an Ordered Alloy," *Scripta Met.* (In press.)

McCormack, M.T., A.G. Khachaturyan, and J.W. Morris, Jr., "Computer Simulation of Coarsing in Elastic Media," *Acta Met.* (Submitted.)

Mei, Z., J.W. Chan, and J.W. Morris, Jr., "The Effects of Temperature of Fatigue Crack Propagation in 310 Austenitic Stainless Steel," *Proc. Int. Cryogenic Mat. Conf.* (In press.)

Mei, Z. and J.W. Morris, Jr., "Influence of Deformation-Induced Martensite on Fatigue Crack Propagation in 304-Type Steels," *Met. Trans. A.* (Submitted.)

Mei, Z. and J.W. Morris Jr., LBL 28009, "Mossbauer Spectrum Curve Fitting with Personal Computer," *Nuclear Instruments and Methods.* (In press.)

Morris Jr., J.W. and A.G. Khachaturyan, "Comment on the Concentration-Wave Model for Oxygen Ordering in $YBa_2Cu_3O_{6+}$," *Phys. Rev. Lett.* (Submitted.)

Sawtell, R.R. and J.W. Morris, Jr., LBL-26913, "The Influence of Ternary Additions on the Strength of Al-Sc Alloys," *Met. Trans. A.* (Submitted.)

Sawtell, R.R. and J.W. Morris, Jr., LBL-27145, "The Microstructures of Al-Sc Alloys with Ternary Additions," *Metal. Trans.* (Submitted.)

Schmitt, J.-H., P.E. Johnson, and J.W. Morris, "Evolution of Dislocation Substructures During Monotonic Deformation of Low Carbon Steels," *Proc. Electron Microscopy Soc. of America.* (In press.)

Sunwoo, A.J., E.L. Bradley, III, and J.W. Morris, Jr., LBL 28010, "Effects of HAZ Thermal Excursions on the Microstructure and Properties," *Met. Trans.* (Submitted.)

Sunwoo, A.J. and J.W. Morris Jr., "Effects of Precipitate Distribution on 293K and 77K Properties of 2090-T81 Weldments," *Proc. Int. Cryogenic Mat. Conf.* (In press.)

Invited Talks

Morris, Jr., J.W., *The Science of Thermomechanical Processing,* First Japan International SAMPE Symposium and Exhibition, Tokyo, Japan, November 1989.

Morris, Jr., J.W., J. Glazer, and J.W. Chang, *The Metallurgical Determinants of Toughness as Cryogenic Temperature,* International Cryogenic Materials Conference, Los Angeles, CA, July 1989. (To be published in the Proceedings.)

Morris, Jr., J.W., D. Grivas, D. Tribula, T.S.E. Summers, and D. Frear, *Research on the Mechanism of Thermal Fatigue in Near-Eutectic Pb-Sn Solders,* Dept. of Navy, 13th Annual Electronics Manufacturing Seminar, China Lake, California, May 1989. (Proceedings of the 13th Annual Electronics Manufacturing Seminar.) (D. Frear, Sandia National Laboratory.)

Tribula, D. and J.W. Morris Jr., *Creep in Shear of Experimental Solder Joints,* Winter Annual Meeting, American Society of Mechanical Engineers, San Francisco, CA, December 1989. (To be published in the Proceedings.)

Tribula, D., T.S.E. Summers, D. Grivas, and J.W. Morris, Jr., *Improving the Fatigue Life of Near-Eutectic Pb-Sn Solders,* ISHM 15th Annual Northern California Microelectronics Symposium, San Jose, California, November 1989.

Contributed Talks

Chan, J.W., J. Glazer, Z. Mei, P. Kramer, and J.W. Morris, Jr., *Fracture Toughness of 304 Stainless in an 8 TESLA Field,* AMIE-TMS Annual Meeting, Las Vegas, Nevada, February 1989.

Chan, J.W., J. Glazer, Z. Mei, and J.W. Morris, Jr., *4.2 K Fracture Toughness of 304 Stainless Steel in a Magnetic Field,* International Cryogenic Materials Conference, Los Angeles, Ca, July 1989. (To be published in the Proceedings.)

Chu, D., *The Cryogenic Mechanical Properties of Advanced Aluminum Alloys,* Westec '89, Los Angeles, California, March 1989.

Chu, D. and J.W. Morris, Jr., *The Effect of Hydrogen Charging on the Mechanical Properties of Aluminum Alloy 2090*, International Cryogenic Materials '89 Conference, Los Angeles, California, July 1989.

Glazer, J. and J.W. Morris, Jr., *Cryogenic Mechanical Properties of Al-Cu-Li-(Mg)-Zr Alloys 2090 and 2091*, AMIE-TMS Annual Meeting, Las Vegas, Nevada, February 1989.

Glazer, J. and J.W. Morris, Jr., *Cryogenic Mechanical Behavior of AA 2090 and 2091 Plate*, 5th International Aluminum-Lithium Conference, Williamsburg, Virginia, March 1989. (Published in the Proceedings, v. 3, p. 1471, 1989.)

Johnson, P.E. and J.W. Morris, Jr., *The Influence of the Dislocation Substructure on Work Hardening During Tensile Deformation of AKDQ Steel Sheets*, AMIE-TMS Annual Meeting, Las Vegas, Nevada, February 1989.

Mei, Z. and J.W. Morris, Jr., *Fatigue Crack Growth in Metastable Austenitic Stainless Steels*, AMIE-TMS Annual Meeting, Las Vegas, Nevada, February 1989.

Miyasato, S. and G. Thomas, *Microstructural Evolution in Al-Li and Al-Li-Cu-Mg Alloys*, Fifth International Aluminum-Lithium Alloy Conference, Williamsburg, VA, March 1989. (Published in the Proceedings, p. 633, 1989.)

Morris, Jr., J.W., D. Tribula, D. Grivas, and T.S.E. Summers, *Research on the Mechanisms of Thermal Fatigue in Near-Eutectic Pb-Sn Solders*, 1989 TMS Fall Meeting, Indianapolis, IN, October 1989.

Philip, A.M., J.-H. Schmitt, and J.W. Morris, Jr., *Local Plastic Behavior of Aluminum Single Crystal Containing a Hole*, AMIE-TMS Annual Meeting , Las Vegas, Nevada, February 1989.

Radmilovic, V., S. Miyasato, and G. Thomas, *Subgrain Boundary Structure in Al-Li-Cu-Zr Alloy*, III Balkan Congress on Electron Microscopy, Athens, Greece, September 1989.

Schmitt, J.-H., P.E. Johnson, and J.W. Morris, Jr., *Evolution of Dislocation Substructures During Monotonic Deformation of Low Carbon Steel*, Electron Microscopy Society of America, San Antonio, Texas, July 1989.

Shaffer, S.J. and J.W. Morris, Jr., *Investigation of Factors Affecting Friction in Electrogalvanized Sheet Steel*, AMIE-TMS Annual Meeting, Las Vegas, Nevada, February 1989.

Shaffer, S.J., A.M. Philip, and J.W. Morris, Jr., *Micromechanisms of Surface Friction in Zinc Electrogalvanized Steel Sheets*, Galvatech '89 Conference, Tokyo, Japan, September 1989. (To be published in the Proceedings.)

Summers, T.S.E. and J.W. Morris, Jr., *Isothermal Fatigue Behavior of Sn-Pb Solder Joints*, ASME Winter Annual Conference, San Francisco, California, December 1989. (To be published in J. of Elec. Pack.)

Sunwoo, A.J., S. Miyasato, and J.W. Morris, Jr., *Effects of Precipitate Distribution on 293 K and 77 K Properties of 2090 T81 Weldments*, International Cryogenic Materials Conference, Los Angeles, CA, July 1989. (To be published in the Proceedings.)

Sunwoo, A.J. and J.W. Morris, Jr., *Microstructure and Properties of AA 2090 Weldments*, Conference of the American Welding Society, New Orleans, Louisiana, April 1989. (Welding Journal, Research Supplement, vol. 65, p 262, 1989.)

Sunwoo, A.J. and J.W. Morris, Jr., *Cryogenic Tensile Properties of AA 2090 Weldments*, 5th International Aluminum-Lithium Conference, Williamsburg, Virginia, March 1989. (Published in the Proceedings, vol. 3, p. 1481, 1989.)

Tribula, D., T.S.E. Summers, and J.W. Morris, Jr., *Creep in Shear of Experimental Pb-Sn Solder Joints*, AMIE-TMS Annual Meeting, Las Vegas, NV, February 1989.

Verzasconi, S.L., J. Glazer, P.A. Kramer, and J.W. Morris, Jr., *Cryogenic Mechanical Properties of Low Density Superplastically Formable Al-Li Alloys*, Presented at the 5th International Aluminum-Lithium Conference, Williamsburg, VA, March 1989; and the International Cryogenic Materials Conference, Los Angeles, CA, July 1989. (Published in the Proceedings, v. 3, p. 1533, 1989.)

Verzasconi, S.L. and J.W. Morris, Jr., *Cryogenic Mechanical Properties of Superplastically Formable Al-Cu-Li-Zr Alloys 2090 and 2090 + In*, AMIE-TMS Annual Meeting, Las Vegas, Nevada, February 1989.

Mechanical Behavior of Materials Project

Refereed Journal Articles

Dauskardt, R.H. and R.O. Ritchie, "Cyclic Fatigue-Crack Growth Behavior in Ceramics," *Closed Loop*, vol. 17, p. 7, 1989.

Dauskardt, R.H., D.K. Veirs, and R.O. Ritchie, "Spatially Resolved Raman Spectroscopy Study of Transformed Zones in Magnesia-Partially-Stabilized Zirconia," *J. Am. Ceram. Soc.*, vol. 72, p. 1124, 1989.

Venkateswara Rao, K.T. and R.O. Ritchie, "Fracture-Toughness Behavior of 2090-T83 Aluminum-Lithium Alloy Sheet at Ambient and Cryogenic Temperatures," *Scripta Metall.*, vol. 23, p. 1129, 1989.

Venkateswara Rao, K.T. and R.O. Ritchie, "Mechanical Properties of Al-Li Alloys, Part I: Fracture Toughness and Microstructure," *Materials Science and Technology*, vol. 5, p. 882, 1989.

Venkateswara Rao, K.T. and R.O. Ritchie, "Mechanical Properties of Al-Li Alloys: Part II: Fatigue-Crack Propagation," *Materials Science and Technology*, vol. 5, p. 896, 1989.

Venkateswara Rao, K.T., W. Yu, and R.O. Ritchie, "Cryogenic Toughness of Commercial Aluminum-Lithium Alloys: Role of Delamination Toughening," *Metall. Trans. A.*, vol. 20, p. 485, 1989.

Ward-Close, C.M., A.F. Blom, and R.O. Ritchie, "Mechanisms Associated with Transient Fatigue Crack Growth during Variable-Amplitude Loading: An Experimental and Numerical Study," *Eng. Fract. Mech.*, vol. 32, p. 613, 1989.

Refereed Conference Proceedings

Dauskardt, R.H., T.W. Duerig, and R.O. Ritchie, "Effects of *in situ* Phase Transformation in Fatigue-Crack Propagation in Titanium-Nickel Shape Memory Alloys," *Shape Memory Materials, Proc. of the MRS International Meeting on Advanced Materials*, vol. 9, p. 243, 1989.

Dauskardt, R.H., D.B. Marshall, and R.O. Ritchie, "Cyclic Fatigue-Crack Propagation in Ceramics: Behavior in Overaged and Partially-Stabilized MgO-Zirconia," *Structural Ceramics/Fracture Mechanics, Proc. of the MRS International Meeting on Adv. Mat.*, vol. 5, p. 543, 1989.

Oh, T.S., R.M. Cannon, and R.O. Ritchie, "On Optimizing the Toughening of Ceramic/Metal Interfaces using Implanted Microcracks," *Joints of Metals and Ceramics, Mat. Res. Soc. Intl. Symp. Proc.*, vol. 8, 1989*.

Oh, T.S., R.M. Cannon, and R.O. Ritchie, "Tailored Microstructures to Control Interfacial Toughness," *Thin Films: Stress and Mechanical Properties, Mat. Res. Soc. Symp. Proc.*, vol. 130, p. 219, 1989*.

Venkateswara Rao, K.T., R.S. Piascik, R.P. Gangloff, and R.O. Ritchie, "Fatigue Crack Propagation in Aluminum-Lithium Alloys: An Overview," in *Aluminum-Lithium Alloys, Proc. 5th Aluminum-Lithium Conf.*, ed. E.A. Starke, and T.H. Sanders, vol. 2, p. 955, 1989.

Venkateswara Rao, K.T. and R.O. Ritchie, "Fatigue-Crack Propagation in Advanced Aerospace Materials: Aluminum-Lithium Alloys," *Advances in Fracture Research, Proc. of the 7th International Conference on Fracture (ICF-7)*, vol. 5, Pergamon Press, Oxford, 1989.

Venkateswara Rao, K.T. and R.O. Ritchie, "Influence of Extrinsic Crack Deflection and Delamination Mechanisms on the Cryogenic Toughness of Aluminum-Lithium Alloy 2090: Behavior on Plate (T81) vs. Sheet (T83) Materials," in *Aluminum-Lithium Alloys, Proc. 5th Aluminum Lithium Conf.*, ed. E.A. Starke, and T.H. Sanders, vol. 3, p. 1501, 1989.

Ward-Close, C.M. and R.O. Ritchie, "Variable Amplitude Fatigue Crack Growth in Ti-4Al-4Mo-2Sn-0.5Si (IMI 550)," *Proc. Sixth World Conference on Titanium*, vol. 1, p. 241, 1989.

LBL Reports (including journal articles submitted or in press)

Dauskardt, R.H., F. Haubensak, and R.O. Ritchie, LBL 25876, "On the Interpretation of the Fractal Character of Fracture Surfaces in Metallic Materials," *Acta Met.* (In press.)

Dauskardt, R.H., D.B. Marshall, and R.O. Ritchie, LBL 26262, "Cyclic Fatigue-Crack Propagation in Mg-PSZ Ceramics," *J. Am. Ceram. Soc.*. (In press.)

Dauskardt, R.H., D.K. Veirs, W.C. Carter, and R.O. Ritchie, LBL 26682, "Transient Subcritical Crack-Growth Behavior in Transformation-Toughened Ceramics," *Acta Met.* (Submitted.)

Marshall, D.B., M.C. Shaw, R.H. Dauskardt, R.O. Ritchie, M. Readey, and A.H. Heuer, LBL 28081, "Crack-Tip Transformation Zones in Toughened Zirconia," *J. Am. Cer. Soc.* (Submitted.)

Steffen, A.A., R.H. Dauskardt, and R.O. Ritchie, LBL 28244, "Cyclic Fatigue-Crack Propagation in Ceramics: Long and Small Crack Behavior," *Proc. 4th Intl. Conf on Fatigue and Fatigue Thresholds.* (In Press.)

Steffen, A.A., R.H. Dauskardt, and R.O. Ritchie, LBL 28364, "Cyclic Fatigue Life and Crack-Growth Behavior in Mg-PSZ Ceramics: Role of Microstructurally Small Cracks," *J. Am. Ceram. Soc.* (Submitted.)

Venkateswara Rao, K.T., R.J. Bucci, and R.O. Ritchie, LBL 28244, "On the Micromechanisms of Fatigue-Crack Propagation in Aluminum-Lithium Alloys: Sheet vs. Plate Materials," *4th Intl. Conf. on Fatigue and Fatigue Thresholds.* (Submitted.)

Venkateswara Rao, K.T. and R.O. Ritchie, LBL 28365, "Fracture Toughness and Fatigue-Crack Propagation Behavior of Powder Metallurgy Aluminum-Lithium Alloys," *Metall. Trans. A.* (Submitted.)

Venkateswara Rao, K.T. and R.O. Ritchie, LBL 28243, "Mechanisms of Cryogenic Toughening in Aluminum-Lithium Alloys," *Acta Met.* (Submitted.)

Invited Talks

Dauskardt, R.H., *Transformation Toughening and its Implications for Crack Growth,* ASM Symposium on Processing and Properties of Structural Ceramics, Indianapolis, IN, October 1989.

Dauskardt, R.H. and R.O. Ritchie, *Cyclic Fatigue-Crack Propagation Behavior in Advanced Ceramics,* 13th Annual Conference on Composites and Advanced Ceramics, Cocao Beach, FL, January 1989.

Dauskardt, R.H., A.A. Steffen, and R.O. Ritchie, *Cyclic Fatigue-Crack Propagation Behavior in Zirconia Ceramics: Long vs. Small Crack Behavior,* Fourth International Science and Technology of Zirconia Conference; First International Ceramics Science and Technology Conference, Anaheim, CA, November 1989.

Ritchie, R.O., *Ceramics and Ceramic Composites: Fatigue and Fracture,* Presented at Pohang Institute of Science and Technology, Pohang, Korea, September 1989; and Materials Research Laboratory, Industrial Technology Research Institute, Hsinchu, Taiwan, September 1989..

Ritchie, R.O., *Behavior of Real Materials: Composites,* Physical Metallurgy Gordon Conference, Tilton, NH, August 1989.

Ritchie, R.O., *Fracture Mechanics: Applications,* Engineering Foundation Conference on Dental Biomaterials, Santa Barbara, CA, August 1989.

Ritchie, R.O., *Mechanisms of Subcritical Crack Growth in Ceramics and Composites: Toughening of Ceramic/Metal Interfaces,* Sandia National Laboratories, Livermore, CA, February 1989.

Ritchie, R.O., *Sub-Critical Cracking Resistance of Bimaterial Interfaces,* Acta/Scripta Metallurgica Conference on Bonding, Structure and Mechanical Properties of Metal/Ceramic Interfaces, University of California, Santa Barbara, CA, January 1989.

Ritchie, R.O., *Fatigue and Fatigue Fracture,* Cryogenic Materials Conference, Los Angeles, CA, July 1989.

Ritchie, R.O., *Cyclic Fatigue Crack Growth,* DOE Workshop on Basic Research Needs and Opportunities Concerning Fracture in Monolithic Ceramics and Ceramic Composites at Temperatures above 1000 ° C, Ithaca, NY, June 1989.

Ritchie, R.O., *Engineering Materials and Technological Development: American Perspective,* Plenary Conference of National Materials Week, Johannesburg, South Africa, June 1989.

Ritchie, R.O., *Mechanics of Fatigue and Fracture in Metallic Alloys: Role of Metallic Ceramic and Polymeric Reinforcements,* Fracture '89, the Third National Conference on Fracture, Johannesburg, South Africa, June 1989.

Ritchie, R.O., *Mechanisms of Fatigue-Crack Growth in Metals, Composites, Ceramics and Ceramic/Metals Interfaces,* Third International Conference on Fundamentals of Fracture, Irsee, F.R. Germany, June 1989.

Ritchie, R.O., *Fatigue-Crack Propagation in Metals, Ceramics and the Interfaces that Separate Them,* Seventh International Conference on Fracture, Plenary Lecture, Houston, TX, March 1989.

Ritchie, R.O., *Fatigue and Fracture in Composite Metals and Ceramics,* Battelle Pacific Northwest Laboratories, Richland, WA, May 1989.

Ritchie, R.O., *Micro-Mechanisms of Fracture in Structural Metals, Ceramics and Composites,* Materials Science and Engineering Department, University of Washington, Seattle, WA, May 1989.

Ritchie, R.O., *Fatigue and Fracture Mechanics,* International Symposium for Testing and Failure Analysis, Amerian Society for Metals, Los Angeles, CA, November 1989.

Ritchie, R.O., *Materials and Materials Testing,* MTS Inc., Minneapolis, MN, November 1989.

Ritchie, R.O., *Ceramic Fatigue,* CSIRO, Clayton, VIC, Australia, October 1989.

Ritchie, R.O., *Mechanics of Cyclic and Monotonic Fracture in Advanced Aluminum-Lithium Alloys*, School of Mechanical and Industrial Engineering, University of New South Wales, Kensington, Australia, October 1989.

Ritchie, R.O., *Mechanism of Cyclic Fatigue-Crack Growth in Ceramic Materials*, Applied Mechanics Colloquium, Department of Mechanical Engineering, University of Sydney, Sydney, Australia, October 1989.

Ritchie, R.O., *Mechanisms of Fracture and Fatigue in Advanced Aerospace Materials*, Australian Aeronautical Conference - 1989: Research and Technology - The Next Decade, Melbourne, Australia, October 1989.

Ritchie, R.O., *Micromechanisms of Fatigue-Crack Growth in Structural Composites*, Materials Research Laboratory of the Defense Science and Technology Office, Melbourne, Australia, October 1989.

Ritchie, R.O., *Ceramic Fatigue*, Government Industrial Research Institute, Nagoya, Japan, September 1989.

Ritchie, R.O., *Cryogenic Toughness Behavior of Aluminum-Lithium Alloys*, Chinese Silicate Society, Beijing, PR China, September 1989.

Ritchie, R.O., *Cyclic Behavior of Ceramics and Ceramic-Matrix Composites: Long vs. Small Crack Behavior*, Institute of Materials Science and Engineering, National Sun-Yat-Sen University, Kaohsiung, Taiwan, September 1989.

Ritchie, R.O., *Fatigue and Fracture of Advanced Composite Materials*, Chinese Silicate Society, Beijing, PR China, September 1989.

Ritchie, R.O., *Fatigue of Aluminum-Lithium Alloys*, Industrial Technology Research Institute, Hsinchu, Taiwan; and Institute of Materials Science and Engineering, National Sun-Yat-Sen University, Kaohsiung, Taiwan, September 1989.

Ritchie, R.O., *Mechanical Behavior of Metal-Matrix Composites*, Korea Institute of Technology, Seoul, Korea, September 1989.

Ritchie, R.O., *Mechanics and Mechanisms of Fatigue in Advanced Materials*, Research Laboratory of Precision Machinery and Electronics, Tokyo Institute of Technology, Yokohama, Japan, September 1989.

Ritchie, R.O. and R.H. Dauskardt, *Cyclic Fatigue of Ceramics and Ceramic-Matrix Composites*, Engineering Foundation Conference on Advanced Structural Ceramics, Palm Coast, FL, March 1989.

Venkateswara Rao, K.T. and R.O. Ritchie, *Fatigue and Fracture in Commerical Aluminum-Lithium Alloys*, Aluminum-Lithium Alloys Session, WESTEC, Los Angeles, CA, March 1989.

Venkateswara Rao, K.T. and R.O. Ritchie, *Fatigue and Fracture of Advanced Aerospace Materials*, Seventh International Conference on Fracture, Keynote Lecture, Houston, TX, March 1989.

Contributed Talks

Dauskardt, R.H., B.J. Dagleish, T.S. Oh, R.M. Cannon, and R.O. Ritchie, *Toughness and Fatigue-Crack Growth Behavior along Ceramic-Metal Interfaces*, First International Ceramics Science and Technology Conference, Anaheim, CA, November 1989.

Dauskardt, R.H., T.S. Oh, R.M. Cannon, R.O. Ritchie, and B.J. Dalgleish, *Toughness and Fatigue-Crack Growth Behavior along Ceramic/Metal Interfaces*, Annual Meeting of the American Ceramic Society, Indianapolis, IN, April 1989*.

Dauskardt, R.H., R.O. Ritchie, and D.B. Marshall, *Cyclic Fatigue-Crack Propagation Behavior in Ceramics*, 1989 Annual Meeting of the American Ceramic Society, Indianapolis, IN, April 1989.

Marshall, D.B., R.H. Dauskardt, R.O. Ritchie, M. Readey, and A.H. Heuer, *Crack Tip Transformation Zones in Toughness* ZrO_2, Annual Meeting of the American Ceramic Society, Indianapolis, IN, April 1989.

Ritchie, R.O. and L.T. Summers, *Fatigue Considerations in the Design of the International Thermonuclear Experimental Reactor*, Cryogenic Materials Conference, Los Angeles, CA, July 1989.

Ritchie, R.O., K.T. Venkateswara Rao, R.P. Gangloff, and R.S. Piascik, *Fatigue Crack Propagation in Aluminum-Lithium Alloys*, Fifth International Aluminum-Lithium Conference, Williamsberg, VA, March 1989.

Venkateswara Rao, K.T. and R.O. Ritchie, *Influence of Extrinsic Crack Deflection and Delamination Mechanisms on the Cryogenic Fracture Toughness of Commercial Aluminum-Lithium Alloys*, Fifth International Aluminum-Lithium Conference, Williamsberg, VA, March 1989.

Venkateswara Rao, K.T. and R.O. Ritchie, *Fatigue of P/M Aluminum-Lithium Alloys*, TMS-AIME Fall Meeting, Indianapolis, IN, October 1989.

Venkateswara Rao, K.T. and R.O. Ritchie, *Mechanisms of Variable-Amplitude Fatigue-Crack Propagation in Advanced Aluminum-Lithium Alloys*, TMS-AIME Annual Meeting, Las Vegas, NV, February 1989.

Venkateswara Rao, K.T. and R.O. Ritchie, *Cryogenic Toughness of Aluminum-Lithium*, Cryogenic Materials Conference, Los Angeles, CA, July 1989.

*Joint study with R.M. Cannon of the CAM Electronic Materials Program.

Ceramic Processing Project

Refereed Journal Articles

Chu, M.-Y. and L.C. De Jonghe, "Effect of Temperature on the Densification/Creep Viscosity During Sintering," *Acta Metall.*, vol. 37, p. 1415, 1989.

De Jonghe, L.C., "Ceramic Processing for Magnetic Applications," *Mater. Sci. & Eng. B.*, vol. 4, p. 427, 1989.

De Jonghe, L.C. and V. Srikanth, "Liquid-Phase Sintering of MgO-Bi_2O_3," *J. Am. Ceram. Soc.*, vol. 71, pp. C-356, 1989.

Refereed Conference Proceedings

De Jonghe, L.C. and M. Rahaman, "Densification of Particulate Composites: the Role of Heterogeneities," *Mat. Res. Socl Symp. Proc.*, vol. 155, p. 353, 1989.

LBL Reports (including journal articles submitted or in press)

De Jonghe, L.C., M.N. Rahaman, M.-Y. Chu, and R.J. Brook, LBL-26823, *The Effect of Heat Rate on Sintering and Coarsening.*

Garg, A. and L.C. De Jonghe, LBL 26051, *Metal-Coated Colloidal Ceramic Particles.*

Naito, N., M.N. Rahaman, and L.C. De Jonghe, LBL-26849, "Pore Size Distribution During Compaction and Early Stage Sintering of Silicon Nitride," *J. Mater. Sci.* (Submitted.) (N. Naito, GTE Laboratories.)

Rahaman, M.N. and L.C. De Jonghe, LBL-26921, "Sintering of Particulate Composites Under a Uniaxial Stress," *J. Am. Cer. Soc.* (Submitted.)

Rahaman, M.N. and L.C. De Jonghe, LBL-26717, "Sintering of Spherical Glass Powder under a Uniaxial Stress," *J. Am. Cer. Soc.* (Submitted.)

Invited Talks

De Jonghe, L.C. and M.N. Rahaman, *Densification of Particulate Ceramic Composites: the Role of Heterogeneities*, Materials Research Society Spring Meeting, San Diego, California, April 1989.

Contributed Talks

Chu, M.-Y. and L.C. De Jonghe, *The Effect of Coarsening on the Sintering Stress and Interpore Spacing During Densification*, Am. Ceram. Soc. Meeting, Indianapolis, IN, April 1989.

De Jonghe, L.C. and M.N. Rahaman, *Constant Heating Rate Sintering of Polycrystalline Ceramics and Glasses*, Am. Ceram. Soc., Indianapolis, IN, April 1989.

De Jonghe, L.C. and M.N. Rahaman, *Effect of Green Density on the Densification Rate/Creep Rate During Sintering*, Am. Ceram. Soc., Indianapolis, IN, April 1989.

De Jonghe, L.C. and M.N. Rahaman, *Effect of Transient Shear Stress on Densification and Microstructure Development*, Am. Ceram. Soc., Indianapolis, IN, April 1989.

Kapolnek, D. and L.C. De Jonghe, *Production and Densification of Al_2O_3-Coated SiC Particles to Fabricate Al_2O_3-SiC Composites*, Am. Ceram. Soc., Indianapolis, IN, April 1989.

Rahaman, M.N. and L.C. De Jonghe, *Sintering of Spherical Glass Powder Under a Uniaxial Stress*, Am. Ceram. Soc., Indianapolis, IN, April 1989.

Surface Science and Catalysis

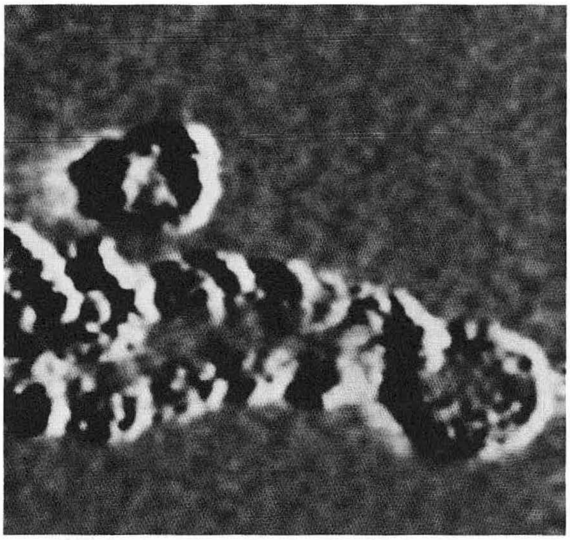
Catalyst Design, Characterization and Applications
Surface and Interface Compounds
Instrumentation for Surface Science

Surface Science and Catalysis

The CAM Surface Science and Catalysis program pursues interdisciplinary, basic research studies of surface and interface materials, phenomena, and processes at the molecular level. The research is focused on the chemical and mechanical properties of surfaces and on the development of new surface instrumentation to permit atomic level characterization of interfaces. Current research focuses on three areas.

The aim of the ***CATALYST DESIGN, CHARACTERIZATION AND APPLICATIONS*** project is to develop a fundamental understanding of the factors governing synthesis and performance of catalysts for a variety of processes. The focus is on the synthesis and characterization of novel microporous materials, including zeolites and transition metal nitrides, carbides, and oxides; the preparation and characterization of single-crystal, model catalysts; and the investigation of the fundamental aspects of the hydrogenation of CO and char gasification. Recent research results include several new findings:

- Cobalt-modified molybdenum crystal surfaces have been found to be more reactive when stepped than when flat, showing structure sensitivity.
- A methodology has been developed to prepare ordered-oxide films by deposition of crystalline monolayers of oxide on metal substrates, layer by layer.
- A powerful automated directed search method has been developed for surface structure determination by low-energy electron diffraction.
- Studies of Cu-containing catalysts have established that Cu^0 and Cu^+ sites are required for methanol synthesis and that Cu^+ sites are stabilized at the adlineation between metallic Cu and basic metal oxides.
- In collaboration with Mobil Research and Development Company, it was discovered that TPA^+ cations form silicate cages containing 22 Si atoms during the initial stages of ZSM-5 synthesis.
- In collaboration with Kodak Research Laboratories, it has been established that the BOC-MP approach provides a realistic description of the energetics of formic acid decomposition on Ag(111), Ni(111) and Fe/W(110) surfaces.



The *SURFACE STRUCTURE AND INTERFACE COMPOUNDS* project consists of three closely-linked efforts. The objective of the ***Surface Structure and Bonding*** group is the development of the molecular science of surface phenomena by means of the understanding of atomic-scale surface structure and chemical bonding of adsorbed monolayers and thin film coatings and their interfaces; the ***Coatings*** effort produces surface films that impart novel mechanical properties (scratch resistance, hardness) and chemical properties (protection against corrosion, diffusion barriers) to the substrate; the ***Surface Compounds*** effort involves studies on submonolayers of atomic and molecular adsorbates, as well as metal oxides (TiO_2, Al_2O_3 and FeO), which can modify the chemical and mechanical properties of metal surfaces.

During the past year:

- Sulfur overlayers on Re (0001) were imaged with atomic resolution with the Scanning Tunneling Microscope (STM) and were shown to form hexagonal aggregates at saturation.
- The changes of surface structure due to repulsive close-range intermolecular interactions has been observed in densely adsorbed monolayers of CO and NO on Rh (111).
- It was found that the hardness of amorphous carbon films grown *in situ* from a plasma could be controlled by variation of the power supplied by the ions.

The *INSTRUMENTATION FOR SURFACE SCIENCE* project is concerned with the development of new techniques and instruments for the study of surfaces. These include the scanning tunneling (STM) and atomic force (AFM) microscopes, nonlinear optical techniques, laser and electron spectroscopies, and low energy electron (LEED) diffraction. A surface analysis facility that provides service for the entire division is also part of this project. During the past year:

- An atomic force microscope with a microfabricated cantilever spring and tip has demonstrated atomic resolution.
- Unenhanced surface Raman spectroscopy was used as a vibrational probe of physisorbed and chemisorbed molecules and films on a variety of surfaces from 14 K to well above room temperature.

Above: Strands of uncoated DNA deposited on graphite and imaged by the STM.

CATALYST DESIGN, CHARACTERIZATION AND APPLICATIONS

MICROPOROUS CRYSTALLINE MATERIALS

Zeolite Synthesis

A.T. Bell, C. Chang*, D. M. Ginter, W. M. Hendricks, R. Mortlock

Zeolites are widely used in industry as catalysts for petroleum processing and chemical synthesis. The aim of this project is to understand the chemical and physical transformations occurring during the synthesis of zeolites from highly alkaline aqueous gels and the function of these processes in determining the structure and composition of the zeolites formed. These questions are being pursued through the use of such modern spectroscopic techniques as nuclear magnetic resonance (NMR) spectroscopy, Raman spectroscopy, x-ray diffraction, and electron microscopy, some of which were specifically modified for these studies at CAM.

In research supported in part by W.R. Grace and Company, studies were carried out to characterize the reactions of well defined silicate anions with aluminate anions. Aluminum wire was dissolved in a tetrapropyl ammonium silicate solution, and the resulting reactions between aluminate and silicate anions were followed by ^{29}Si and ^{27}Al NMR spectroscopy (Figure 1). The aluminate anions were found to react preferentially with low-molecular-weight silicate anions to form aluminosilicate anions. These reactions cause an imbalance in the equilibrium distribution of silicate anions and cause a depolymerization of higher-molecular-weight oligomers to replace the low-molecular-weight oligomers lost by reaction with aluminate anions. ^{27}Al NMR spectroscopy reveals that after reaction, most of the aluminum is present in aluminosilicate structures. The predominant structures are those in which an aluminum atom

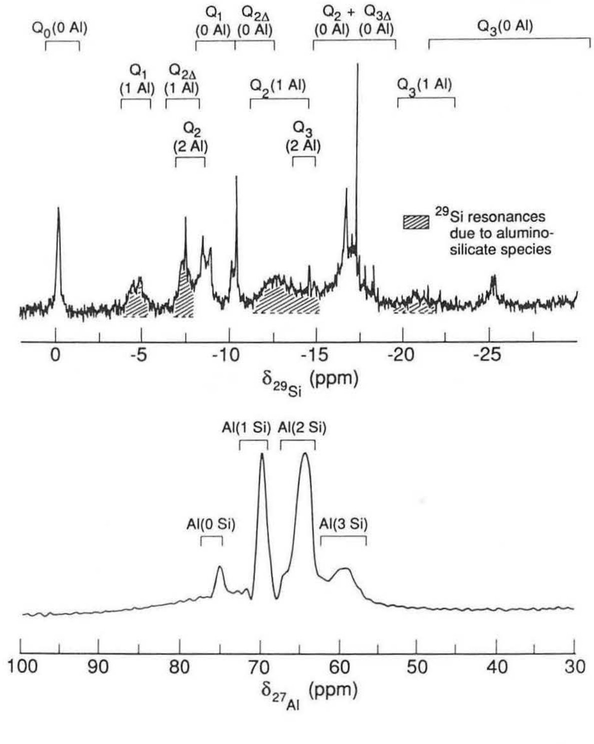


Figure 1

^{29}Si and ^{27}Al NMR spectra of silicate and aluminosilicate species produced by the reaction of metallic aluminum with a tetra propyl ammonium silicate solution. The shaded regions of the ^{29}Si NMR spectrum identify Si resonances in aluminosilicate anions, whereas the unshaded portions of the spectrum are due to Si in silicate anions. The connectivity of Si is designated by Q_i where i is the number of nearest neighbor Si or Al atoms. The number of nearest neighbor Al atoms in aluminosilicate species is given by the numbers in parentheses. The ^{27}Al NMR spectrum shows well defined peaks for Al bonded to 0, 1, 2 and 3 nearest neighbors. (XBL 903-1000)

---

* CAM Industrial Fellow, Mobil Research and Development Corporation.

has one or two nearest neighbor silicon atoms. No evidence was found for isomorphic substitution of aluminum for silicon in preformed single- or double-ring silicate structures. These results indicate that larger aluminosilicate structures are built up by reaction of aluminate anions with small silicate anions.

In a collaborative study with C. Chang of Mobil Research and Development Corporation, the synthesis of ZSM-5 was investigated as a function of time using ^{29}Si NMR spectroscopy and other techniques. Immediately upon preparation, most of the silicon in the synthesis gel was found to be in Q_4 environments, with a smaller proportion present in Q_3 environments. As synthesis proceeded, the proportion of silicon in Q_3 environments declined and an x-ray diffraction pattern characteristic of ZSM-5 could be observed. Ion exchange experiments revealed that shortly after the onset of heating, a ratio of 22 silicon atoms per TPA^+ cation was established. This ratio was then maintained until all of the synthesis gel had been converted to crystalline zeolite. The observed Si/TPA^+ ratio can be attributed to the formation of silicate cage structures around each TPA^+ cation.

Transition Metal Nitrides and Carbides

P. A. ARMSTRONG, K. S. LEE, A.T. BELL, J. A. REIMER

Transition metal nitrides and carbides, such as Mo_2N, Mo_2C, W_2C, and WC, have been shown to be effective catalysts for a variety of reactions, including CO hydrogenation, olefin hydrogenation, hydrocarbon reforming, ammonia synthesis, and hydrodenitrogenation (HDN). The transition metals are cheaper and more abundant than the noble metals which are now used for the above reactions. Little is known about the reaction chemistry on these nitrides and carbides, however. The aim of this research is to study the surface chemistry of γ-Mo_2N during representative hydrodenitrogenation reactions. The HDN reaction is important in the refining of petroleum to produce cleaner-burning fuels.

NMR spectroscopy has previously been shown by this group to be an effective technique for identifying surface species on γ-Mo_2N. In particular, adsorbed ammonia, carbon monoxide, hydrogen, and acetonitrile have been studied successfully by NMR spectroscopy. These investigations have laid the groundwork for continuing studies of adsorbed nitrogen heterocycles, such as pyridine and quinoline, and the species formed from these reactants during HDN. The selectivity of an HDN catalyst is determined by the ability of the catalyst to promote hydrogenation of only the heterocyclic rings of nitrogen heterocycles, and not other aromatic rings or olefinic groups. Experiments are currently in progress to observe per-deuterated quinoline adsorbed on γ-Mo_2N to establish the mode of bonding and the motion of the adsorbate. These experiments will then be extended to observe the effects of hydrogenation. Model compound studies of HDN over high surface area γ-Mo_2N have also been initiated recently.

Supported Vanadia

G. T. WENT, M. S. WENT, J. A. REIMER, A.T. BELL, S.T. OYAMA,
K.B. LEWIS, J. ODRIOZOLA*, H. HEINEMANN, G.A. SOMORJAI

Oxide catalysts are used for oxidation reactions that account for more than 25% by volume of the top 20 chemicals produced worldwide. Their use to catalyze NO_x and SO_x reductions will increase in the US in the next few years as more stringent air pollution laws are enacted. Until recently most of these oxide catalysts, consisting of transition metal oxides in bulk or supported on other oxides (i.e., V_2O_5/TiO_2), have been designed empirically. In a joint program with the Spanish Catalysis Institute, the mechanism of the ammonia-NO_x reaction on vanadia titania catalysts has been identified. It is a redox mechanism in which vanadium V is reduced by ammonia to vanadium IV, which in turn is oxidized by NO_x. Vanadia cannot sorb NO_x, but titania can sorb it. There is, therefore, a spillover of NO_x from titania to reduced vanadia. In other words, spectroscopic studies have been aimed at understanding how surface geometry affects activity and selectivity, the structure of the catalyst on the support and how it is affected by dispersion, and the mechanism by which the support affects activity and selectivity.

Raman and NMR spectroscopy are being used to characterize the geometry and dynamics of several small molecules adsorbed on supported vanadia catalysts. ^1H, ^{15}N, and ^{17}O NMR spectroscopy are being used to study NH_3 and NO on V_2O_5/TiO_2 in an attempt to understand the catalytic chemistry of NO reduction. Raman spectroscopy complements these studies. One goal of this work is to observe reaction dynamics by detecting oxygen exchange between adsorbed species and oxygen in the catalyst.

NO Reduction by Ammonia over Platinum

M. VAN TOL†, G.A. SOMORJAI

The catalytic removal of nitric oxide by ammonia is an important reaction to prevent air pollution. This process occurs readily over a small area (~2cm^2) platinum foil or single crystal in the range of 200-250 °C near atmospheric pressures. The reaction is first order in NO, zero order in NH_3 and its activation energy is 27kcal/mole. The platinum catalyst is much more active (by at least two orders of magnitude) than the oxide catalyst (V_2O_5/TiO_2) that is utilized presently in the technology.

Oxygen Chemisorption and Laser Raman Spectroscopy of Unsupported and Silica-Supported Vanadium Oxide Catalysts

S.T. OYAMA§, G.T. WENT, K.B. LEWIS**, A.T. BELL, G.A. SOMORJAI

An oxygen chemisorption method was developed for measuring the active surface area of supported and unsupported V_2O_5 following reduction in hydrogen. It is shown that to achieve complete reduction of the vanadia surface without reducing the bulk, reduction must be carried out at 640 K. Oxygen uptakes of unsupported samples reduced at close to this temperature yield an oxygen atom site density of 3.2×10^{18} m^{-2}, a value near that expected for a monolayer. The same oxygen-chemisorption technique is applied to silica-supported V_2O_5. Laser Raman spectroscopy confirms that near 640 K oxygen chemisorbs primarily at the surface of the dispersed vanadia, but does not exchange with the bulk of the oxide. For very low weight loadings, a limiting stoichimetry of one adsorbed oxygen atom per vanadium atom is obtained. This stoichiometry is used to calculate dispersions ranging from 93% to 50% for supported V_2O_5 samples of 0.3% to 9.8% weight loading.

---

* University of Seville, Spain
† University of Leiden, Netherlands
§ Catalytica Associates
** University of Washington

CATALYTIC HYDROGENATION OF CO*

The purpose of this project is to develop an understanding of the fundamental processes involved in the catalytic conversion of carbon monoxide and hydrogen to gaseous and liquid fuels. Attention is focused on defining the factors which limit catalyst activity, selectivity, and resistance to poisoning, and the relationship between catalyst composition/structure and performance. To meet these objectives, a variety of surface diagnostic techniques are used to characterize supported and unsupported catalysts before, during, and after reaction. The information is combined with detailed studies of reaction kinetics to elucidate reaction mechanisms and the influence of modifications in catalyst composition and/or structure on the elementary reactions involved in carbon monoxide hydrogenation.

CO and CO_2 Hydrogenation Over $LaMn_{1-x}Cu_xO_{3+\lambda}$ Perovskites and Related Catalysts

J. A. Brown Bourzutschky, N. Homs, A. T. Bell

CO hydrogenation was investigated over perovskites with the composition $LaMn_{1-x}Cu_xO_{3+\lambda}$ (x = 0, 0.2, 0.4, 0.5, 0.6, 1.0); Cu supported on SiO_2, unpromoted and promoted with La_2O_3; Cu supported on La_2O_3 and on MnO_2/La_2O_3; and unsupported Cu metal powder containing traces of sodium oxide (NaO/Cu). The x = 0 perovskite ($LaMnO_{3.24}$) is weakly active for CO hydrogenation, and produces only hydrocarbons, whereas all the other perovskites are more active and display > 90% selectivity to alcohols (80% methanol and 20% C_{2+} alcohols) (Figure 2). The C_{2+} alcohols follow a distribution characteristic of alkali-promoted copper catalysts. Cu/SiO_2 is > 80% selective to hydrocarbons, and < 5% selective to methanol. Introduction of La_2O_3 or NaO into the copper catalyst increases the CO hydrogenation activity and selectivity to alcohols. The activities and product distributions of the Cu-containing perovskites (x > 0) are similar to those of NaO/Cu and the La_2O_3-containing catalysts, suggesting that the active sites in all of the catalysts are similar. It is proposed that hydrocarbon synthesis occurs at Cu^0 sites, but that Cu^0 and Cu^+ sites are required for the synthesis of methanol and C_{2+} alcohols. It is also proposed

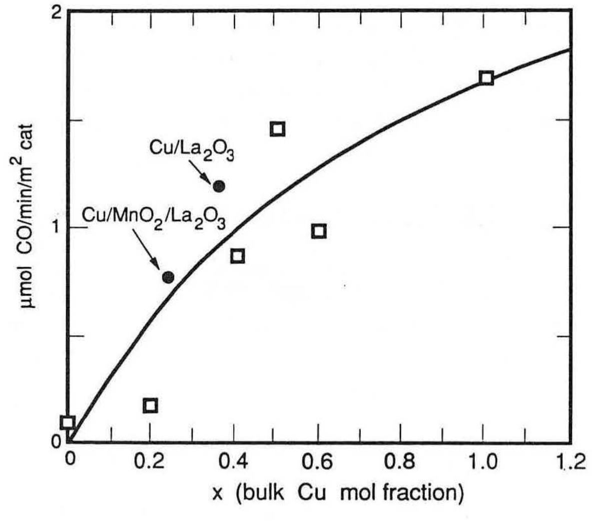


Figure 2
Correlation of CO hydrogenation activity with bulk Cu mole fraction, for perovskite (□) and lanthanum–supported (●) catalysts ($H_2/CO = 2$, $\underline{P} = 10.6$ atm, T = 573K).
(XBL 901-332)

---

*This work was supported by the Division of Chemical Sciences.

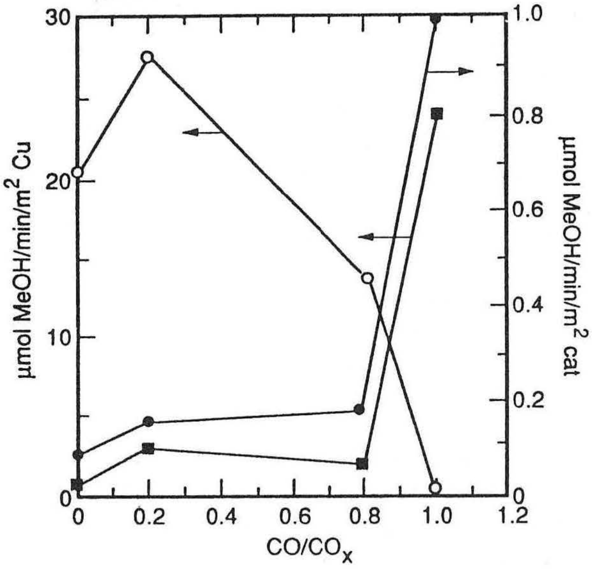


Figure 3
Hydrogenation of CO_2 and CO over copper catalysts: effects of CO/CO_x ratio on the methanol activity ($H_2/CO_x = 3$, $P = 13.4$ atm, $T = 573K$). (■) NaO_x/Cu, (○) Cu/SiO_2, (●) Cu/La_2O_3. (XBL 901-333)

that Cu^+ sites are stabilized at the adlineation between metallic copper and lanthana (or soda).

CO_2 hydrogenation was carried out over Cu/SiO_2, $La_2O_3/Cu/SiO_2$, Cu/La_2O_3, $Cu/MnO_2/La_2O_3$, and NaO/Cu powder. The major products are methanol and methane. Methyl formate was also produced at temperatures below 523K. In terms of oxygenate yield, the catalysts ranked in the order: $La_2O_3/Cu/SiO_2 > Cu/SiO_2 > Cu/La_2O_3 > Cu/MnO_2/La_2O_3 >> NaO/Cu$. Lanthana promotion of Cu/SiO_2 increases the formation of methanol but not of the other products. The selectivity patterns of the lanthana-supported catalysts are similar to that of Cu/SiO_2. Addition of Mn to Cu/La_2O_3 decreases the selectivity to methanol. Hydrogenation of CO_2/CO mixtures was studied over NaO/Cu, Cu/SiO_2, and Cu/La_2O_3(Figure 3). The NaO/Cu powder displayed higher selectivity to methanol in CO/H_2 than in CO_2/H_2. The activity and selectivity to methanol decreased with increasing CO fraction over Cu/SiO_2. Both activity and oxygenate selectivity increased with CO fraction over Cu/La_2O_3. C_{2+} alcohols are produced in CO-rich atmospheres. The observed effects of catalyst composition and feed composition on the activity and selectivity of Cu for methanol synthesis are attributable to the distribution of Cu^0 and Cu^+ sites.

METAL AND BIMETALLIC SINGLE CRYSTAL CATALYST SYSTEMS: (Pt, Pt-Re, Fe, Mo, Mo-Co)

Fundamental aspects of catalysis are investigated by the use of well-characterized single-crystal metal surfaces. Bimetallic surfaces are produced in ultra-high vacuum by deposition of a second metal. This procedure can generate a variety of bimetallic systems (Figure 4).

Platinum-Rhenium Bimetallic System

C. KIM, G.A. SOMORJAI

The isomerization and hydrogenolysis of light alkanes (ethane, n-hexane) were studied over platinum single crystal surfaces that were modified by the deposition of rhenium. The (111) face of platinum was used in most of these studies. The Pt-Re bimetallic system with one monolayer of ordered rhenium is a superior hydrogenolysis catalyst. The results suggest that a strong electronic interaction exists between the two metals that strongly influences the catalytic properties. The co-deposition of sulfur over the Pt-Re bimetallic system has been investigated in order to develop a Pt-Re-S model catalyst that was found to have superior activity and selectivity for dehydrocyclization in the petroleum refining technology. The sulfur surface coverage and hydrogenation rate have been determined over the bimetallic system in preparation for the catalytic hydrocarbon conversion studies.

Molybdenum Modified by the Epitaxial Deposition of Cobalt

C. Knight, G.A. Somorjai

Molybdenum modified by the epitaxial deposition of cobalt was utilized for the hydrodesulfurization of thiophene to butenes and butane. Cobalt did not improve the reaction rate when it was deposited on the Mo(100) crystal face. However, when a stepped molybdenum single crystal was used, the deposition of less than a monolayer of cobalt increased the reaction rate over that of clean Mo. The formation of a Mo-Co compound at the stepped surface is indicated, which has superior catalytic activity. The roles of sulfur and carbon, which deposit during the reaction over the bimetallic interface, are being explored by pre-sulfiding or pre-carbiding the bimetallic system. We aim to prepare a Mo-Co-S catalyst to model one that has been found superior for the HDS reaction in petrochemical technology.

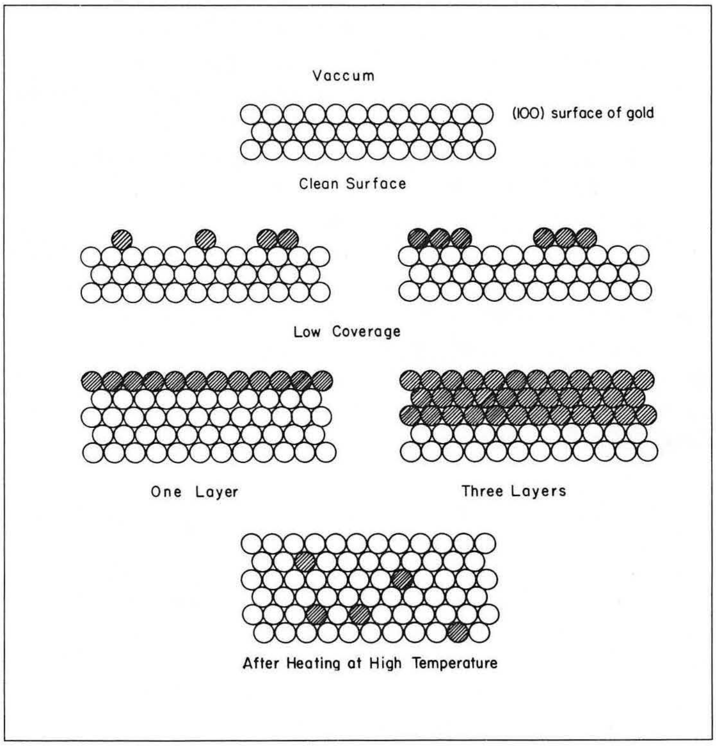


Figure 4
Different bimetallic growth modes are depicted, when one metal is deposited on a clean single-crystal substrate of another metal (shown on top panel). With increasing deposition, submonolayers become single and then multiple layers. At higher temperatures, an alloy may form.
(XBL 7810-6070)

Effects of Ammonia Pretreatment on the Structure and Activity of Iron Single Crystal Surfaces for Ammonia Synthesis

D.R. STRONGIN, G.A. SOMORJAI

Treatment of the (110), (100), and (111) planes of iron with 5 Torr or 50 Torr of ammonia (at 723K for 30 minutes) causes surface restructuring, as evidenced by changes in ammonia synthesis activity (20 atm total pressure), temperature programmed desorption and the appearance of new surfaces as seen by scanning electron microscopy (Figure 5). The Fe(110) and Fe(100) surfaces are restructured to surfaces containing C_7 sites, such as Fe(111) and Fe(211). A stereographic analysis of the restructured Fe(111) surface, using scanning electron microscopy, taken together with the reaction rate measurements, suggest that (211) surface planes are formed upon ammonia treatment. The high concentrations of near-surface nitrogen that is deposited by the ammonia pretreatment does not block catalytic sites for the synthesis of ammonia. The presence of aluminum oxide on any of the iron single crystal surfaces inhibits the ammonia induced restructuring process, while the presence of potassium has no observable effect on the process. These results suggest a method of activating iron with both ammonia and water vapor restructuring in the presence of aluminum oxide and potassium to achieve a catalyst with optimal activity for ammonia synthesis.

OXIDE AND OXIDE-METAL SINGLE CRYSTAL CATALYST SYSTEMS—Fe_2O_3, V_2O_3, Cu_xO, Rh/TiO_2, Cu/V_2O_3, Cu/ZrO)

Oxides are usually insulating materials and in many cases they are utilized in amorphous or polycrystalline form. To study the surfaces of such materials, and in particular, to study the structure and chemical properties of metal-oxide interfaces, we have developed a new methodology for sample preparation (Figure 6). In this method, single crystalline thin oxide films of Fe_2O_3, V_2O_3, Cu_xO, TiO_2, Al_2O_3 and ZrO_x are deposited by the condensation and subsequent oxidation of a metal monolayer to build up the oxide thin film layer by layer. The substrate is usually a single crystal face of a noble metal, such as Rh, Pt, Au, etc. This method permits the control of the surface structure and composition of the growing oxide film and allows the use of electron spectroscopies that necessitate conductive substrates for their proper operation. It also enables one to change the physical properties of the oxide (crystalline structure, stoichiometry) and to study the interface with the metal substrate.

Oxide islands are deposited in submonolayer coverage on single crystal surfaces or on polycrystalline foils of transition metals by depositing the metal from the vapor and subsequently oxidizing it. The surface coverage of the oxide is monitored by selective chemisorption, electron and ion spectroscopies (AES, ISS). The chemisorption and catalytic behavior of the oxide-metal systems is compared with that of the clean metal as a function of oxide coverage.

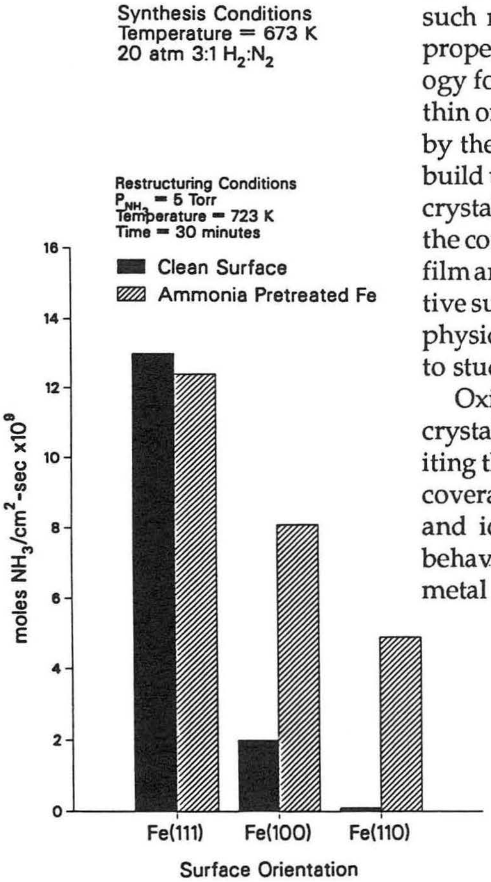
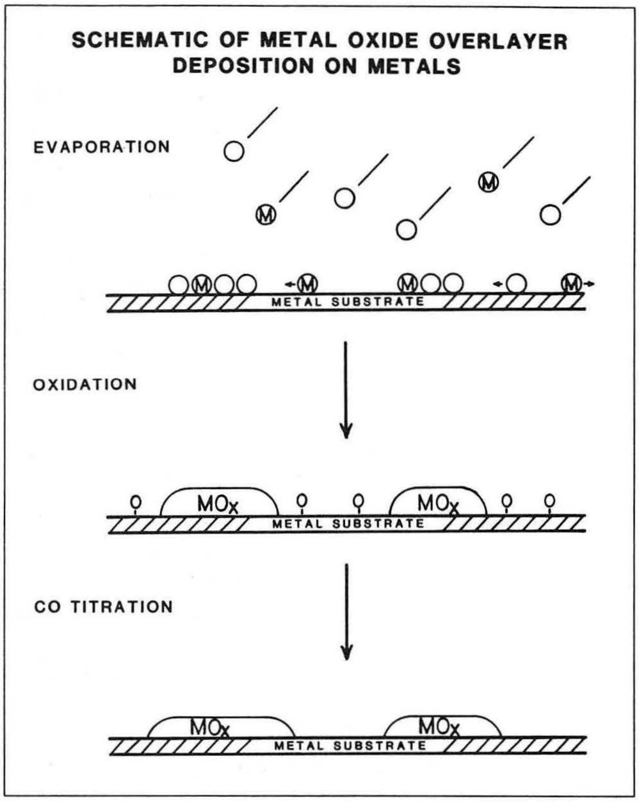


Figure 5
Comparison of ammonia synthesis over clean Fe single crystals and ones pretreated in ammonia prior to ammonia synthesis. Ammonia pretreatment restructures Fe(110) and Fe(100) to surfaces containing C_7 sites. Restructuring of Fe(111) has little change in ammonia synthesis activity. (XBL 8811-3901)

Figure 6
Thin metal oxide layers are grown on a metal substrate by deposition of evaporated metal, followed by oxidation and CO titration to remove excess oxygen. (XBL 8611-4263)



Preparation and Reactivity of Thin Ordered Films of Iron Oxide on Platinum

G. Vurens, M. Salmeron, G.A. Somorjai

Iron oxide has been grown on Pt(111) and Pt(100) in a two-dimensional fashion, at least for the first atomic layer. A combination of auger electron spectroscopy (AES), ion scattering spectroscopy (ISS), x-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), low energy electron diffraction (LEED) and temperature programmed desorption (TPD) was used to study these iron oxide overlayers. AES shows that the stoichiometry of the iron oxide is approximately Fe:O = 1:1, and XPS shows that the iron is in the Fe^{2+} oxidation state. However, the overlayer on Pt(100) contains less oxygen than the overlayer on Pt(111). On both platinum surfaces the oxide overlayers form an ordered structure. An incommensurate overlayer is formed on the Pt(111) surface, while a c(10x2) structure is formed on the Pt(100) substrate.

The iron oxide overlayer on Pt(100) showed little reactivity towards water as determined with water TPD. Two desorption features were obtained, associated with a chemisorbed monolayer (190K) and a physisorbed multilayer (170K). The physisorbed multilayer shows zero order desorption kinetics, while the chemisorbed peak showed half order desorption kinetics. This is explained by desorption from the edges of two-dimensional water islands on the surface. The influence of sodium oxide overlayers on the iron oxide on Pt(111) and Pt(100) was studied. After heating to 850K, the two-dimensional overlayer on Pt(111) restructured (i.e., the overlayer formed three-dimensional crystallites), while on Pt(100) this restructuring did not occur.

Preparation and Reactivity of Thin Ordered Films of Vanadium Oxide on Au(111)

K.B. Lewis, S.T. Oyama, G.A. Somorjai

Ordered vanadium oxide films can be grown on an Au(111) substrate. These films are formed when an evaporated layer of metallic vanadium is oxidized and annealed in UHV. A $(\sqrt{3} \times \sqrt{3})R30°$ LEED pattern is observed for submonolayer to multilayer coverages of vanadium oxide on Au(111), and AES shows that the vanadium in the film is in the +3 oxidation state. Hydrogen, ethanol, and ethylene adsorption on the oxide films was studied with temperature-programmed desorption. Oxidized molecules (H_2O, CO, and CO_2) were the primary desorption products. Oxygen became more difficult to extract as the vanadium oxide film was reduced during successive TPD experiments.

Preparation of Thin Ordered Films of ZrO_2 on Pt (111)

V. Maurice, M. Salmeron, G.A. Somorjai

Zirconium was deposited from the vapor phase on Pt (111) single crystal surfaces and oxidized to ZrO_2. When heated to 700°C the oxide film orders. This way an ordered ZrO_2 thin film can be grown layer by layer. Upon heating in vacuum the zirconium dissolves in platinum to form an intermetallic compound. The oxide film can be regrown by heating the Pt-Zr intermetallic in oxygen.

Rh/TiO_2 System

H.C. Wang, K. Williams, A.T. Bell, G.A. Somorjai

The hydrogenation of CO_2 to alkanes and the hydrogenation of acetone to iso-propanol was studied over the Rh-TiO_2 system. A large enhancement in the reaction rate is observed at about one-half monolayer oxide coverage on the rhodium surface (Figure 7). The carbon-oxygen bond is being activated at the oxide-metal interface rather than the H-H bond, since hydrogenation of olefins and the hydrogenolysis of light alkanes are unaffected by the presence of the oxide. STM studies are being carried out to investigate the oxide-metal interface structure on the atomic scale. These studies explore the molecular ingredients of the so called strong metal-support interaction.

Pt/Al_2O_3 System

I. Bozormenyi, G.A. Somorjai

The isomerization of n-hexane and the ring opening of methyl-cyclopentane was investigated over the Pt-Al_2O_3 system. Enhanced isomeri-

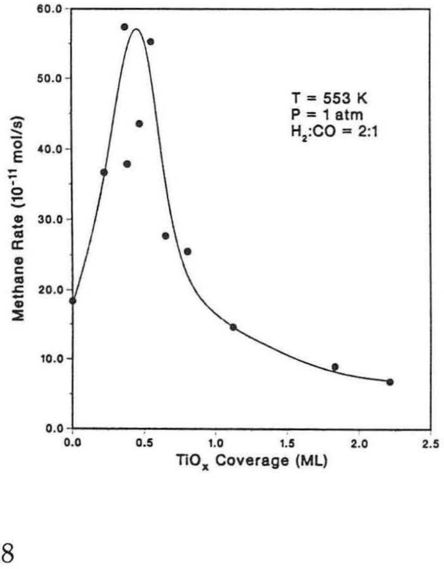


Figure 7
The rate of methane formation is shown on thin alumina layers deposited on a rhodium substrate, as a function of the oxide coverage on the surface.
(XBL 896-2171)

zation activity has been detected in the presence of the oxide. The effect of chlorine as a reaction promoter when adsorbed on the oxide is being investigated. The purpose of these studies is to delineate the catalytic reactions that occur over the oxide and over the oxide metal interface as compared to the metal during petroleum refining to high-octane fuels.

Cu/ZrO System

S. FU, G.A. SOMORJAI

The formation of methanol from CO and H_2 was explored over the Cu-ZnO system. The chemisorption properties of CO, H_2, CH_3OH, CO_2 and H_2O are markedly altered in the presence of zinc oxide. The existence of Cu_xZn_yO compounds at the interface could be detected. CO_2 only chemisorbs over the oxide while CO adsorbs on both Cu and ZnO. Our aim is to build a model catalyst that exhibits the same activity for methanol production as the Cu/ZnO system that is utilized in the chemical technology.

MODELING

Adsorbate-Induced Restructuring of Surfaces: Catalytic Implications

M.A. VAN HOVE, G.A. SOMORJAI

Chemisorbed atoms and molecules frequently restructure metal surfaces. Recent surface crystallography studies revealed the structural changes that occur on the atomic scale. The metal atoms relocate around the adsorbate accompanied by changes of bond distances and bond angles for both substrate and adsorbate. The restructuring may occur on the time scale of chemisorption ($\sim 10^{-3}$ seconds), of catalytic reactions (seconds) or by slower mass-transport (diffusion) controlled processes (days). Often, restructuring is necessary to create the catalytically active sites. Adsorbate-induced restructuring can explain the existence of classes of structure-sensitive and structure-insensitive reactions. Slow deactivation and regeneration processes observed and utilized in catalytic technologies can be interpreted as caused by adsorbate-induced restructuring.

*Analysis of Formic Acid Decomposition on Metal Surfaces by the BOC-MP Approach**

E. SHUSTOROVICH†, A.T. BELL

The bond-order-conservation–Morse-potential (BOC-MP) approach, extended to treat the heat of chemisorption of bidentate species and of molecular radicals, has been used to analyze the energetics of formic acid decomposition at low coverages on Ag(111), Ni(111), and Fe/W(110) surfaces. These calculations project that on all three surfaces formate species are produced with a parallel formation of formyl plus hydroxyl species on Ni and Fe/W. Bidentate coordination of formate species is preferred over monodentate coordination, the energy difference increasing in the order Ag < Ni < Fe/W. The decomposition of formate species leads mainly to atomic hydrogen and CO_2 on Ag, whereas on Ni and especially on Fe/W, formate decomposition leads mainly to atomic oxygen and formyl species, the latter of which decomposes practically without activation to CO and atomic hydrogen. The findings of this study are in general agreement with experimental observation.

---

* This work was supported by the Division of Chemical Sciences.

† Corporate Research Laboratories, Eastman Kodak Company

*Monte Carlo Simulation of Temperature-Programmed Desorption of Coadsorbed Species**

S. J. Lombardo, A.T. Bell

A Monte Carlo model has been developed for describing the temperature-programmed desorption of coadsorbed species from single-crystal surfaces. Interactions between the adsorbates and the metal surface as well as interactions between the adsorbates are taken into account using the bond-order-conservation–Morse-potential (BOC-MP) approach. The number, shape, and location of the peaks is found to be sensitive to the binding energy, coverage, and coordination of each coadsorbed species. The presence of a strongly bound coadsorbate on a bcc(100) surface is shown to shift the desorption spectrum for associative desorption of adsorbed atoms to lower temperatures. TPD spectra for the concurrent associative desorption of A atoms and the desorption of B molecules from a fcc(100) surface are of two types: in one case, both species exhibit new low-temperature features far removed from their pure component spectra (Figure 8); in the second case, only the species undergoing associative desorption display new spectral features. The simulated TPD spectra are in qualitative agreement with experimental results for H_2 coadsorbed with strongly bound atomic species on Mo(100) and Fe(100) surfaces as well as for CO and H_2 coadsorbed on Ni(100) and Rh(100) surfaces.

Directed Search Methods for Surface Structure Determination by LEED

P.J. Rous, M.A. Van Hove, G.A. Somorjai

Conventional surface crystallography by low-energy electron diffraction (LEED) employs a trial-and-error search controlled at each step by a human being. This trial-and-error approach becomes very cumbersome and unreliable when it is applied to complex surfaces with a large number of unknown structural parameters. An automatic optimization procedure has been developed for LEED which combines the complementary techniques of Tensor LEED and a numerical search algorithm. This approach can reduce the computer time required for an entire structure determination by several orders of magnitude. It also allows all structural parameters to be found simultaneously; in particular, complex non-symmetric

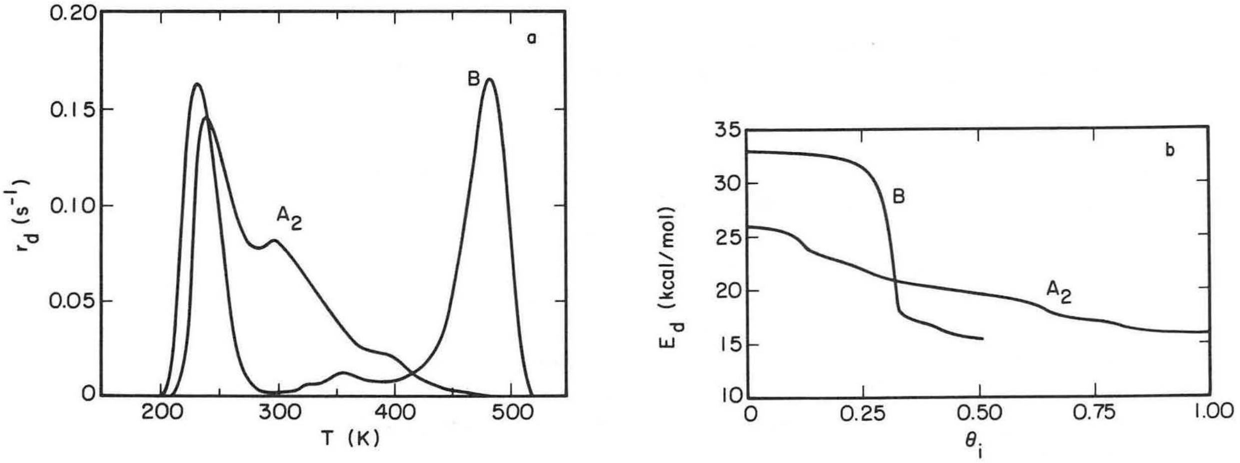


Figure 8
(a) Monte Carlo simulations of A_2 and B codesorption. (b) Variation of activation energy, E_d, as a function of adsorbate coverage. (XBL 897-2824)

---

*This work was supported by the Division of Chemical Sciences.

structures and adsorbate-induced substrate distortions can be readily determined. This method has been applied to the determination of the surface structures of clean Pd(111), and CO-covered Pd(111), as well as C- and S-covered Mo(100).

First-Principles Studies of Surface Structures and Properties

S.G. LOUIE, X.-W. WANG

First-principles studies are carried out to explain and predict the structures and properties of surfaces and chemisorption systems. Emphasis is on providing a microscopic understanding of the scanning tunneling microscopy (STM) images and the optical and photoemission spectra of systems of particular relevance to the experimental efforts in CAM. The theoretical methods employed include *ab initio* pseudopotential density functional calculations for ground-state properties and many-body quasiparticle calculations for excitation spectra. These methods allow accurate determination of solid state and surface properties from those of the atoms. Application to sulfur overlayers on Mo surfaces is reported under Surface Structure and Bonding.

Hydrogen Chemisorption on Diamond Surfaces

S.G. LOUIE, X.-W. WANG

We have initiated a project to investigate the properties of H chemisorption on the diamond (100) surface. The work is motivated by the observed differences in the behavior of this system from those of diamond (111) and other covalent semiconductor surfaces and by the current interest in the role of H in diamond film growth.

Hydrogen-Hydrogen Interactions in Palladium

S.G. LOUIE, X.-W. WANG, D. TOMANEK

The Pons-Fleischmann claim that cold fusion could occur in metal hydrides motivated our investigation of hydrogen interactions in and on palladium. Calculations have been carried out to evaluate the energetics and electronic structure of PdH_n where n is varied from 1 to 4. The interaction between a pair of hydrogen atoms in various locations in the Pd lattice was studied. This work was among the first to show that the separation between the hydrogens in Pd remained much larger than the value required for a significant fusion rate. The results, however, did indicate that, with a moderate chemical potential shift, a high density of hydrogen can be achieved inside the Pd crystal.

Dynamics of Deuterium Interstitials in Metals

K.B. WHALEY

Dynamics of atomic hydrogen and its isotopes in and on metals is dominated by quantum effects. Deuterium shows anomalous behavior in several instances, e.g., D/W(110) and D/Pd. We have developed a tight-binding theoretical approach to the coherent many-particle dynamics of strongly interacting tunneling particles, which is appropriate for analysis of deuterium dynamics at high concentrations. This model shows the marked effects of nuclear statistics in enhancing local site density fluctuations for deuterium in small clusters of interstitial sites. This leads to a new type of screening of the deuteron-deuteron interaction, namely 'boson screening,' which has important consequences for deuterium dynamics at high concentrations. Application to the nuclear regime shows that finite temperature bosonic collective effects can enhance nuclear reaction rates involving deuterons in palladium deuterides. It is now being applied to the study of anomalous isotope effects for low temperature tunneling diffusion.

FUNDAMENTALS OF CATALYTIC GASIFICATION*

H. Heinemann, P. Pereira, G.A. Somorjai

It is the purpose of this project to achieve steam gasification of carbonaceous materials at temperatures below 1000K and to produce essentially only hydrogen and carbon dioxide and further to understand the reaction mechanism.

Earlier work in this laboratory had shown that catalysts of binary metal oxides such as alkali-transition metal oxides or alkali-earth alkali oxides can promote the gasification of graphite and of chars at temperatures of about 800-1000K and atmospheric pressure. It was also shown that for catalysts to be active at those conditions, they had to be able to dissociate water providing hydrogen and giving oxygen to the carbonaceous substrate. It had been concluded that the attack of a potassium-nickel oxide catalyst on the carbonaceous substrate proceeded by edge recession rather than by channeling. It was also found that potassium-nickel oxide catalysts are more subject to poisoning by ash components than alkali-earth alkali such as potassium-calcium oxide catalysts.

During 1989 it was demonstrated that poisoning of the potassium-nickel oxide catalysts was largely due to organic sulfur compounds in the ash. Against expectations pyrite was not a poison. Organic sulfur compounds did not appreciably poison potassium-calcium oxide catalysts. Additional electron microscopy work indicated that the mechanism of attack on the carbon is the same for potassium-calcium oxide as for potassium-nickel oxide catalysts (Figure 9). This work also demonstrated that each catalyst particle derived from impregnation of the carbonaceous substrate with nitrates of the metals followed by decomposition contains both potassium and calcium, regardless of the size of the particle.

The gasification work was extended to coals. It was found that coals impregnated with either of the catalysts could be gasified at much higher

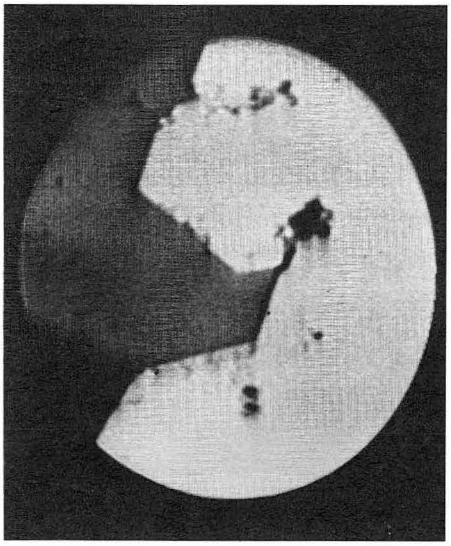


Figure 9
Controlled atmosphere electron micrograph of graphite gasification in presence of K–NiO catalyst showing catalyst wetting surface and edge recession.
(XBB 876-5379A)

---

*This work was supported by the Office of Fossil Energy.

rates than the chars derived from the coals. The order of gasification rate for coals and chars was lignite > subbituminous > bituminous > graphitic.

Since catalysts of the alkali-alkali earth oxide type have previously been found to be active for oxidative coupling of methane, experiments were undertaken to carry out the gasification in the presence of steam, methane, and small amounts of oxygen. No conversion of methane to products other than carbon dioxide was observed until about 90% of the char had been gasified. At this point C_2 hydrocarbons were formed from methane and continued to be formed after 100% gasification of the char. Yields of about 10-15% of C_2 hydrocarbons were formed at temperatures which are about 200 °C lower than those described in the literature for similar yields with other catalysts. This phenomenon is being further investigated.

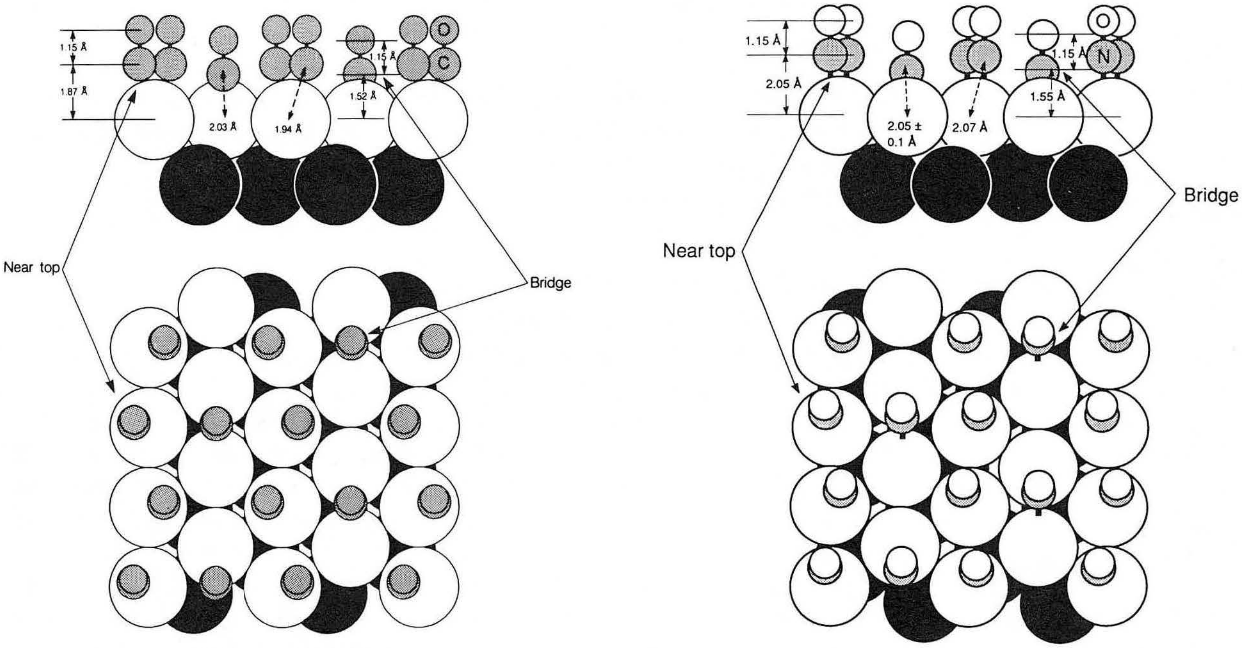
SURFACE AND INTERFACE COMPOUNDS

SURFACE STRUCTURE AND BONDING

Structure of Disordered Molecular Adsorbates: CO and Benzene on Pt (111)

G.S. Blackman, P. De Andres, R.Q. Hwang, D.F. Ogletree, G.A. Somorjai,
M.A. Van Hove, A. Wander, M.-L. Xu

The use of low-energy electron diffraction (LEED) in determining bond distances and angles of adsorbates on surfaces has been greatly extended in this laboratory in recent years, both experimentally and theoretically. It is now possible to determine the surface structure of disordered monolayers on ordered substrates using a new digital-LEED apparatus and a new diffuse-LEED theory. For example, the disordered structures of benzene and carbon monoxide adsorbed on the Pt(111) single-crystal surface were determined. This involved the measurement and calculation of diffuse LEED intensities in order to determine the molecular adsorption sites, metal-carbon bond lengths and internal distortions of the molecules.



Rh(111) + (2X2) 3CO

Rh(111) + (2 X 2) 3NO

Figure 10
Side and near-perpendicular views of the best-fit models for dense structures of CO (left) and NO (right) on Rh(111). (left: XBL 895-6910; right: XBL 888-8950)

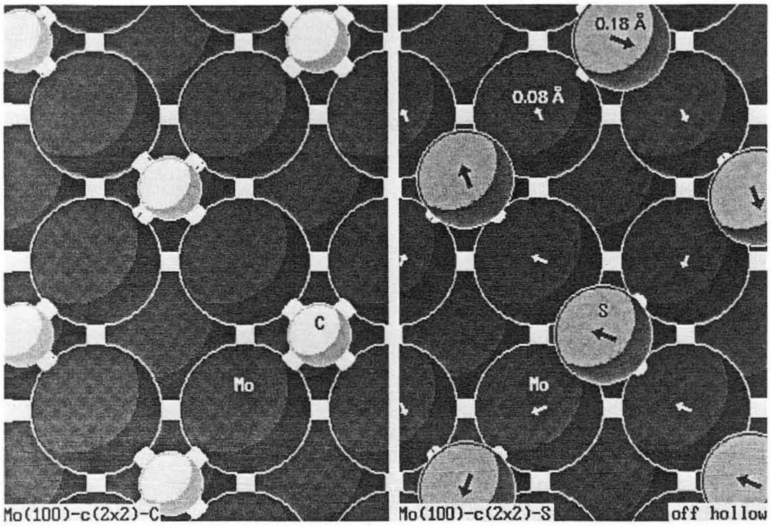


Figure 11
At left: top view of a highly symmetric overlayer of carbon on Mo(100). At right: top view of c(2x2) sulfur overlayer on Mo(100) with asymmetric lateral shifts as shown by arrows. These shifts point in random directions.
(XBB 895-4262)

High-Density Molecular Monolayers on Metal Surfaces: CO and NO on Rh (111)

G.S. Blackman, C.-M. Chan, C.-T. Kao, G.A. Somorjai, M.A. Van Hove

At high densities, close to saturation coverage, molecular monolayers exhibit strong adsorbate-adsorbate interactions. Such effects can involve charge transfer between inequivalent adsorbates, much studied in this laboratory in the past. Another type of interaction occurs with like adsorbates, as with a monolayer consisting of only NO molecules. Here non-ionic forces dominate which are repelling at close separations, defining van der Waals radii. Structural analysis by LEED and high-resolution electron energy loss spectroscopy (HREELS) has exhibited this behavior for both a NO monolayer and a CO monolayer deposited on Rh(111). At saturation coverage a well-ordered (2 x 2) structure exists in both cases, with all molecules closely perpendicular to the surface. In each (2 x 2) unit cell, one molecule resides on a bridge site (two-fold coordination) (Figure 10) It pushes two neighboring molecules away from symmetrical top sites (one-fold coordination) by an amount closely related to the van der Waals radii of the carbon atoms. This finding gives a direct measure of interactions between admolecules and points to the validity of the conventional concept of van der Waals radii when applied to adsorbed molecules.

Atomic Adsorption Structures on Metal Surfaces: Sulfur and Carbon on Mo (100) and Re (0001)

D. Jentz, D.G. Kelly, S.G. Louie, D.F. Ogletree, C. Ocal, B. Marchon, P.J. Rous, M. Salmeron, G.A. Somorjai, M.A. Van Hove, X.-W. Wang

Structures of sulfur and carbon adsorbed on Mo(100) and Re(0001) were studied with LEED and STM as well as with total-energy calculations. Half-monolayer c(2x2) structures of sulfur or carbon atoms on Mo(100) have been investigated by LEED, allowing complete relaxation of the atoms in the first 3 layers (Figure 11). Whereas the carbon atoms nestle symmetrically at the center of the four-fold coordinated hollows of the substrate, the sulfur atoms are found to shift laterally and also induce marked lateral displacements in the topmost metal layer. With both C and S adsorption, significant changes in metal-metal interlayer spacings are observed, illustrating the phenomenon of adsorbate-induced restructuring. Corresponding total-energy calculations (keeping a rigid bulk-like substrate) predict no lateral shift of sulfur, and find S-Mo bond lengths

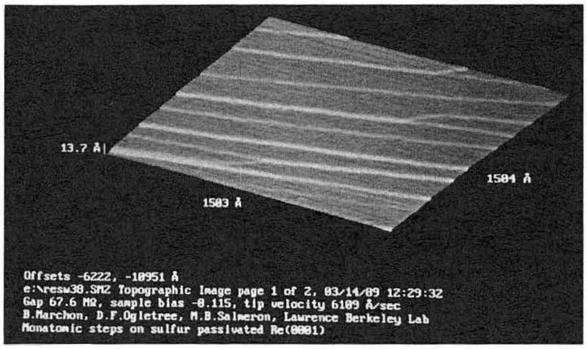


Figure 12
Steps of 2 atoms height and also 1 atom height are seen to separate terraces of (0001) orientation in this STM image of Re covered with a saturation layer of sulfur. Notice also the emergence of a screw dislocation in the lower right of the image giving rise to steps. (XBB 896-5072)

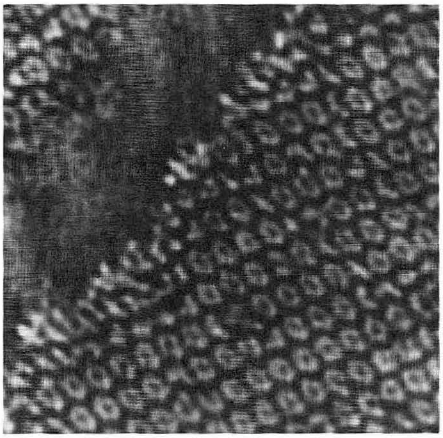


Figure 13
Scanning tunneling microscopy image of the $(2\sqrt{3} \times 2\sqrt{3})$ R30° structure of sulfur on Re(0001). Sulfur forms rings of 6 atoms that cover the surface. The distance between ring centers is 9.5Å. Two terraces are shown separated by a blurred region at the step. The size of this region is due to the finite tip radius. Notice also defects in the layer (broken rings, phase boundary crossing the middle part of the image perpendicular to the step). The corrugation height across sulfur rings (black to white) is about 2.4Å. (XBB 888-8469)

closely similar to the LEED result. Calculations were also performed for the full-monolayer p(2x1) structure of S on Mo(100), to be compared with earlier STM images taken in this laboratory. The theory predicts a bridge-hollow chemisorption geometry as the most stable structure. This result is compatible with the STM data only if one assumes that STM is not sensitive to the difference in the heights of bridge-S and hollow-S above the metal. Further STM work has focused on sulfur layers on Re(0001), observed both in air and in ultra-high vacuum. A rich set of sulfur structures is obtained. For example, a $(2\sqrt{3}x2\sqrt{3})$R30° sulfur overlayer chemisorbed on Re(0001) was prepared in UHV and then transferred through air to a scanning tunneling microscope (STM) operating at a vacuum of 10^{-7} Torr. This $(2\sqrt{3}x2\sqrt{3})$R30° sulfur overlayer passivates the rhenium substrate in air. STM images show steps and dislocations on the metal surface (Figure 12). The atomic structure of the overlayer unit cell is shown to be a hexagonal ring of six sulfur atoms (Figure 13). Defect structures in the two-dimensional lattice of sulfur hexagons and overlayer domain boundaries can also be observed.

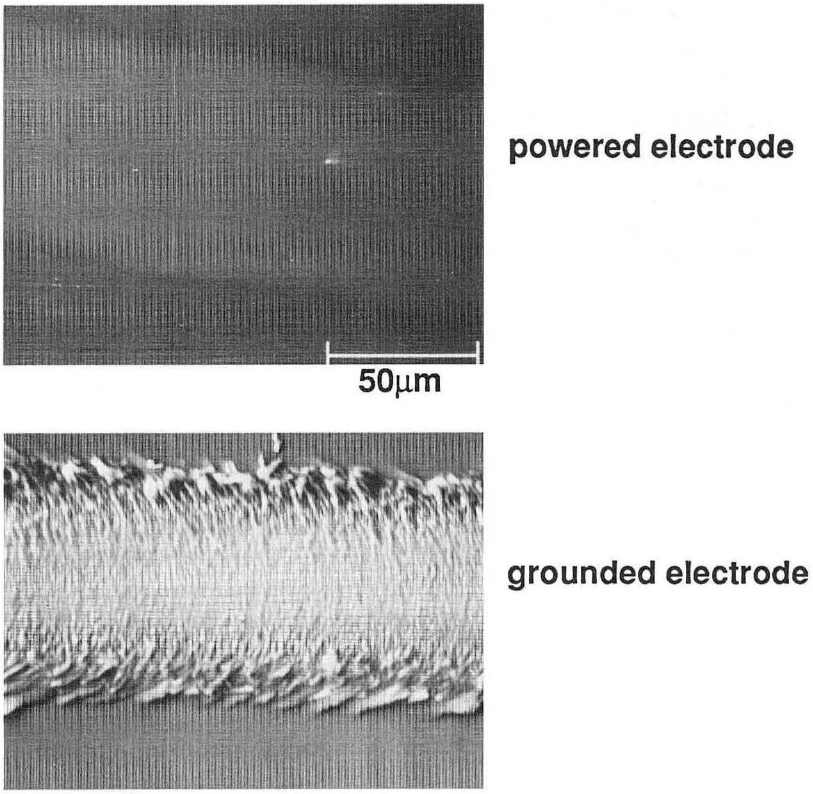
COATINGS AND INTERFACE COMPOUNDS: AMORPHOUS CARBON FILMS

Formation of Hydrogenated Amorphous Carbon Films of Controlled Hardness from a Methane Plasma

G.J. Vandentop, M. Kawasaki, R.M. Nix, I.G. Brown, M. Salmeron, G.A. Somorjai

Studies of amorphous hydrogenated carbon (αC:H) film deposition revealed that methyl radicals are the precursor species responsible for the bulk mass deposition of the films, while the ions act to improve the mechanical properties. The films were deposited on Si(100) substrates both on the powered (negatively self-biased) and on the grounded electrodes from a methane rf plasma (13.56 MHz) at 68 to 70 mTorr and 300 to 370K. The films produced on the powered electrode exhibited superior

Figure 14
Secondary electron microscope images of scratch tracks made with a Rockwell C diamond tip at a load of 830g, for films formed on the powered and grounded electrodes. Little damage is apparent on the hard film formed on the powered electrode, while the soft film formed on the grounded electrode has suffered noticeable damage. (XBB 897-5454)



mechanical properties, such as high hardness and scratch resistance (Figure 14). A mass spectrometer was used to identify neutral species and positive ions incident on the electrodes from the plasma, and also to measure ion energies. Methyl radicals were incident on the electrode surface with an estimated flux of $10^{16}cm^{-2}s^{-1}$, for an rf power of 50 W. Methyl radicals appear to be the dominant intermediates in the growth of the soft carbon polymer, and there is a remarkable decrease in deposition rate due to the introduction of NO, a radical scavenger. A novel pulsed biasing technique was used so that the role of ions in the plasma could be studied separately. It was found that the hardness of the films depends on the power supplied by the ions to the growing film surface (the time

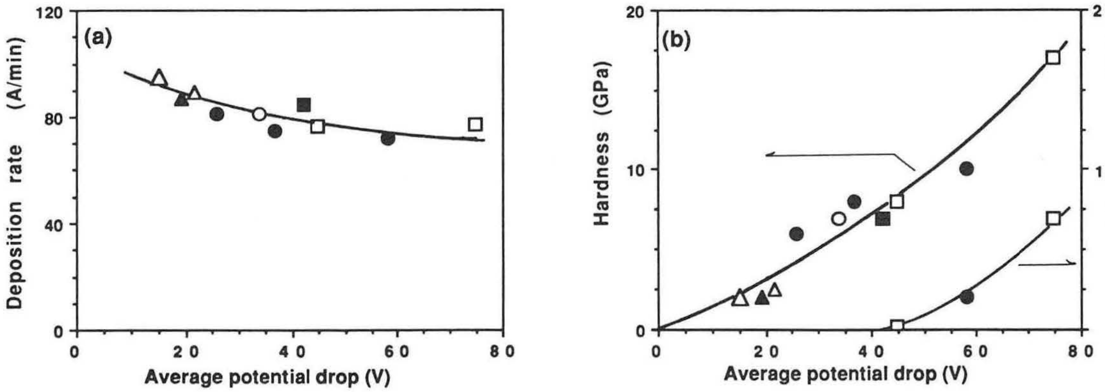


Figure 15
The dependence of hardness and compressive stress on the time averaged potential drop between the plasma bulk and the substrate. Hardness depends monotonically on the average potential drop between the plasma and the electrode; i.e., the power delivered to the film surface by ions as controlled by pulsed biasing. Deposition rate is independent of the average potential drop. The pulse frequencies are 25, 12.5, and 6.25 kHz for the -800 V pulses, 25 and 12.5 kHz for -1100 V, 25 kHz for -500 and -200 V, and 100 kHz for -20 and -800 V. (XBL 8911-4162)

averaged difference between the plasma potential and the electrode potential), but not on the energy of individual ions (Figure 15). The pulsed biasing technique offers an efficient method to adjust the film hardness by independent control of the neutral radical and ion fluxes to the surface.

Analysis of the Interface of Hydrogenated Amorphous Carbon Films on Silicon by Angle-Resolved X-Ray Photoelectron Spectroscopy

M. KAWASAKI, G.J. VANDENTOP, M. SALMERON, G.A. SOMORJAI

Thin amorphous hydrogenated carbon films were deposited from a methane rf plasma (13.56 MHz) at 68 mTorr on Si(100) substrates both on the powered (negatively self-biased) and on the nonpowered (grounded) electrode. The interface was analyzed with angle-resolved X-ray photoelectron spectroscopy. An approximately stoichiometric silicon carbide layer was found at the interface of a hard carbon film produced on the powered electrode. The thickness of the interfacial carbide as estimated from the angle resolved spectra was approximately 7Å, which is much thinner than previously reported by other workers. There was no interfacial silicon carbide formation evident for a soft polymer-like film produced on the grounded electrode. Instead, a submonolayer amount of oxide which showed poor adhesion was detected at the interface of the soft carbon film . Our results indicate that the high energy ions incident on the powered electrode in the rf plasma are responsible for the production of the interfacial silicon carbide and are also likely responsible for the good adhesion of the film to the silicon substrate.

Oxidation of SiC Single Crystal Surfaces

J. POWERS, M. SALMERON, G.A. SOMORJAI

AES and LEED have been utilized to monitor the kinetics of oxidation of silicon carbide single crystals. Oxidation is faster in the presence of large concentrations of surface defects that can be produced by argon ion bombardment. At low oxygen partial pressures, the surface is covered by graphite after SiO is removed by heating above 600°C. At high oxygen partial pressures (near one atmosphere), the SiC surface is covered by silicon dioxide.

INSTRUMENTATION FOR SURFACE SCIENCE

OPTICAL SURFACE STUDIES

Determination of Surface pH Values by Optical Second Harmonic Generation

X.-D. XIAO, V. VOGEL, Y.R. SHEN

Optical second harmonic generation from protonable dye molecules at a lipid/water interface can be employed to determine the surface pH values (proton excess) at interfaces. This has been demonstrated on a stearic acid monolayer/water interfacial system. The surface proton concentration changes in response to variation of the bulk proton and salt concentration as shown in Figure 16 and can differ from the bulk proton concentration by 6 or 7 orders of magnitude. Probing the surface pH value by SHG provides the possibility for investigation of fast dynamic processes involving protons at interfaces.

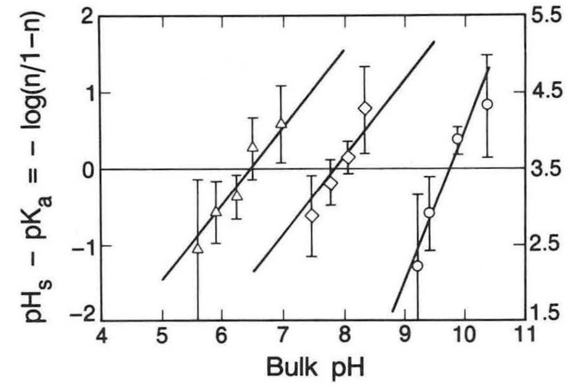


Figure 16
The effective molecular hyperpolarizability β of the hemicyanine dye deduced from the SHG results is plotted against pH_b for different salt concentrations. The hemicyanine dye is embedded into a negatively charged monolayer matrix of stearic acids in the molar ratio of 1/15. The symbols "○" and "Δ" represent the experimental data on 0, 5.6, and 100 mM NaCl solutions, respectively (200°C). The solid lines are theoretical curves. (XBL 895-5094)

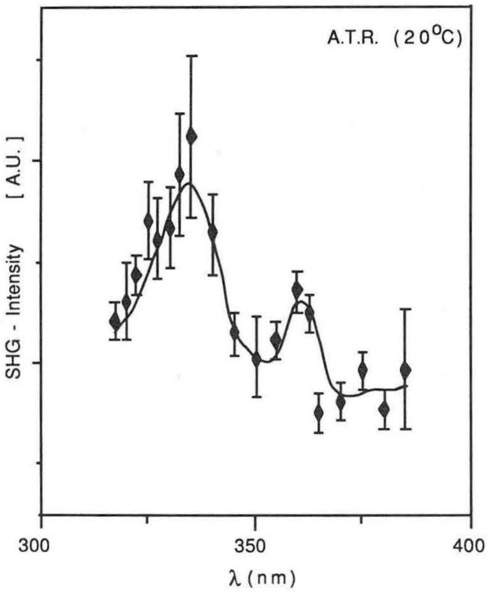


Figure 17
SHG spectrum of all-trans retinal at an air-water interface. (XBL 897-3927)

A New Vision on Vision

Th. Rasing, J.Y. Huang[†], A. Lewis, T. Stehlin, Y.R. Shen

The orientation, hyperpolarizability, and spectrum of retinal chromophores were studied for monolayers of the pure chromophore and for the chromophore embedded in the purple membrane of *Halobacterium halobium* spread at the air-water interface using the technique of optical second harmonic generation. The hyperpolarizability in the membrane appears to be identical to that of the free chromophore. The spectrum of all-trans retinal monolayers exhibits a subsidiary one-photon forbidden peak in addition to the main absorption peak (Figure 17).

Study of Conformation, Orientation, and Interaction in Molecular Monolayers by IR-Visible Sum-Frequency Generation[*]

R. Superfine, J.Y. Huang[†], Y.R. Shen

We have used sum-frequency generation to study the order in a silane monolayer. We observe an increase in the order of the chain of the silane molecule induced by the interpenetration of the liquid crystal molecules. By using SHG and SFG, we have studied the orientation and conformation of the liquid crystal molecule on clean and silane coated glass surfaces. On both surfaces, the biphenyl group is tilted by 70° with the alkyl chain end pointing away from the surface. The shift in the C-H stretch frequencies (Figure 18) in the coadsorbed system indicates a significant interaction between molecules.

---

[*] Supported by 3M Corporate Research Laboratories

[†] IBM Postdoctoral Fellow

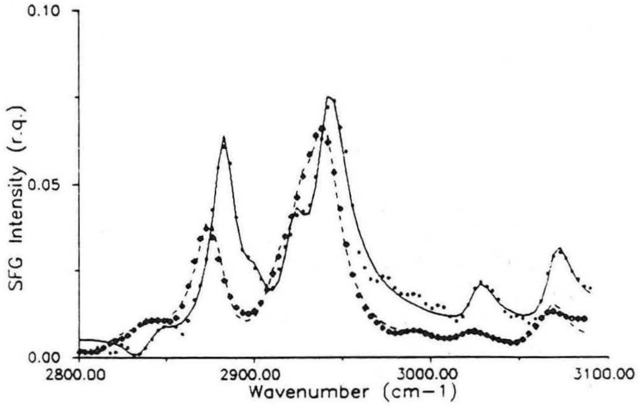


Figure 16
SFG spectrum of 8CB monolayer on clean glass (solid curve) is compared to 8CP deposited on DMPOAP coated surface (dashed curve). (XBL 901-120)

Interference between Second Harmonic Generation from a Substrate and an Adsorbate Layer

G. Berkovic, Y.R. Shen, G. Marowsky, R. Steinhoff

Several experiments on surface second harmonic generation have been carried out to show how the contribution from a transparent substrate can interfere with that from an adsorbate monolayer. The interference depends on the relative phase of the two contributions, which varies with the molecular orientation, the laser frequency, the polarization, and the optical geometry.

Polymer Concentration Profile near a Liquid-Solid Interface: Evanescent Wave Ellipsometry Study

M.W. Kim, D.G. Peiffer, W. Chen, H. Hsiung, Th. Rasing, Y.R. Shen

The phase retardation angle, $\Delta\Phi$, as a function of the incident angle was measured by evanescent wave ellipsometry technique to study adsorption and depletion of polymers near a solid substrate from a solution. A lightly sulfonated ionomer dissolved in a polar solvent displayed an appreciable interfacial adsorption layer, while the nonionic precursor in ethyl acetate exhibited a depleted concentration profile. The results are in good agreement with adsorption or depletion layer profiles obtained previously by other techniques, i.e., X-ray fluorescence for polymer adsorption and optical fluorescence wave technique for depletion.

Unenhanced Surface Raman Spectroscopy

J.W. Ager III, G.M. Rosenblatt, D.K. Veirs

Unenhanced surface Raman spectroscopy is used as a vibrational probe of physisorbed and chemisorbed molecules and films on a variety of surfaces from 14K to well above room temperature

Recent developments in two-dimensional single-photon sensitive detectors, as implemented in our laboratory, allow unenhanced surface Raman spectroscopy of physisorbed and chemisorbed adsorbates and of thin films. The sensitive Raman apparatus is coupled with an ultrahigh vacuum chamber capable of cooling samples to 14K and equipped with LEED/Auger surface characterization and ion bombardment and heating for surface cleaning to study the vibrational-rotational energy levels of low temperature adsorbates.

Following the first Raman measurements of a physisorbed system at low, near-monolayer coverages—N_2 adsorbed on Ag(111)—we have studied thicker adsorbed films of α-N_2 in order to examine optical polarization and film orientation. In contrast to near-monolayer films, where the

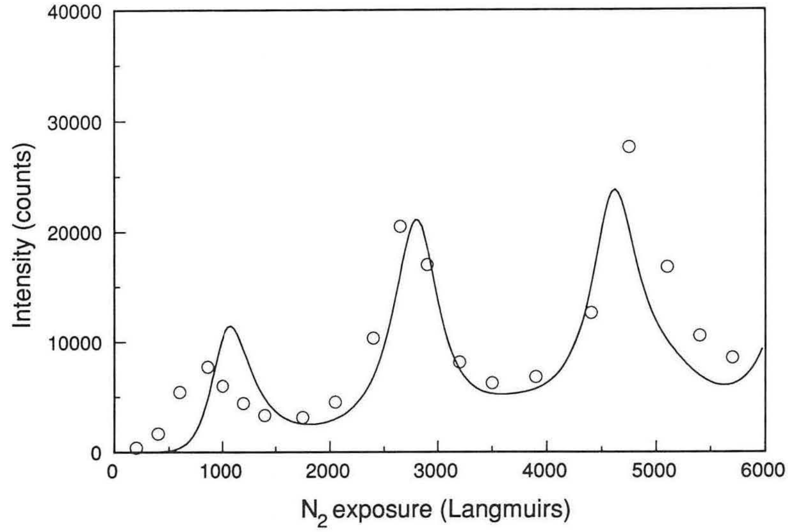


Figure 19
The Raman intensity at 2325 cm^{-1} of N_2 physisorbed on Ag(111) at 14 K as a function of N_2 exposure. The intensity shows oscillations arising from interference effects. The experimental data are indicated by circles and the solid line is the theoretical prediction. The spacing between maxima is a measure of the film thickness and yields the sticking coefficient. (XBL 899-3324)

Raman intensity varies linearly with coverage, large oscillations in the vibrational Raman intensity are observed as a function of film thickness (Figure 19). The observed oscillations are due to multiple beam interference caused by reflections at the vacuum-film and metal-film boundaries of the incident laser light and the Raman scattered light.

To describe the interference, we have extended the available theoretical development for Raman scattering in thin films to the general three-dimensional experimental geometry and have derived expressions for the total intensity as a function of film thickness, incident laser polarization and angle, and scattered light polarization and angle. As the film gets thicker, the theoretical development and the experimental observations show enhanced intensity from laser light polarized parallel to the surface (solid line in Figure 20), whereas scattering from laser light polarized perpendicular to the surface, which completely dominates at near monolayer coverages, is enhanced less by interference effects (dotted line in Figure 20). The calculated Raman intensities are in excellent agreement with the experimental results (solid line in Figure 19).

The observed period of the intensity oscillation relates the film thickness to the exposure allowing the sticking probability of N_2 on α-N_2 to be determined: 0.84±0.2 at 14±1K (for α-N_2 one monolayer requires 3.3 L). In similar experiments, the sticking coefficient of O_2 on O_2 was found to be 0.82±0.2 at 14±1K.

The unique Raman apparatus used in these studies was also applied to collaborative studies of crack propagation in zirconia (see R.H. Dauskardt and R.O. Ritchie's work in the Structural Materials Program) and of carbon films for Seagate Magnetics and IBM Corporation.

SCANNING TUNNELING MICROSCOPY

Application of STM to Studies of Organic and Bio-Organic Materials

J. Clarke, M. Salmeron, T. Beebe, J. Odriozola, T. Wilson, D.F. Ogletree,
W. Siekhaus, K.A. Fisher*, M.B. Shattuck*, R. S. Bhatnagau*, S. Whitfield, R.E. Thomson

The ability of the scanning tunneling microscope (STM) to resolve the atomic structure and electronic properties of metal and semiconductor surfaces is now well established. More recently, the performance of the

---

* University of California, San Francisco

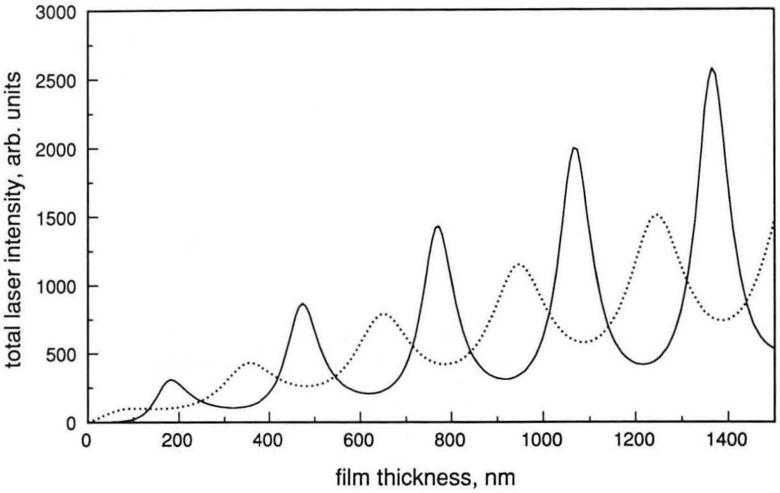


Figure 20
The illumination intensity with an N2 film on Ag as a function of coverage. The solid line is for 2-polarized incident light. For our experimental conditions the Raman intensity follows the illumination intensity. Note that at very low coverages, Raman scattering is prodiced only by p-polarized light and at higher coverages interference effects from s-polarized light dominate. (XBL 899-3322)

STM on various organic materials has been an area of intense interest. The use of STM on native biological materials has been limited by their inherent non-conductivity and relative mobility. Two approaches have been adopted in our laboratories. In one set of experiments, we have performed investigations of membranes coated with thin conducting metal overlayers as well as begun experiments on native uncoated collagen.

For this study, we used Halobacterium halobium purple membrane (PM) prepared by planar membrane monolayer techniques. These techniques produce large, optically flat areas of oriented membrane which can be coated with metals (usually Pt-Ir-C) for examination by both TEM and STM. STM top-view images (Figure 21) show membranes similar in size and shape to those imaged by TEM.

The exact height (or thickness) of the membrane is difficult to quantify with traditional techniques such as TEM. However, the STM is an ideal instrument for height measurements because the tunneling current is exponentially dependent on the tip-to-sample distance. After a careful calibration of the STM and determination of the effects of contamination-mediated surface deformation, we were able to measure the thickness of the PM both before and after a treatment with the proteolytic enzyme, papain. The apparent thickness of enzymatically modified PM increased after papain treatment from 46Å to 54Å on glass substrates and from 46Å to 48Å on mica substrates.

In a different approach, we have also imaged native, uncoated molecules of collagen. Figure 22 shows a top view of an image of a single molecule of collagen taken in air at room temperature. The collagen molecule has a right-handed helical structure which, although it is somewhat variable, gives the molecule an average periodicity of 30Å. This periodicity is clearly resolved in our STM images. We are also able to see regions where the helix is nonuniform, regions where the helix is not present and regions where the collagen molecule appears to be flexible.

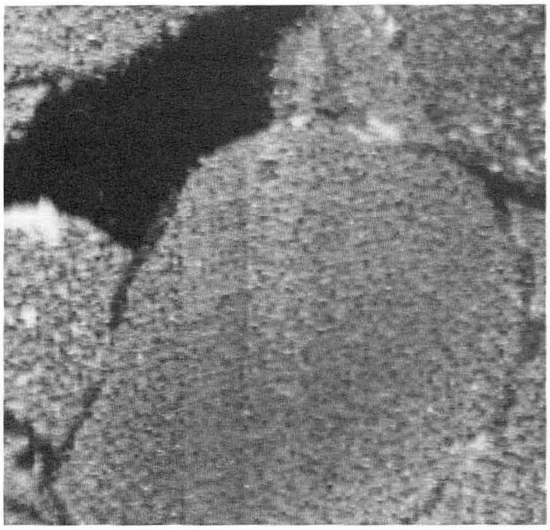


Figure 21
Top view of STM image of Pt-Ir-C coated purple membrane (PM). Large flat pieces of PM are visible as well as crevices between adjacent PM patches and areas without membrane. (XBB 890-10060)

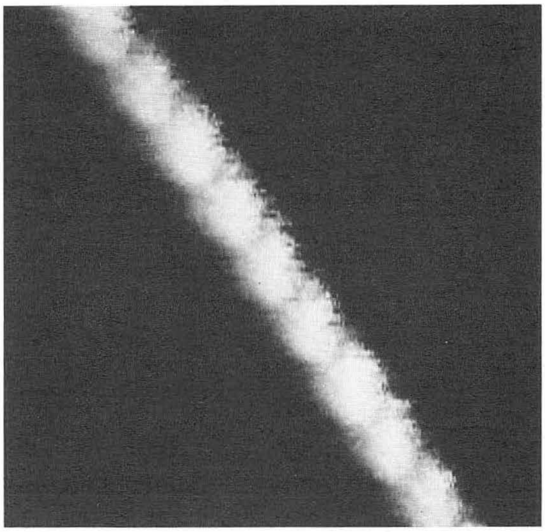


Figure 22
Top view of STM image of native uncoated collagen. The periodic repeat of the helix of the molecule is clearly resolved as well as other details of the molecule's morphology even though mobility and lack of conductivity are significant problems in STM of uncoated biological samples. (XBB 890-10040)

In a further set of experiments, we deposited DNA on graphite, and were able to image several isolated strands such as those shown in Figure 23. The resolution in some cases was such that the major and minor grooves in the DNA spiral could be distinguished. In order to make STM a routine technique for biological applications, however, methods of fixation of the biomolecules to the substrate must be developed to ensure that the non-negligible forces exerted by the tip do not displace the molecules during scanning. The example illustrates how DNA fragments are displaced by the forces exerted by the scanning tip.

INSTRUMENT DEVELOPMENT

Atomic Force Microscopy

J. Clarke, M. Salmeron, W. Kolbe, M. Gustafsson, K.A. Fisher*

The atomic force microscope (AFM) is an instrument similar to the STM, but with the ability to image insulating as well as conducting samples. Like the STM, it generates atomic resolution images by scanning a sharp tip over the sample surface. Instead of sensing a tunneling current, the AFM senses the force between the tip and the sample, by detecting sub-Angstrom deflections of a cantilever spring on which the tip is mounted.

In one system under development in our laboratory, this spring motion is detected by measuring the angular deflection of a laser beam which is reflected off the back side of the spring (Figure 24). For high sensitivity and low noise, the AFM spring should have a low force constant and a high resonance frequency, which implies a low mass. We use microfabrication techniques to manufacture silicon nitride springs with masses below 10^{-11} kg, achieving resonance frequencies of 201kHz at a force constant of 1 N/m.

---

* Biochemistry Department, University of California, San Francisco

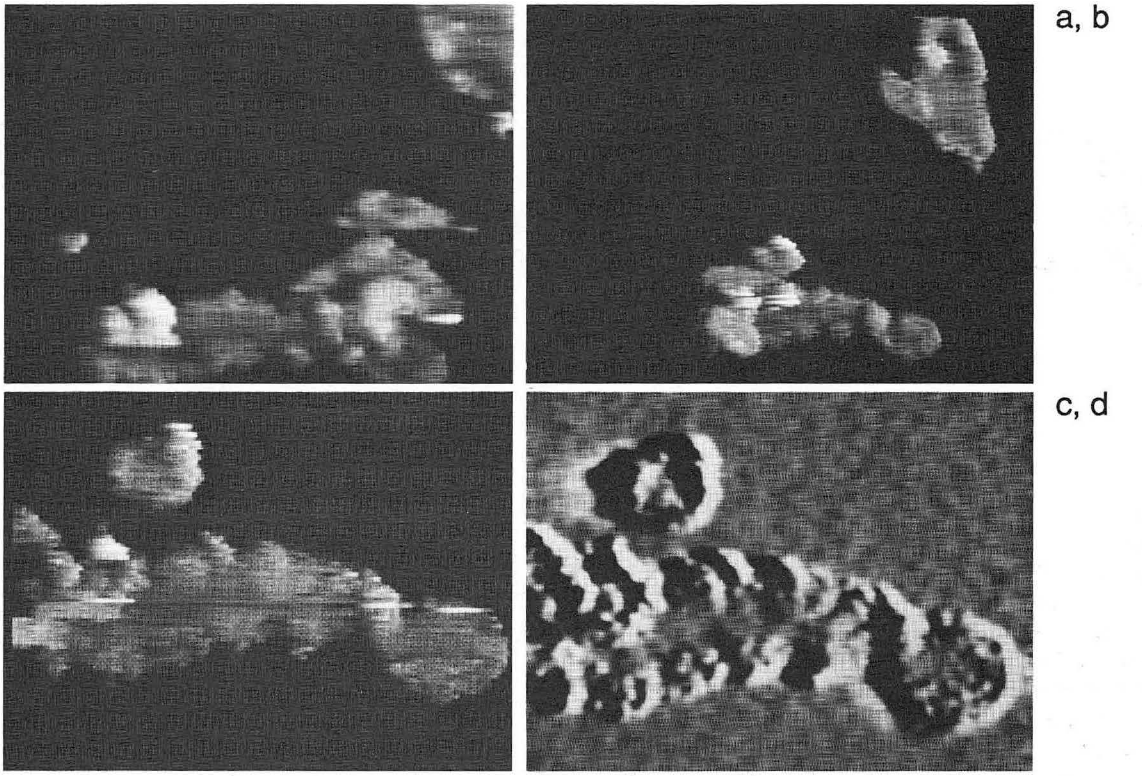


Figure 23
Strands of uncoated DNA deposited on graphite and imaged by the STM. Notice the displacement of material from image to image due to the forces exerted by the tip. These images are 400 x 400 Å (a, c, d) and 600 x 600 Å (b). Fig. 5d shows the processed image from Fig. 5c after smoothing and artificial light source illumination. (BBC 893-1854; BBC 893-1852; BBC 893-1848; XBB 8810-9840)

The sharpness of the tip is of great importance for high resolution AFM. Existing approaches to tip manufacturing involve attaching a fragment of a crushed diamond, or using etching techniques. The diamond, while quite sharp, seriously lowers the resonance frequency of the spring-tip system by its added mass. The etching methods, while adding only

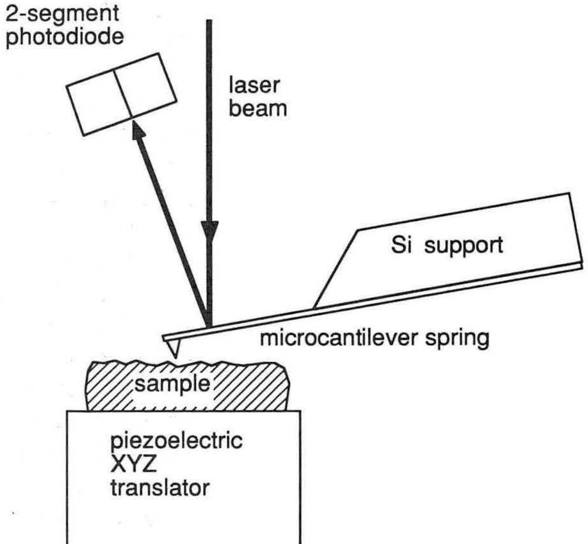


Figure 24
The AFM principle: Short range forces between the sample and a sharp tip deflect a microcantilever spring on which the tip is mounted. This deflects a laser beam which is reflected off the back of the spring. As the sample is scanned, a feedback loop regulates the tip-sample distance to keep the force constant. Thus an image of a surface of constant force is generated. (XBL 8911-4118)

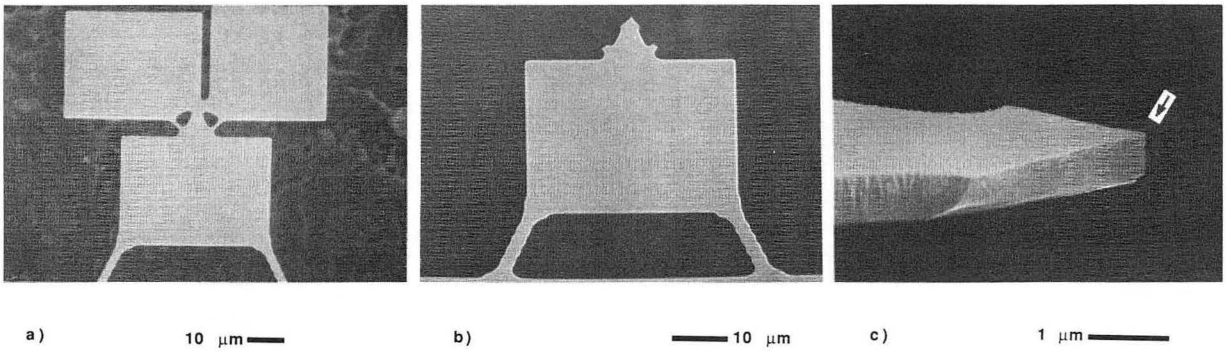


Figure 25
The micro springs are patterned from a 0.8µm thick Si_3N_4 film, supported at the base by a silicon chip. As the last processing step, the two plates shown in (a) are mechanically broken off (b). The sharp corner thus created is used as the AFM tip. Figure (c) is an 80° side view of the tip region. (XBB 8911-9922)

negligible mass, have not yet yielded tips sharper than 300 Å in radius. We have developed a simple method that attempts to combine negligible mass with the sharpness of intersecting fracture planes. The microcantilever springs are designed so that the spring material itself can be fractured in a controlled way (Figure 25 a, b), leaving a corner shaped tip (Figure 25 c). SEM images put an upper limit on the radius of this tip at below 100Å.

Figure 26 is an image of the honeycomb-shaped atomic lattice of the surface of muscovite mica, acquired with this system.

A different AFM system, based on interferometry to measure the deflection of the cantilever spring, is also in its final stages of construction. This instrument will be used to study biological material that cannot be studied with the STM. It will also be used to study mechanical properties of surfaces by measuring the forces between tip and surface in the vertical direction (adhesion) and in the horizontal direction (friction).

DEVELOPMENT OF A COMBINED DIGITAL-LEED/STM INSTRUMENT

R.Q. Hwang, M. Salmeron, G.A. Somorjai

Recently it has been shown in our laboratory that measurements of diffuse LEED intensities can be used to extract structural information of disordered chemisorption systems. Our digital LEED system, with its high sensitivity pulse counting detector, is well suited for these measurements. However, initial guesses of the adsorbate geometry must come from other techniques. Scanning Tunneling Microscopy (STM) would allow us to directly image the adsorbate and hopefully the substrate simultaneously. This would give immediate information of adsorbate sites, and even crude estimates of bond lengths could be made. In addition, by imaging as a function of adsorbate coverage, short range order phenomena such as island formation can be studied and compared with the digital LEED information.

We are building and inserting an STM into the system that now contains the digital LEED apparatus. This will allow STM and digital LEED measurements to be made on the same surfaces. Modifications to the sample manipulator must be made to allow interchange of the sample between the two techniques. In addition, improved cooling capabilities are presently being added to the manipulator that will allow sample temperatures to reach approximately 100K. This will allow studies of molecular systems, such as ice grown on Pt(111), that require low temperatures for adsorption.

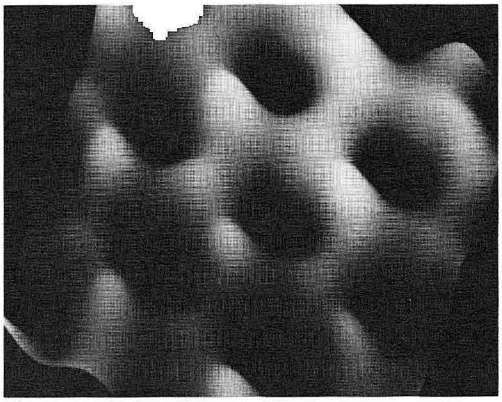


Figure 26
AFM image of the surface of muscovite mica, showing the honeycomb lattice of SiO_4 tetrahedra. The spacing between holes is 5.2Å.
(XBB 8911-9921)

Development of Instrumentation for Studies of Liquid-Phase Catalytic Reactions

M. Quinlan, G.A. Somorjai

The techniques of surface science which have been successful in the elucidation of the mechanisms and adsorbed intermediates in the metal surface catalyzed hydrogenation of gaseous hydrocarbons will be applied to the study of hydrogenation reactions occurring at the liquid-solid interface. The added constraint of measuring meaningful specific catalytic reaction rates in the presence of the diffusional resistances commonly encountered in the liquid phase requires that a novel catalytic reactor geometry be used. Consequently, a rotating disk reactor employing a single crystal metal substrate is being designed and constructed. The impetus for the use of a rotating disk reactor to study liquid phase hydrogenation reactions arises from the formation of a well characterized one-dimensional, equiaccessible diffusion field to complement the well characterized atomic composition and geometry of the single crystal metal substrate. The thickness of the diffusion boundary layer varies inversely with the rotational rate of the disk, allowing the reaction kinetics to be determined under conditions free of mass transfer influences. The hydrogenation of liquid cyclohexane will be the initial reaction to be studied.

STAFF

Program Leader
Gabor Somorjai

Project Leaders
Alex T. Bell—Catalyst Design and Characterization
John Clarke—Instrumentation for Surface Science
Heinz Heinemann—Coal Gasification
Miquel Salmeron—Surface and Interface Compounds

Scientific Staff
Steven Louie
Jeffrey Reimer
Gerd Rosenblatt
Yuen-Ron Shen
Michel Van Hove
Birgitta Whaley
Frank Ogletree
Kirk Veirs

Visiting Scientists
Piotr Badzaig, University of South Africa
Pedro de Andres, CSIC, UAM, Spain
Mordaci Folman, Technion, I.I.T., Haifa, Israel
Konrad Hayek, University of Innsbruck, Austria
M.J. Yacaman, University of Mexico
Mitsuo Kawasaki, Kyoto University, Japan
Kazuhisa Kobayashi, Mitsubishi Paper Mills, Ltd., Japan
Juoko Lahtinen, University of Helsinki, Finland
Francis Luck, Rhone Poulenc, France
Taisei Nakayama, Mitsubishi, Japan
Pedro Pereira, INTEVEP, Venezuela
Pedro Schabes, University of Mexico
Jose Velasquez, INTEVEP, Venezuela
Hongchuan Wang, Fudan University, Shanghai, PRC
Barry Yang, National Central University, Taiwan, ROC

Postdoctoral Fellows
Greg Blackman
Marie-Paule Delplancke
Robert Q. Hwang
Mark Johnson
Vincent Maurice
Philip Rous
Adrian Wander
X.-W. Wang
Xiaoguang Zhang

Graduate Students
Joel Ager, III
Phillip Armstrong
Reha Bafrali
Alex Boffa
Istvan Böszörmenyi
Judith Brown Bourzutschky
Dean Clarke
Sabrina Fu
Denis Gardin
David Ginter
Janet Griffiths
Mats Gustafsson
William Hendricks
David Jentz
Glenn Jernigan
Changmin Kim
Colette Knight
Marc Kollrack
Kamala Krishna
Kenneth Lee
Stephen Lombardo
Peter Macanally
Brian McIntyre
Robert Mortlock
Chris Mullin
Pedro Nascente
James Powers
Michael Quinlan
Richard Superfine
Ruth Ellen Thomson
Gilroy Vandentop
Gerard Vurens
Marjorie Went
Gregory Went
Kevin Williams
Xu-Dong Xiao
David Zeglinski

Technical Support
Wini Heppler
Travis Palomares
Heather Rumsey
Sue Whitfield

Student Assistant
Troy Wilson

Administrative Support
Gloria Osterloh
Brigid Tung

AWARDS

- Gabor Somorjai was awarded the Peter Debye Award of the American Chemical Society; the E.W. Müller Award from the University of Wisconsin; the Alexander von Humboldt Award for U.S. Senior Scientists; and an honorary doctorate degree from the Technical University of Budapest, Hungary.

- Stephen Louie was awarded a Guggenheim Fellowship.

- John Clarke was elected a Visiting Fellow at Clare College, Cambridge, England.

INDUSTRY INTERACTIONS

Industrial Fellows

- David Denley of Shell Development Company joined the Surface and Interface Compounds group in a study of the design, construction, and use of the Scanning Tunneling Microscope and the Atomic Force Microscope

- Clarence D. Chang, Mobil Research and Development Corporation, worked with the Catalyst Design and Characterization Project on the use of MAS-NMR spectroscopy to characterize the composition of aluminosilicate gels used in the synthesis of zeolites.

- Bharat Bhushan of IBM Almaden Research Center is working with the Surface and Interface Compounds group studying plasma coatings and the tribological properties of surfaces.

- Mahn Won Kim of Exxon Research and Engineering worked with the Instrumentation for Surface Science Project on the application of second harmonic generation to the study of surfaces and monolayers.

Advisory Board

Roger Baetzold, Chairman	Eastman Kodak Company
S.K. Alley	Union Oil of California
Michel Boudart*	Stanford University
L. Louis Hegedus†	W.R. Grace & Co.
Jerry Meyer	Chevron Research Company
Robert Nowak†	Dow Chemical
Jule Rabo*	Union Carbide Corporation
Kathleen Taylor	General Motors Technical Center
J.J. Wise	Mobil Research and Development Corporation

---

* Retired in 1989.
† New member in 1989.

Gifts

- Gifts from Chevron Research Corporation and IBM were used to support the Surface Science and Catalysis Seminars.
- Gifts from E.I. DuPont de Nemours, Inc., provided support for research in nonlinear optics and microporous crystalline catalysts.
- A gift from Exxon was used to support studies of molecular diffusion in the 2–D and 3–D bioptical second harmonic generation (SHG).
- A gift from Mobil Research and Development Corporation will be used for travel to scientific meetings.
- A gift from Rhône Poulenc was used to perform experimental surface science studies of the catalytic oxidation of light alkanes.
- A gift from Shell Oil Development was used to support research on Atomic Force Microscope development and applications to zeolites.

Contracts

- 3M provided support for research on the development of the techniques of second harmonic generation and sum-frequency generation to study monolayers on surfaces.
- IBM Corporation provided support for research on the properties of polymer coatings on surfaces.
- Dow Chemical Corporation provided support for studies of oxide surface structure using STM and AFM.
- E.I. DuPont de Nemours, Inc., provided support for research in electro-optics.
- Grants from Harshaw/Filtrol, and W.R. Grace were used to support research on zeolite synthesis.

Collaborations

- In collaboration with Mobil Research and Development Company, it was discovered that TPA^+ cations form silicate cages containing 22 Si atoms during the initial stages of ZSM-5 synthesis.
- In collaboration with Kodak Research Laboratories, it was established that the BOC-MP approach provides a realistic description of the energetics of formic acid decomposition on Ag(111), Ni(111) and Fe/W(110) surfaces.
- Francis Luck of Rhone Poulenc worked on the surface science of the catalytic oxidation of light alkanes.

Technology Transfer

- Y. Ron Shen was awarded U.S. Patent No. 4,829,505 for Multiple Layer Optical Memory System using Second-Harmonic Generation Readout.

Surface Science and Catalysis Seminars

(Supported in part by gifts from Chevron Research Corporation and IBM)

F.T. Wagner - GM Research, Warren, MI, "Modeling the Electrochemical Double Layer in UHV"

U. Starke - University of Erlangen-Germany, "Reliability of Diffuse LEED Intensity Measurements"

B.E. Bent - Dept. of Chem., Columbia Univ., NY, "Surface Reactions in the Chemical Vapor Deposition of Aluminum Using Triisobutylaluminum"

M.P. Soriaga - Dept. of Chem.,Texas A&M,TX, "Surface Chemical Studies of Noble-Metal Electrocatalysts"

R.J. Koestner - Texas Instruments, Dallas, TX, "Molecular Beam Epitaxial Growth of HgCdTe Semiconductor Films"

R. Szostak - Georgia Tech Research Institute, Atlanta, GA, "Non-aluminosilicate Molecular Sieves: New Compositions, Novel Applications"

P.S. Bagus - IBM-Almaden, CA, "Core Level Binding Energy Shifts of Surface Atoms: A Theoretical Analysis"

F. Zaera - UC-Riverside, CA, "Selectivity Between C-H Bond Breaking and Hydrogen Migration: C_2 Moieties on Pt (111) Surfaces"

I. Horvath - Exxon Research Corporation-Annandale, NJ, "Mechanistic Studies of Hydroformylation Under Pressure With NMR and IR"

H. Ibach - Jülich, Germany, "Surface Phonon Dispersion as a Measure of Surface Stress with Special Applications to Epitaxial Metal Overlayers"

M. Halmann - Weizmann Institute, Israel, "Photosensitized Oxidation of Bromide Ion to Bromine in Aqueous Solution"

Y. Murata - The Institute for Solid State Physics, Tokyo, Japan, "Dynamical Behavior of Hydrogen Adsorbed on W(110) Studied by Resonance Nuclear Reaction of $^{1}H(^{15}N,\alpha\Gamma)^{12}C$.

S.M. Csicsery - retired from Chevron Research Corporation, "New Developments in Shape Selective Catalysts in Zeolites"

J. Fripiat - University of Wisconsin, "Strange Coordination of Aluminum in Alumina and Silica-Alumina"

J.G. McCarty - SRI International, Menlo Park, CA, "Interaction of Homogeneous and Heterogeneous Reactions During Methane Dimerization"

J.B. Pendry - Imperial College, London, "Surface Structure and Catalysis"

H. Holleck - Kernforschungszentrum, Karlsruhe, Germany, "Advanced Concepts in PVD Hard Coatings"

C.-M. Chan - Raychem Corp., Menlo Park, CA, "Surface Oxidation of Nickel-Titanium Alloy"

P.W. Davies - Intel Corp., Santa Clara, CA, "Applications of Surface Science in Microelectronics"

T.N. Taylor - Los Alamos National Laboratory, "The Ag/Cu(110) Interface: Surface Properties and Their Correlation with Second Harmonic Generation"

Prof. Howard W. Pickering - Penn State, "A New Field Ion-Scanning Tunneling Microscope and Its Application For the Study of Semiconductor and Metal Surfaces"

S. Han - Mobil Research and Development Corporation, Princeton, NJ, "Direct Methane Conversion - Fame and Misfortune"

J. Blakely - Cornell Univ., Ithaca, "Composition and Ionic Transport at Sapphire Surfaces"

S. Topham - ICI, Bellingham, England, "Recent Developments in Syn-Gas Technology"

A. Kaldor - Exxon Research & Engineering Co., "Dissociative Chemisorption on Noble Metal Gas Phase Clusters: The Connection to Supported Cluster Materials"

P. Blau - Oak Ridge National Laboratory, "Tribology Research on Nickel Ni_3Al Alloys"

G. Pirug - Jülich, Germany, "The Coadsorption of CO and H_2O with Alkali Metals on Transition Metal Surfaces"

J.P. Biberian - Univ. of Marseille, France, "Field Emission Microtips: A New Technology in Microelectronics"

A. Vehanen - Helsinki Univ. of Technology, Finland, "Probing Solid Surfaces with Monoenergetic Positron Beams"

B. Tonner - University of Wisconsin, Milwaukee, "Photoelectron Microscopy of Reactions at Surfaces: Current Status and Future Prospects"

M. Wuttig - KFA, Jülich, Germany, "Structure, Dynamics, and Oxidation Behavior of Ni Alloys"

K. Trabelsi - French Institute of Petroleum, "Solid-Liquid Interactions In Oil Reservoir Rocks"

M. Folman - Technion I.I.T.-Haifa, Israel, "Some Aspects of I.R. Spectroscopy of Physically Adsorbed Molecules"

N. Roesch - Technical University, Munich, "CO+K Coadsorption on Transition Metal Surfaces: Insights from Computational Chemistry"

X.D. Zhu - UC Berkeley/UC Davis, "Surface Diffusion of CO on Ni(111)"

W. Ellis - Los Alamos National Laboratory, "Surface Stabilities of Fluoritic Oxides"

X.W. Wang - Center for Advanced Materials, Lawrence Berkeley Laboratory, "First-Principles Calculations of Sulfur on Mo(100)"

A. Gonis - Lawrence Livermore National Laboratory, "A New Method for the Determination of Electronic Structure for Surfaces and Interfaces"

O. Krause - Neste Co., Finland, "Components for the Unleaded Gasoline; Production and Properties"

A. Baiker - Federal Institute of Technology-Zurich, "New Perspectives in the Design of Solid Catalysts"

R. Kaplan - Naval Research Laboratory, "SiC Surface Structure and Composition and the Relation to Oxidation and Metallization"

S.M. Davis - Exxon, Baton Rouge, "Surface Science of Iron-Based Denitrogenation Catalysts"

R. Stulen - Sandia National Laboratory, Livermore, "Interaction of Hydrogen with Diamond(111) and (100) Surfaces"

N. Kruse - ETH-Zurich, "Kinetics of Surface Reactions on the Atomic Scale"

J.J. Barton - IBM-Yorktown Heights, "Photoelectron Holography"

C.S. Fadley - Univ. of Hawaii, "Recent Surface Structure Studies Using Photoelectron Diffraction"

M. Ishikawa - Hokkaido Univ., Sapporo, Japan, "Molecular Approaches in Heterogeneous Catalysis - Surface-Bound Metal Clusters, Their Structural Characterization and Catalysis"

K. Baberschke - Free University, Berlin, "Surface EXAFS: Local Bond Geometry, Debye-Waller Factor and Anharmonic Pair Potential"

S. Bernasek - Princeton University, "Small-Molecule Chemistry on Fe Surfaces"

L. Atanasoska - Univ. of Belgrade, Yugoslavia, "XPS Study of Chemical Bonding at Polyimide Interfaces with Metal and Semiconductor Overlayers"

P. Badziag - University of South Africa, "Atomic Cluster Calculations of Semiconductor Surface Structure"

BIBLIOGRAPHY

Catalyst Design, Characterization, and Applications Project

Refereed Journal Articles

Bell, A.T., "The Solution Chemistry of Zeolite Precursors," *Catal. Rev. - Sci. Eng.*, vol. 31, p. 97, 1989.

Bell, A.T., J.S. Papanu, D.W. Hess, and D.S. Soane, "*In Situ* Ellipsometry to Monitor Swelling and Dissolution of Thin Polymer Films," *J. Electrochem. Soc.*, vol. 136, p. 1195, 1989.

Blanco, J., P. Avila, C. Barthelemy, A. Bahamonde, J.A. Odriozola, J.F. Garcia de la Banda, and H. Heinemann, "Influence of Phosphorus in Vanadium-Containing Catalysts for NO_x Removal," *J. Applied Cat.*, vol. 55, p. 151, 1989.

Bussell, M.E. and G.A. Somorjai, "Thiophene Hydrodesulfurization over Rhenium Surfaces: The Effects of Structure and Adsorbates (C and S)," *J. Phys. Chem.*, vol. 93, p. 2009, 1989.

Bussell, M.E. and G.A. Somorjai, "Thiophene Hydrodesulfurization over Transition Metal Foils: Comparison with Metal Sulfides," *Catal. Lett.*, vol. 3, p. 1, 1989.

Ginter, D.M., A.T. Bell, and C.J. Radke, "Magic-Angle-Spinning NMR Spectroscopy of Gels," *J. Magnetic Resonance*, vol. 81, p. 217, 1989.

Godbey, D.J., F. Garin, and G.A. Somorjai, "The Hydrogenolysis of Ethane over Re-Pt(111) and Pt-Re(0001) Bimetallic Crystal Surfaces," *J. Catal.*, vol. 117, p. 144, 1989.

Haddix, G.W., A.T. Bell, and J.A. Reimer, "NMR Studies of Model Hydrodenitrogenation Catalysis: Acetonitrile Hydrogenation on γ-Mo$_2$N," *J. Phys. Chem.*, vol. 93, p. 5859, 1989.

Lombardo, S.J. and A.T. Bell, "Monte Carlo Simulation of Temperature-Programmed Desorption of Coadsorbed Species," *Surface Science*, vol. 224, p. 451, 1990.

McCormick, A.V., A.T. Bell, and C.J. Radke, "Evidence from Alkali-Metal NMR Spectroscopy for Ion Pairing in Alkaline Silicate Solutions," *J. Phys. Chem.*, vol. 93, p. 1733, 1989.

McCormick, A.V., A.T. Bell, and C.J. Radke, "Influence of Alkali-Metal Cations on Silicon Exchange and Silicon-29 Spin Relaxation in Alkaline Silicate Solutions," *J. Phys. Chem.*, vol. 93, p. 1737, 1989.

McCormick, A.V., A.T. Bell, and C.J. Radke, "Multinuclear NMR Investigation of the Formation of Aluminosilicate Anions," *J. Phys. Chem.*, vol. 93, p. 1741, 1989.

Morrison Jr., P.W. and J.A. Reimer, "Silane Pyrolysis in a Piston Reactor," *AIChE Journal*, vol. 34, p. 783, 1989.

Odriozola, J.A., H. Heinemann, J.F. Garcia de la Banda, P. Pereira, and G.A. Somorjai, "AES and TDS Study of the Adsorption of NH$_3$ and NO on V$_2$O$_5$ and TiO$_2$ Surfaces: Mechanistic Implications," *J. Catal.*, vol. 119, p. 71, 1989.

Oyama, S.T., G.T. Went, K.B. Lewis, A.T. Bell, and G.A. Somorjai, "Oxygen Chemisorption and Laser Raman Spectroscopy of Unsupported and Silica-Supported Vanadium Oxide Catalysts," *J. Phys. Chem.*, vol. 93, p. 6786, 1989.

Prins, R. and V.H.J. de Beer, "Structure and Function of the Catalyst and the Promoter in Co-Mo Hydrodesulfurization Catalysis, Proceedings in Analytical Chemistry in Honor of Professor Kovats, Lucerne Switzerland," *Cat Review Sci. Eng.*, vol. 31, p. 41, 1989.

Shustorovich, E. and A.T. Bell, "An Analysis of Formic Acid Decomposition on Metal Surfaces by the Bond-Order-Conservation-Morse-Potential Approach," *Surface Science*, vol. 222, p. 371, 1989. (E. Shustorovich, Corporate Research Laboratories, Eastman Kodak Company.)

Somorjai, G.A. and D.R. Strongin, "Ammonia-Pretreatment-Induced Restructuring of Iron Single-Crystal Surfaces: Its Effect on Ammonia Synthesis and on Coadsorbed Aluminum Oxide and Potassium," *J. Catal.*, vol. 118, p. 99, 1989.

Somorjai, G.A. and M. Van Hove, "Adsorbate-Induced Restructuring of Surfaces," *Progress in Surface Science*, vol. 30, p. 201, 1989.

Soria, J., J.C. Conesa, M. Lopez Granados, R. Mariscal, J.L.G. Fierro, J.F. Garcia de la Banda, and H. Heinemann, "Phase Transformations of Vanadia-Titania Catalysts Induced by Phosphoric Acid Additive," *J. Catal.*, vol. 120, p. 457, 1989.

Strongin, D.R. and G.A. Somorjai, "Ammonia Pretreatment Induced Restructuring of Iron Single Crystal Surfaces: Its Effects on Ammonia Synthesis and on Coadsorbed Aluminium Oxide and Potassium," *J. Catal.*, vol. 118, p. 99, 1989.

Wang, X.W. and S.G. Louie, "First Principles Studies of S/Mo(001) Surfaces," *Bull. Am. Phys. Soc*, vol. 34, p. 863, 1989.

Wang, X.W., S.G. Louie, and M.L. Cohen, "Hydrogen Interactions in PdH$_n$ ($1 \leq n \leq 4$)," *Phys. Rev. B*, vol. 40, p. 5822, 1989.

Yokomizo, G.H. and A.T. Bell, "Isotopic Tracer and NMR Studies of Carbonaceous Species Present during CO Hydrogenation over Ru/TiO$_2$," *J. Catal.*, vol. 119, p. 467, 1989.

Yokomizo, G.H., C. Louis, and A.T. Bell, "An Infrared Study of CO Adsorption on Reduced and Oxidized Ru/SiO$_2$," *J. Catal.*, vol. 120, p. 1, 1989.

Yokomizo, G.H., C. Louis, and A.T. Bell, "Thermal Desorption and Disproportionation of Co Adsorbed on Ru/SiO$_2$," *J. Catal.*, vol. 120, p. 15, 1989.

Zhang, S.B., D. Tomanek, M.L. Cohen, S.G. Louie, and M.S. Hybertsen, "Evaluation of Quasiparticle Energies for Semiconductors without Inversion Symmetry," *Phys. Rev. B*, vol. 40, p. 3162, 1989.

Refereed Conference Proceedings

Bell, A.T., "Applications of NMR Spectroscopy to the Study of Zeolite Synthesis," in *Proc. ACS Symposium Series 398: Zeolite Synthesis*, ed. M.L. Occelli, H.E. Robson, p. 66, 1989.

Heinemann, H., P. Pereira, J. Carrazza, and G.A. Somorjai, "Catalytic Gasification of Graphite and Chars," *American Chemical Society Division of Fuel Chemistry*, vol. 34, p. 121.

Louie, S.G., "Variational Quantum Monte Carlo Calculations of Materials Properties," *Atomic Scale Calculations in Materials Science, Mat. Res. Soc. Symp. Proc.*, vol. 141, p. 3, 1989.

Other Publications

Chmelka, B.F., R.R. Rosin, G.T. Went, A.T. Bell, C.J. Radke, and E.E. Petersen, "The Chemistry of Pt-NaY Zeolite Preparation," in *Zeolites: Facts, Figures, Future*, ed. P.A. Jacobs, and R.A. van Santen, p. 955, Elsevier, 1989.

Garfunkel, E.L. and G.A. Somorjai, "Alkali Metals as Structure and Bonding Modifiers of Transition Metal Catalysts," in *Alkali Adsorption on Metals and Semiconductors*, ed. H.P. Bonzel, A.M. Bradshaw, G. Ertl, p. 319, Elsevier Science Publishers, 1989. (In press.)

Ginter, D.M., C.J. Radke, and A.T. Bell, "Applications of MAS-NMR Spectroscopy to the Study of Faujasite Synthesis," in *Zeolites: Facts, Figures, Future*, ed. P.A. Jacobs, and R.A. van Santen, p. 161, Elsevier Science Publishers, 1989.

LBL Reports (including journal articles submitted or in press)

Bustillo, K.C., M.A. Petrich, and J.A. Reimer, "Microstructure of Amorphous Hydrogenated Carbon using Solid State Nuclear Magnetic Resonance Spectroscopy," *Chemistry of Materials.* (Submitted.)

Fish, R.H., J.N. Michaels, R.S. Moore, and H. Heinemann, "Gas Phase Hydrodenitrogenation Reactions of Polynuclear Heteroaromatic Nitrogen Compounds and Selected Intermediates over 50 percent-Nickel Oxide/Aluminate Supported on Silica-Alumina," *J. Catal.* (In press.)

Fish, R.H., J.N. Michaels, R.S. Moore, and H. Heinemann, LBL 28186, "Hydrodenitrogenation Chemistry 2: Gas Phase HDN Reacions of Polynuclear Heteroaromatic Nitrogen Compounds and Selected Intermediates over 500%-Nickel Oxide/Aluminate Supported on Silica-Alumina," *J. Cat.* (In press.)

Heinemann, H. and G.A. Somorjai, LBL-26891, LBL-27330, "Fundamental Studies of Catalytic Gasification," *Quarterly Reports: January 1 - March 31, 1989; April 1 - June 30, 1989.*

Heinemann, H. and G.A. Somorjai, "Fundamental Studies of Catalytic Gasification," *Annual Report: October 1, 1988 - September 30, 1989.*

Heinemann, H. and G.A. Somorjai, "Fundamental Studies of Catalytic Gasification," *Annual Report: October 1, 1989 - December 31, 1989.*

Heinemann, H., G.A. Somorjai, and J. Garcia de la Banda, LBL-26850, *Improved Industrial Catalysts: Part 1. Catalysts for NO and NO_x Removal - Final Report.*

Pereira, P., R. Csencsits, G. Somorjai, and H. Heinemann, LBL 27655, "Steam Gasification of Graphite and Chars at Temperatures $<$ 1000 K Potassium-Calcium-Oxide Catalysts," *J. Catal.* (In press.)

Somorjai, G.A., LBL-27396, "Modern Concepts in Surface Science and Heterogeneous Catalysis," *J. Phys. Chem.* (Submitted.)

Somorjai, G.A., "The Production of High Octane Gasoline and Hydrodesulfurization by Transition Metal Catalyst," *Proc. Catalysts in Petroleum Refining Conference, Kuwait.* (In press.)

Somorjai, G.A., "The Surface Science of Catalytic Hydrocarbon Conversion over Platinum," *Proc. Kendall Award Lecture.* (In press.)

Went, G.T., S.T. Oyama, and A.T. Bell, LBL 27687, "Laser Raman Spectroscopy Studies of Supported Vanadium Oxide Catalysts," *J. Phys. Chem.* (In press.)

Whaley, K.B., "Boson Enhancement of Finite Temperature Coherent Dynamics for Deuterium in Metals," *Phys. Rev. B.* (Submitted.)

Invited Talks

Bell, A.T., *Applications of NMR Spectroscopy to the Study of Zeolite Synthesis*, Union Carbide Corporation, South Charleston, W. VA, 1989.

Bell, A.T., *The Genesis and Structural Characterization of Dispersed Metal Oxides*, ACS Meeting, Dallas, TX, April 1989.

Bell, A.T., *NMR Studies of Model HDN Catalysts*, ACS Meeting, Dallas, TX, April 1989.

Bell, A.T., *Synthesis of Alcohols over Cu-Containing Catalysts*, California Catalysis Society Meeting, Stanford, CA, April 1989.

Bell, A.T., *Adsorption and Catalysis on Molybdenum Carbides and Nitrides*, Frontiers in Chemical Research Series, Department of Chemistry, Texas A & M University, College Station, TX, August 1989.

Bell, A.T., *Catalysis at Metal-Metal Oxide Boundaries*, Frontiers in Chemical Research Series, Department of Chemistry, Texas A & M University, College Station, TX, August, 1989.

Bell, A.T., *Applications of MAS-NMR Spectroscopy to the Study of Faujasite Synthesis*, 8th International Zeolite Conference, Amsterdam, the Netherlands, July 1989.

Bell, A.T., *Applications of NMR Spectroscopy to the Study of Zeolite Synthesis*, University of Paris, Department of Chemistry, Paris, France, July 1989.

Bell, A.T., *Isotropic Tracer Studies of CO Hydrogeneration over* Ru/TiO_2, 4th Japan-China-USA Symposium on Heterogeneous Catalysis, Sapporo, Japan, July 1989.

Bell, A.T., *Prediction of Sorption and Diffusion in Zeolites*, UOP, Tarrytown, NY, March 1989.

Bell, A.T., *Prediction of Sorption and Diffusion in Silicalite*, North American Catalysis Society Meeting, Dearborn, MI, May 1989.

Bell, A.T., *The Relationship of Catalyst Science to Catalyst Development*, Korea/USA Catalysis Workshop, Tesquesquitengo, Mexico, May 1989.

Bell, A.T., *Sythesis and Characterization of Dispersed Metal Oxides*, Dearborn, MI, May 1989.

Louie, S.G., *Quantum Monte Carlo Simulations and Electron Correlations in Solids*, General Meeting of the Topical Group on Computational Physics, Boston, MA. (Bull. APS, Vol. 34, p. 1435, 1989.)

Louie, S.G., *Supercomputing and Materials Research*, DOE Computational Materials Science Meeting, Chicago, IL, April 1989.

Louie, S.G., *Recent Progress in Predicting Materials Properties*, Solid State Seminar, LURE, University of Paris, Orsay, France, January 1989.

Louie, S.G., *Variational Quantum Monte Carlo Calculation of Materials Properties*, International Workshop on Computational Condensed Matter Physics: Total Energy Force Methods, Trieste, Italy, January 1989.

Louie, S.G., *Quasiparticle Excitations at Semiconductor Surfaces*, March Meeting APS, St. Louis, MO, March 1989. (Bull. APS, Vol. 34, p 814, 1989.)

Louie, S.G., *Electronic Excitations in Solids*, Seminar Series on Electronic Materials: A New Era in Material Science, Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN, May 1989.

Reimer, J.A., *On the Application of Solid-State NMR to the Study of Polymers*, Annual Meeting of the American Institute of Chemical Engineers, November 1989.

Somorjai, G.A., *The Structure and Bonding of Organic Monolayers on Metal Surfaces*, Presented at the Universite Catholique de Louvain, Belgium, January 1989; Burgenstock Conference, Switzerland, May 1989; University of Innsbruck, Austria, May 1989.

Somorjai, G.A., *Surface Science Studies of Solid-Liquid and Solid-Solid Interfaces*, Presented at the KFA Surface and Vacuum Physics Institute, Julich, Germany, January 1989; Institute de Recherches sur la Catalyse Villeurbanne, France, Febrary 1989; University of Copenhagen, Denmark, March 1989; University of Clausthal, Germany, July 1989; Ecole National Superieure de Chimie, Paris, France, July 1989.

Somorjai, G.A., *The Concepts of Modern Surface Chemistry: A Historical Perspective*, University of Illinois, Urbana, IL, April 1989.

Somorjai, G.A., *Molecular Concepts of Surface Chemistry and Catalysis*, Finnish Chemical Society Meeting, Helsinki, Finland, April 1989.

Somorjai, G.A., *Chemical and Mechanical Properties of Surfaces*, University of Michigan, Ann Arbor, MI, August 1989.

Somorjai, G.A., *Case Histories in the Surface Science of Heterogeneous Catalysis, Hydrodesulfurization, Ammonia Synthesis and Ethylene Hydorgenation*, Leiden University, The Netherlands, January 1989.

Somorjai, G.A., *The Role of Steps as Active Sites for Adsorption and Catalysis*, Conference on Atomic Steps at Surfaces and Interfaces, Ringberg Schloss, Germany, January 1989.

Somorjai, G.A., *The Oxide-Metal Interface in Catalysis: A Modern View of the Old Puzzle*, Second European Conference on Catalysis, Berlin, Germany, July 1989.

Somorjai, G.A., *Structure of Surfaces and Catalysis*, Ecole Polytechnique, Paris, France, July 1989.

Somorjai, G.A., *Alkalai Metals as Bonding and Structure Modifiers in Adsorption and Catalysis*, Conference on Alkali Metal Roles in Surface Science, Bad Hoffef, Germany, March 1989.

Somorjai, G.A., *Structure Sensitive and Insensitive Catalytic Reactions: Building the Bridge to Homogeneous Catalysis*, International Conference on Homogeneous and Heterogeneous Catalysis, Pisa, Italy, September 1989.

Whaley, K.B., *Dynamics of Deuterium in Metals: Is Cold Nuclear Fusion Possible?*, Presented at IBM Research Center, Almaden, CA, May 1989; and Raychem Corporation, Menlo Park, CA, August 1989.

Whaley, K.B., *Cold Nuclear Fusion: A Possible Theoretical Explanation*, Spring National Meeting of the ACS, Dallas, TX, April 1989.

Whaley, K.B., *Boson Screening of Deuterium in Metals*, Spring National Meeting of the APS, Baltimore, MD, May 1989.

Contributed Talks

Fu, S.S. and G.A. Somorjai, *The Effect of Oxygen on CO Desorption and CO_2 Decomposition over Copper Polycrystalline Foil and Copper Oxide*, California Catalysis Society, Stanford, CA, April 1989.

Heinemann, H., G.A. Somorjai, P. Pereira, and J. Carrazza, *Catalytic Gasification of Graphite and Chars*, 197th ACS National Meeting, Dallas, Texas, April 1989. (American Chemical Society Division of Fuel Chemistry, vol. 34, p. 121, 1989.)

Knight, C., M. Bussell, and G.A. Somorjai, *Hydrodesulfurization over Molybdenum Single Crystal Catalysts: A Surface Science Investigation of the Effect of Sulfur, Carbon, and Cobalt*, 11th North American Meeting of the Catalysis Society, Dearborn, MI, May 1989.

Reimer, J.A., *NMR Studies of Solids, Thin Films, and Surfaces*, Colloquium, Department of Chemical Engineering, Purdue University, February 1989.

Reimer, J.A., *NMR Studies of the Structure of Plasma-Deposited Silicon-Carbide, Silicon-Nitride, and Diamond-Like Carbon*, IBM Almaden Research Center, San Jose, CA, February 1989.

Reimer, J.A., *Nuclear Magnetic Resonance in Chemical Engineering Research: The History, The Promise, and The Practice*, Colloquium, Department of Chemical Engineering, University of Wisconsin, March 1989.

Reimer, J.A., *NMR Studies of Model Hydrodenitrogenation Catalysis*, X National Meeting on Catalysis, INTEVEP, Caracas, Venezuela, May 1989.

Reimer, J.A., *NMR Studies of Molecules Reacting on Catalytic Surfaces*, Colloquium, Department of Chemical Engineering, MIT, November 1989.

Reimer, J.A., Colloquium, Department of Chemical Engineering, University of California, Santa Barbara, September 1989.

Surface and Interface Compounds Project

Refereed Journal Articles

Beebe, Jr., T.P., T.E. Wilson, D.F. Ogletree, J.E. Katz, R. Balhorn, W. Siekhaus, and M. Salmeron, "Direct Observation of Native DNA Structures with the Scanning Tunneling Microscope," *Science*, vol. 243, p. 370, 1989.

Cronacher, H., E. Lang, K. Heinz, K. Muller, M.-L. Xu, and M.A. Van Hove, "Forward Focusing of Auger and Kikuchi Electrons for Surface Structure Determination: Ni(100) and Oxidized Mg (0001)," *Surf. Sci.*, vol. 209, p. 387, 1989.

Felter, T.E., E.C. Sowa, and M.A. Van Hove, "The Location of Hydrogen Adsorbed on Palladium (111) Studied by Low-Energy Electron Diffraction," *Phys. Rev. B*, vol. 40, p. 891, 1989.

Kao, C.-T., G.S. Blackman, M.A. Van Hove, and G.A. Somorjai, "The Surface Structure and Chemical Reactivity of Rh(111)-(2x2)-3NO by HREELS and Dynamical LEED Analysis," *Surface Science*, vol. 224, p. 77, 1989.

Kelly, D.G., R.F. Lin, M.A. Van Hove, and G.A. Somorjai, "Disordered Asymmetrical Surface Structures of Clean Mo(100)-"(1x1)" and of "c(2x2)" Sulfur on Mo(100) from Dynamical LEED Analyses," *Surface Science*, vol. 224, p. 97, 1989.

Marchon, B., M. Salmeron, and W. Siekhaus, "Observation of Graphitic and Amorphous Structures on the Surface of Hard Carbon Films by Scanning Tunneling Microscopy," *Phys. Rev. B*, vol. 39, p. 12907, 1989.

Rous, P.J., M.A. Van Hove, and G.A. Somorjai, "Directed Search Methods for Surface Structure Determination by LEED," *Bull. Am. Phys. Soc*, vol. 34, p. 1555, 1989.

Salmeron, M., B. Marchon, D.F. Ogletree, M.E. Bussell, G.A. Somorjai, and W. Siekhaus, "STM Study of the Structure of the Sulfur (1x2) Overlayer on Molybdenum (001) in Air: Ordered Domains, Phase Boundaries and Defects," *J. of Microscopy*, vol. 152, p. 427, 1989.

Somorjai, G.A., S.W. Wang, D.F. Ogletree, and M.A. Van Hove, "The State of Surface Structural Chemistry: Theory and Experiment," *Adv. in Quantum Chem*, vol. 20, p. 147. (In press.)

Xu, M.-L., J.J. Barton, and M.A. Van Hove, "Electron Scattering by Atomic Chains: Multiple-Scattering Effects," *Phys. Rev. B*, vol. 39, p. 8275, 1989. (J.J. Barton, IBM.)

Xu, M.-L. and M.A. Van Hove, "Surface Structure Determination with Forward Focused Electrons," *Surf. Sci.*, vol. 207, p. 215, 1989.

Refereed Conference Proceedings

Salmeron, M., B. Marchon, and W. Siekhaus, "Surface Modifications by STM on a Passivated Re(0001) Surface," *Proc. 15th Int. Conf. on Met. Coatings*, vol. 36, p. 319, 1989.

Other Publications

Salmeron, M., "Espectroscopia de Superficies: Utilizacion de tecnicas modernas para la caracterizacion de su estructura y propiedads quimicas," in *Nuevas Tendencias en Quimica Teorica: Estructura, Interacciones y Reactividad*, ed. Servicio de publicaciones del Consejo Superior de Investigaciones Cientificas, Madrid, Spain, vol. 3, 1989.

Williams, K.J., M.E. Levin, M. Salmeron, A.T. Bell, and G.A. Somorjai, "Surface Characterization of Metal Oxide Overlayers," in *Characterization and Catalyst Development*, p. 183, American Chemical Society, 1989.

LBL Reports (including journal articles submitted or in press)

Kawasaki, M., G.J. Vandentop, M. Salmeron, and G.A. Somorjai, LBL 27757, "Analysis of the Interface of Hydrogenated Amorphous Carbon Films on Silicon by Angle-Resolved X-ray Photoelectron Spectroscopy," *Surface Science*. (Submitted.)

Rous, P.J., M.A. Van Hove, and G.A. Somorjai, "Directed Search Methods for Surface Structure Determination by LEED," *Surface Science*. (Submitted.)

Salmeron, M., "Scanning Tunneling Microscopy and Potential Aplication of STM in Catalyst Characterization," in *Emerging Methods of Catalyst Characterization*, ed. Catalytica, 1989. (In press.)

Salmeron, M., T. Beebe, J. Odriozola, T. Wilson, D.F. Ogletree, W. Siekhaus, and G.A. Somorjai, LBL-27566, "Imaging of Biomolecules with the Scanning Tunneling Microscope: Problems and Prospects," *J. of Vac. Sci.* (In press.)

Salmeron, M. and D.F. Ogletree, "The Structure of Solid Surfaces by Scanning Tunneling Microscopy," *Progress in Solid-State Chemistry.* (Submitted.)

Salmeron, M., D.F. Ogletree, C. Ocal, B. Marchon, G.A. Somorjai, T. Beebe, and W. Siekhaus, LBL 27563, "STM Study of the Structure of Sulfur $(2\sqrt{3} \times 2\sqrt{3})\ R30^{\circ}$ *Overlayer on Rhenium (0001)," J. Vac. Sci. & Tech., Proc. 4th Int. Conf. on STM.* (In press.)

Salmeron, M., G.J. Vandentop, M. Kawasaki, R.M. Nix, I.G. Brown, and G.A. Somorjai, LBL 27526, "The Formation of Hydrogenated Amorphous Carbon Films of Controlled Hardness from a Methane Plasma," *Phys. Rev. B.* (Submitted.)

Salmeron, M., G. Vurens, and G.A. Somorjai, "The Preparation of Thin Ordered Transition Metal Oxide Films on Metal Single Crystals for Surface Science Studies," *Prog. in Surf. Sci.* (Submitted.)

Van Hove, M.A., LBL 27158, "A Glimpse of Solid Surfaces," in *L. Van Hove Festschrift*, ed. A. Giovannini and W. Kittel, World Science Publishing Co.. (In press.)

Invited Talks

Bent, B.E. and G.A. Somorjai, *Bonding and Chemistry of Hydrocarbon Monolayers on Metal Surfaces*, Catalysts in Petroleum Refining Conference, Kuwait, March 1989. (J. Adv. Coll. Interface Sci., vol. 29, p. 223, 1989.)

Salmeron, M., *Application of the Scanning Tunneling Microscope to the Study of Surface Structures and Processes in Gaseous and Liquid Environments*, NACE Corrosion Research Symposium, New Orleans, LA, April 1989.

Salmeron, M., *The Structure of Chemisorbed Layers on Metal Surfaces Studied by Means of the Scanning Tunneling Microscope*, American Chemical Society Meeting, Surface Science and Debye Award Symposium, Dallas, TX, April 1989.

Salmeron, M., *The Structure of Chemisorbed Layers on Metal Surfaces Studied with the Scanning Tunneling Microscope*, 9th National Meeting on Surface Science of the Sociedad Mexicana de Ciencia de Superficies y Vacio, Zacatecas, Mexico, August 1989.

Salmeron, M., *Atomic Scale Imaging of Solid Surfaces with the Scanning Tunneling Microscope*, UOP Research Center, Des Plaines, IL , January 1989.

Salmeron, M., *Imaging of Biomolecules with STM: Problems and Prospects*, Oarai, Ibaraki, Japan, July 1989.

Salmeron, M., *Structures Formed by DNA Deposited on Graphite: An STM Study*, 12th Surface/Interface Research Meeting of the NCCAVS, Stanford, CA, June 1989.

Salmeron, M., *Tunneling Microscopy*, Wolf Trap Genome Sequencing Conference, Rockville, MD, October 1989.

Salmeron, M., D.F. Ogletree, B. Marchon, C. Ocal, T.P. Beebe, and W. Siekhaus, *Determination of the Ordered* $(2\sqrt{3} \times 2\sqrt{3})\ R30^{\circ}$ *Sulfur Overlayer Structure on Re (0001) by STM*, March Meeting of the APS, St. Louis, MO, March 1989.

Van Hove, M.A., *Complex and Disordered Surface Structures from LEED*, 197th ACS Meeting, Dallas, TX, April 1989.

Van Hove, M.A., *Complex Surface Structures from LEED*, NSF Science and Technology Center Workshop, Milwaukee, WI, February 1989.

Van Hove, M.A., *Diffuse LEED and Disordered Surface Structure*, LATSIS Symposium, Lausanne, Switzerland, October 1989.

Van Hove, M.A., *LEED Theory for Complex Molecular Systems Applied to Chemisorption on Pt, Rh and Pd (111)*, Workshop on Structure and Reactivity of Small Molecules on Surfaces, Ofir, Portugal, September 1989.

Van Hove, M.A., *Recent Complex Surface Structure Determinations by LEED*, Imperial College, London, GB, September 1989.

Contributed Talks

Ogletree, D.F., C. Ocal, T.P. Beebe, W. Siekhaus, and M. Salmeron, *Studies of Contacts between Pt-Rh tips and S covered Re(0001) Surfaces in the STM*, March Meeting of the APS, St. Louis, Missouri, March 1989.

Ogletree, D.F., C. Ocal, B. Marchon, G.A. Somorjai, and M. Salmeron, *STM Study of the Structure of Sulfur* $(2\sqrt{3} \times 2\sqrt{3})\ R30^{\circ}$ *Overlayer on Rhenium (0001)*, IV International Conference on STM, Oarai, Japan, July 1989. (To be published in the J. Vac. Sci. and Tech.)

Salmeron, M., T.P. Beebe, T. Wilson, R. Balhorn, D.F. Ogletree, and W. Siekhaus, *Observation of Nanometer Structures of Uncoated DNA Adsorbed on Graphite with the Scanning Tunneling Microscope*, March Meeting of the APS, St. Louis, MO, March 1989.

Siekhaus, W., T. Beebe, T. Wilson, D.F. Ogletree, R. Balhorn, and J. Katz, *Imaging DNA with the Scanning Tunneling Microscope*, AAAS Annual Meeting, January 1989.

Instrumentation for Surface Science Project

Refereed Journal Articles

Andres, R.P., R.S. Averback, W.L. Brown, L.E. Brus, W.A. Goddard, III, A. Kaldor, S.G. Louie, M. Moscovits, P.S. Peercy, R.J. Riley, R.W. Siegel, F. Spaepen, and Y. Wang, "Research Opportunities on Clusters and Cluster-Assembled Materials," *J. Mat. Res.*, vol. 4, p. 704, 1989.

Berkovic, G., Y.R. Shen, G. Marowsky, and R. Steinhoff, "Interference between Second-Harmonic Generation from a Substrate and from an Adsorbate Layer," *J. Opt. Soc. of Am. B*, vol. 6, p. 205, 1989.

Chen, W., M. Feller, J. Huang, R. Superfine, and Y.R. Shen, "Nonlinear Optical Studies of Molecular Orientation and Alignment at Interfaces," *Bull. Am. Phys. Soc*, vol. 34, p. 1678, 1989.

Chia, V.K.F., D.K. Veirs, and G.M. Rosenblatt, "Cryogenic Sample Manipulator for Multipurpose Sample Analysis," *J. Vac. Sci. Tech. A.*, vol. 7, p. 108, 1989.

Chia, V.K.F., D.K. Veirs, and G.M. Rosenblatt, "Ultrahigh Vacuum Apparatus for Unenhanced Surface Spectroscopy and Characterization at Cryogenic Temperatures," *Rev. Sci. Instr.*, vol. 60, p. 1161, 1989.

Fisher, K.A., R.E. Thomson, S. Whitfield, and J. Clarke, "Scanning Tunneling Microscopy of Planar Membrane Monolayers," *J. Cell Biol.*, vol. 107, p. 213a, 1989.

Ganz, E., K. Sattler, and J. Clarke, "Scanning Tunneling Microscopy of Cu, Ag, Au, and Al Adatoms, Small Clusters, and Islands on Graphite," *Surf. Sci.*, vol. 219, p. 33, 1989.

Kim, M.W., D.G. Peiffer, W. Chen, H. Hsiung, Th. Rasing, and Y.R. Shen, "Polymer Concentration Profile Near a Liquid/Solid Interface: Evanescent Wave Ellipsometry Study," *Macromolecules*, vol. 22, p. 2682, 1989. (M.W. Kim, CAM Industrial Fellow, Exxon Research and Engineering Company; D.G. Peiffer, Exxon Research and Engineering Company)

Northrup, J.E., M.S. Hybertsen, and S.G. Louie, "Quasiparticle Excitation Spectrum for Nearly-Free-Electron Metals," *Phys. Rev. B*, vol. 39, p. 8198, 1989.

Rasing, Th., J. Huang, A. Lewis, T. Stehlin, and Y.R. Shen, "*In-situ* Determination of Induced Dipole Moments of Pure and Membrane-bound Retinal Chromophores," *Phys. Rev. A*, vol. 40, p. 1684, 1989.

Shen, Y.R., "Surface Properties Probed by Second-Harmonic and Sum-Frequency Generation," *Nature*, vol. 337, p. 519, 1989.

Veirs, D.K., V.K.F. Chia, and G.M. Rosenblatt, "Unenhanced Surface Raman Spectroscopy of Nitrogen Physisorbed on Ag(111)," *Langmuir*, vol. 5, p. 633, 1989.

Xiao, X.-D., V. Vogel, and Y.R. Shen, "Probing the Proton Excess at Interfaces by Second Harmonic Generation," *Chem. Phys. Lett.*, vol. 163, p. 555, 1989.

Zettl, A., L.C. Bourne, J. Clarke, M.F. Crommie, M.F. Hundley, R.E. Thomson, and U. Walter, "Electric Interference, Elasticity and Scanning Tunneling Microscopy Studies of the Charge Density Wave Conductor $K_{0.3}M_0O_3$," *Syn. Met.*, vol. 29, p. F445, 1989.

Zhu, X., S. Fahy, and S.G. Louie, "*Ab initio* Calculation of Pressure Coefficients of Band Gaps of Silicon: Comparison of the Local-Density Approximation and Quasiparticle Results," *Phys. Rev. B*, vol. 39, p. 7840, 1989.

Refereed Conference Proceedings

Fisher, K.A., R.E. Thomson, K. Yanagimoto, M. Gustafsson, and J. Clarke, "Scanning Tunneling Microscopy of Planar Biomembranes," *Proc. of the 47th Annual Meeting of the Electron Microscopy Society of America*, vol. 14, 1989.

Guyot-Sionnest, P., Y.R. Shen, R. Superfine, and J.H. Hunt, "Sum-Frequency Generation for Surface Vibrational Spectroscopy," *Proc. Topical Meeting on Laser Materials and Laser Spectroscopy*, p. 283, 1989.

LBL Reports (including journal articles submitted or in press)

Ager, III, J.W., D.K. Veirs, and G.M. Rosenblatt, "Raman Intensities and Interference Effects for Thin Films Adsorbed on Metals," *J. Chem. Phys.* (In press.)

Johnson, M. and J. Clarke, "Spin Polarized Scanning Tunneling Microscope: Concept, Design and Preliminary Results from a Prototype Operated in Air," *J. Appl. Phys.* (Submitted.)

Shattuck, M.B., S.L. Whitfield, J. Clarke, and R.S. Bhatnagar, "Scanning Tunneling Microscopy of Collagen," *Proc. 3rd Symp. of the Protein Soc.* (In press.)

Superfine, R., J. Huang, and Y.R. Shen, LBL 26490, "Conformation, Orientation and Interaction on Molecular Monolayers: A Surface Second Harmonic and Sum Frequency Generation Study," in *Laser Spectroscopy IX*, ed. M. Feld, A. Mooradian, and J.E. Thomas, Academic Press.

Invited Talks

Chen, W., M. Feller, J. Huang, R. Superfine, and Y.R. Shen, *Nonlinear Optical Studies of Molecular Orientation and Alignment at Interfaces*, 5th Interdisciplinary Laser Science Conference, Stanford, CA, August 1989. (Bull. Am. Phys. Soc., vol. 34, pg. 1678, 1989.)

Fisher, K.A., R.E. Thomson, S. Whitfield, and J. Clarke, "Scanning Tunneling Microscopy of Planar Membrane Monolayers," *J. Cell Biol.*, vol. 107, p. 213a, 1989.

Kim, M.W., D. Peiffer, H. Hsiung, Th. Rasing, W. Chen, and Y.R. Shen, *Study of Polymer Adsorption Phenomena on a Solid Substrate*, Fall Meeting, Materials Research Society, Boston, MA, November 1989. (M.W. Kim, CAM Industrial Fellow, Exxon Research and Engineering Company)

Shen, Y.R., *Surface Studies by Nonlinear Optics*, Presented at Tsinghua University, Taiwan, Republic of China, May 1989; Department of Physics, Korea University, Seoul Korea, May 1989; and Digital Equipment Corporation, Palo Alto, CA, March 1989.

Shen, Y.R., *Nonlinear Optical Probing of Surfaces*, IBM Almaden Research Center, Seminar, San Jose, CA, April 1989.

Shen, Y.R., *Optical Second Harmonic and Sum-Frequency Generation for Surface Studies*, American Chemical Society Meeting (Debye Award Symposium), Dallas, TX, April 1989.

Shen, Y.R., *Optical Studies of Molecules at Interfaces*, Gordon Research Conference on Electrochemistry, Ventura, CA, January 1989.

Shen, Y.R., *Applications of Nonlinear Optics to Interfacial Studies*, Symposium on Interfacial Phenomena: Structure and Thermal Properties, Victoria, British Columbia, Canada, June 1989.

Shen, Y.R., *Nonlinear Optical Surface Probes*, Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlanta, GA, March 1989.

Shen, Y.R., *Introduction to Nonlinear Optics*, Department of Physics, Seoul National University; and Korea Advanced Energy Research Institute, Seoul, Korea, Seoul, Korea, May 1989.

Superfine, R., J.Y. Huang, and Y.R. Shen, *Conformation, Orientation and Interaction in Molecular Monolayers: A Surface Second Harmonic and Sum Frequency Generation Study*, 9th International Conference on Laser Spectroscopy, Bretton Woods, NH, June 1989.

Veirs, D.K., G.M. Rosenblatt, and J.W. Ager III, *Raman Spectroscopy of Adsorbed Films and Advanced Materials*, Chemistry Seminar, UC Davis, September 1989.

Vogel, V., *Adsorbates at Liquid Interfaces Studied by SHG*, Physics Colloquium, Case Western University, Cleveland, OH, December 1989.

Vogel, V., *Adsorbates Studied by Optical Second Harmonic Generation*, Exxon Research Division, Annadale, NJ, June 1989.

Vogel, V., *Surfactants Studied by Second Harmonic Generation*, Union Carbide, Research Division, Tarrytown, NJ, June 1989.

Contributed Talks

Johnson, M., *Ferromagnet-Air-Ferromagnet Tunneling and Application to a Spin Polarized Scanning Tunneling Microscope*, Presented at Naval Research Labs, Washington, DC, November 1989; Massachusetts Institute of Technology, Francis Butler National Magnet Laboratory, Boston, MA, November 1989; National Institute of Standards and Technology, Washington, DC, November 1989; Polytechnic University, New York, NY, November 1989.

Kim, M.W., D.G. Peiffer, W. Chen, H. Hsiung, Th. Rasing, and Y.R. Shen, *Polymer Concentration Near Liquid/Solid Interfaces by an Evanescent Wave Ellipsometry*, 4th International Conference on Langmuir-Blodgett Films, Tsukuba, Japan, April 1989. (M.W. Kim, CAM Industrial Fellow, Exxon Research and Engineering Company; D.G. Peiffer, Exxon Research and Engineering Company.)

Kim, M.W., D.G. Pfeiffer, W. Chen, H. Hsiung, Th. Rasing, and Y.R. Shen, *Polymer Concentration Measurements near Liquid/Solid Interfaces by an Evanescent Wave Ellipsometry*, Fourth International Conference on Langmuir-Blodgett Films, Tsukuba, Japan, April 1989. (M.W. Kim, CAM Industrial Fellow, Exxon Research and Engineering Company; D.G. Pfeiffer, Exxon Research and Engineering Company.) (Submitted to Macromolecules.)

Kim, M.W., Th. Rasing, and Y.R. Shen, *Two-Dimensional Phase Transitions of a Surfactant Monolayer*, Conference on Phase Transitions in Soft Condensed Matter, Geilo, Norway, April 1989. (M.W. Kim, CAM Industrial Fellow, Exxon Research and Engineering Company.)

Kim, M.W., P. Valint, C. Mullin, Th. Rasing, T. Stehlin, and Y.R. Shen, *Adsorption Kinetics of Soluble Surfactants at a Liquid-Air Interface*, Fourth International Conference on Langmuir-Blodgett Films, Tsukbua, Japan, April 1989. (M.W. Kim, CAM Industrial Fellow, Exxon Research and Engineering Company; P. Valint, Exxon Research and Engineering Company.)

Kim, M.W., P. Valint, Th. Rasing, T. Stehlin, and Y.R. Shen, *Study of Surfactant Adsorption Kinetics at an Air/Water Interface by Second Harmonic Generation,* XVI International Quantum Electronics Conference, Tokyo, Japan, July 1989. (M.W. Kim, CAM Industrial Fellow, Exxon Research and Engineering company.)

Shattuck, M., S. Whitfield, R.E. Thomson, J. Clarke, and R.S. Bhatnagau, *Scanning Tunneling Microscopy of Collagen,* Third Annual Symposium of the Protein Society, Seattle, WA, July 1989.

Superfine, R., J. Huang, and Y.R. Shen, *Molecular Conformation and Ordering in a Monolayer Determined by Simultaneous Surface Infrared-Visible Sum Frequency and Second Harmonic Generation,* Ninth International Conference on Laser Spectroscopy, Bretton Woods, New Hampshire, June 1989.

Thomson, R.E., J.B. Liu, M.F. Crommie, B. Burke, A. Zettl, and J. Clarke, *Charge Density Waves in a o-TaS*$_3$ *Studied by Scanning Tunneling Microscopy,* Meeting of the American Physical Society, St. Louis, MO, March 1989.

Vogel, V., C.S. Mullin, Y.R. Shen, and M.W. Kim, *Surface Adsorption Studied by Optical SHG,* Fall Meeting of the Materials Research Society, Boston, MA, November 1989.

Vogel, V., X.-D. Xiao, and Y.R. Shen, *Probing the Proton Excess at Interfaces by Second Harmonic Generation,* 5th Interdisciplinary Laser Science Conference, Stanford, CA, August 1989.

Wang, X.W. and S.G. Louie, *First-Principles Study of S/Mo(001) Systems,* March Meeting APS, St. Louis, MO, March 1989. (Bull. APS, Vol 34, p. 863, 1989.)

Xiao, X.-D., V. Vogel, and Y.R. Shen, *Environmental Effects on Hemicyanine Dye Monolayers at the Air/Water Interface Studied by SHG,* 5th Interdisciplinary Laser Science Conference, Stanford, CA, August 1989.

IndustryParticipation

Advisory Boards
Workshops
Industrial Fellows
Research Contracts and Gifts
Publications
Visits
Collaborations

Advisory Boards
Workshops
Industrial Fellows
Research Contracts and Gifts
Publications
Visits
Collaborations

Industry Participation

CAM's mission statement calls for basic research in materials science. The research programs described in the preceding sections of this report are devoted to increasing our understanding of the fundamental properties of materials and materials systems. The mission statement also states that this research should support U.S. industry and that there be direct and continuing collaboration between CAM and U.S. industrial research laboratories. The selection of CAM research topics and the design of its programs are governed by the basic materials research needs of industry and a major thrust of the programs involves information flow to and from industry. This includes discussions, research collaborations, gifts, contracts, industrial fellowships, visits, publication of results in the scientific journals, and publications from the Center, such as Research Notes, and this Annual Report.

The CAM Industry Participation Office, in the office of the CAM Director, is charged with the development and management of these interactions with industry. Activities supported by that office include:

- program advisory board meetings
- industry participation workshops
- research collaborations
- CAM Industrial Fellows
- research contracts, gifts and fellowships
- publications
- visits of industry scientists and research managers

ADVISORY BOARDS

Each CAM program, and some projects, are supported by an advisory board made up of industrial research managers serving two or three year renewable terms. The boards meet formally once each year to review the focus and goals of the program and the research progress made since the last meeting. A report is prepared on these aspects of the program with specific suggestions and criticisms, primarily focused on the question of which research directions are appropriate to CAM and of greatest potential benefit to U.S. industry. Members of the advisory board also consult with the program and project leaders informally throughout the year. Listings of the advisory board members follow each chapter of this report.

WORKSHOPS

Each CAM program holds, at two to three year intervals, a formal workshop for industry. These are open to all interested representatives of U.S. industry. The workshops, which usually run for two days, involve presentations by the CAM investigators of the research of their programs, and their planned directions for the following few years. Industrial scientists attending the workshop are invited to discuss the research and to express their views on appropriate directions of the research programs—directions that will produce beneficial results for their own companies and for U.S. industry in general. The workshops also include visits to the CAM laboratories and informal discussions with its scientists and students.

INDUSTRIAL FELLOWS

The Industrial Fellows Program at CAM is one of our most effective means of technology transfer to industry. Under the program, industrial scientists come to CAM to spend from one month to a year as integral members of one of the research programs. The fellowships can also be arranged for one week each month for a year, or, with local companies, for one or two days each week during the year. Industrial Fellows not only pursue research projects while in residence, adding their own background and experience to that of the program's staff, but also serve as excellent technology transfer agents when they return to their company's laboratories. Some of the Fellows devote their time at CAM to the development and design of collaborative research programs between their laboratories and the CAM Program. Six Industrial Fellows worked at CAM during 1989. Six are scheduled for appointment in 1990 and more are planned for 1991.

1989 Industrial Fellows

M.W. Kim	Exxon Research and Engineering
G.Elliot	Hewlett-Packard Optoelectronics Division
K.T. Chan	Hewlett-Packard Microwave Technology Division
D. Denley	Shell Development Company
C.D. Chang	Mobil Research and Development
B.Bhushan	IBM Almaden Research Center

The value of this program has been recognized by the Department of Energy. Arrangements have been made for DOE support of the laboratory, living, and travel expenses of many of the Industrial Fellows while at work at CAM through the Industry-Laboratory Technology Exchange Program of the DOE Office of Energy Research. In 1989, C.D. Chang, and G. Elliot were supported under this program.

GIFTS

Unrestricted gifts to CAM during 1989 totaled $295,000, raising the six year total to $632,000. This type of funding is the most valuable to the CAM programs because it gives them the required flexibility to deal with important and unexpected research needs as they arise.

FELLOWSHIPS

A number of CAM students are supported on industrial and other types of fellowships. Fellowship support is free of Laboratory overheads and can include funds for the purchase of supplies. Fellowships are listed in each program chapter.

GIFTS OF MATERIAL AND EQUIPMENT

Programs at the Center benefit greatly from donations of used or new processing or analytical equipment, or materials that are unavailable commercially. The value of donated materials and equipment at CAM exceeds two million dollars.

RESEARCH CONTRACTS

1989 research contracts totaled $285,000, bringing that six year total to $794,000. The contracts allow for focused work on specific projects of direct interest to the company involved, and enable the sponsors to maintain close contact with the investigators and students.

CALIFORNIA COMPETETIVE TECHNOLOGY PROGRAM

This year, a group in the CAM program on High-T_c Superconductivity, with support from the U.S. Department of Energy has joined in a collaborative effort with the State of California and Conductus, Inc., a start-up company in California's Silicon Valley. The goal of the project is to transfer to Conductus, results of the fundamental research supported by DOE that will allow the development of Superconducting QUantum Interference Devices (SQUIDs) using the new high-T_c superconducting materials. The California Competitive Technology Program will contribute close to one half million dollars over an eighteen month period to support the effort. Conductus will send one of its senior scientists to work with the research group at CAM with support of the DOE Research Program on Industry-Laboratory Technology Exchange.

PUBLICATIONS

All CAM work is published in the open literature. This year CAM researchers published 172 articles in books, journals and conference proceedings, 9 doctoral or masters theses, 176 invited papers, 113 contributed papers. An additional 137 journal articles are now in press. The Center also produces a number of its own publications throughout the year. These include this Annual Report, and the triannual Research Notes describing recent research highlights. Research Notes also includes the list of recent journal articles. These CAM publications are sent, along with announcements of workshops and other meetings, to those on our mailing list. The attached form should be used for adding names to that list.

INDUSTRIAL VISITORS

Representatives from U.S. industrial companies are encouraged to visit the Center; visits range from one day to a week or more. First visits usually involve discussions with CAM management, industry participation officials, and selected program leaders. Subsequent visits are focused on more detailed scientific discussions with program staff and often lead to continuing relationships including periodic exchanges of ideas and results, or active, formal collaborations.

COLLABORATIONS

CAM programs have established research collaborations with scientists in many U.S. industrial laboratories. These are described in detail in the preceeding sections of this report and involve companies in areas from petrochemical to automobile manufacturing to biotechnology. In some cases, the collaboration involves exchange of proprietary information or materials. Results of this work are published in the open literature by University of California and Lawrence Berkeley Laboratory policy, but only after protection of the proprietary information is assured. Currently, there are 39 active industrial collaborations.

STUDENTS AND POSTDOCTORAL FELLOWS

During the past six years, 90 students received their masters or doctoral degrees (18 in 1989) and 13 completed postdoctoral fellowships. Of this group, 56 have moved on to industrial research positions, 8 have gone to work at a National Laboratory, and 12 more have taken University teaching positions. Others continued their studies after leaving CAM.

1989 DEGREE RECIPIENTS

Name	*Degree*	*Current Employer*	*CAM Program*
K.R. Amundson	Ph.D	AT&T Bell Laboratories	Polymers and Composites
J.B. Bourzutschky	Masters	Exxon	Surface Science and Catalysis
R.P. Caron	Ph.D	LBL	Electronic Materials
J. Ding	Ph.D	Applied Materials	Electronic Materials
M.L Galiano	Masters	Continuing studies for Ph.D	Electronic Materials
J. Glazer	Ph.D	Hewlett-Packard	Structural Materials
W. Ham	Ph.D	LBL	High-T_c Superconductivity
D. Hill	Ph.D.	LBL	Polymers and Composites
C.J. Jou	Ph.D	Ecole Polytechnique, France	Electronic Materials
T. Kenny	Ph.D	Jet Propulsion Lab	High-T_c Superconductivity
P.S. McAnnally	Masters	Texas Instruments	Surface Science and Catalysis
L.T. McKnelly, Jr.	Ph.D	Vitesse Semiconductors	Structural Materials
M.S. Mastandrea	Masters	Oracle Corporation	Enzymatic Synthesis of Materials
H. Menendez	Masters	LRA Laboratories	Structural Materials
A. Michiels	Masters	Applied Magnetics	Enzymatic Synthesis of Materials
W.E. Tegrotenhuis	Ph.D	Dow Chemical	Polymers and Composites
S.L Verzasconi	Masters	Alcoa	Structural Materials
D.J. Weitz	Masters	Continuing Studies	Enzymatic Synthesis of Materials

Index to Investigators

☆U.S. GOVERNMENT PRINTING OFFICE: 1990 785-130 - 1015

CENTER FOR ADVANCED MATERIALS

In our effort to keep the scientific community informed of research activities at the Center for Advanced Materials, we produce and distribute publications during the year. In addition to this Annual Report, the Center publishes Research Notes along with a publications update three times yearly. Notices of workshops and seminars held at the Center are also sent. If you wish to receive our publications and notices of our workshops and seminars, please fill out this form and return it to the CAM office.

Last name :
First name :
Middle name :
(Mr, Ms, Dr) :
Title :
Company :
Address 1 :
Address 2 :
City :
State :
Zip Code :
Phone :

Please mark the appropriate interest areas:

CAM (General) __
Ceramics __
Enzymatic Synthesis of Materials __
High-T_C Superconductivity __
Instrumentation for Surface Science __

Interconnects __
Metals/Alloys __
Polymers and Composites __
Semiconductors/Crystal Growth __
Surface Science and Catalysis __

Return this page to:

Meg Holm
Center for Advanced Materials
Lawrence Berkeley Laboratory
One Cyclotron Rd., 66-200
Berkeley, CA 94720

Center for Advanced Materials
CAM

DISCLAIMER

Available to DOE and DOE Contractors
from the Office of Scientific and Technical Information
P.O. Box 62, Oak Ridge, TN 37831
Prices available from (615) 576-8401, FTS 626-8401

Available to the public from the
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, VA 22161
Price: Printed Copy A09, Microfiche A01

LAWRENCE BERKELEY LABORATORY
CENTER FOR ADVANCED MATERIALS
1 CYCLOTRON ROAD
BERKELEY, CALIFORNIA 94720