

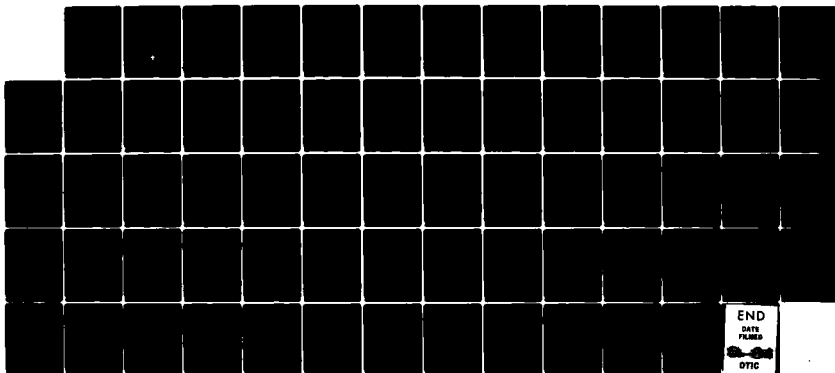
AD-A140 898

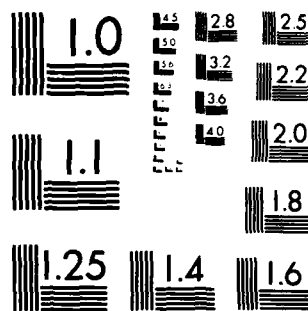
ANNUAL TECHNICAL REPORT MATERIALS RESEARCH LABORATORY 1 1/1
JULY 1982 - 30 JUNE 1983(U) BROWN UNIV PROVIDENCE RI
MATERIALS RESEARCH LAB 30 JUN 83 NSF-DMR79-235702

UNCLASSIFIED

F/G 20/12

NL



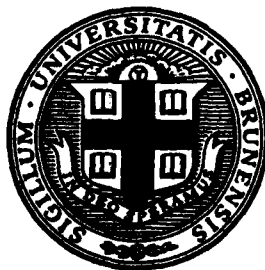


MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

ANNUAL TECHNICAL REPORT
Materials Research Laboratory
July 1, 1982 - June 30, 1983

AD-A140 898

DTIC FILE COPY



DTIC
MAY 10 1984
A

This document has been approved
for public release and sale; its
distribution is unlimited.

Brown University
Providence, Rhode Island
02912

84 04 27 021

**ANNUAL TECHNICAL REPORT
MATERIALS RESEARCH LABORATORY**

**Brown University
Providence, RI 02912**

**A Report on Grant No. DMR-792357 02
from the
National Science Foundation
Washington, DC 20550**

**Reproduction in whole or in part is permitted for any
purpose of the United
States Government.**

Distribution of this document is unlimited.



AD 000000	6
DTIC 011001	
DTIC TAB	
Unannounced	
Justification	
By	
Distribution/	
Availability Codes	
Avail and/or	
Dist Special	
AI	

Additional Sources of Support for the Research Described in this Report

Air Force Office of Scientific Research

Exxon Research Laboratories

Gas Research Institute

General Telephone Laboratories, Inc.

Jet Propulsion Laboratory

Mobil Oil Foundation

National Bureau of Standards

National Science Foundation

Naval Research Laboratory ✓

Office of Naval Research ✓

Owens-Corning Fiberglass, Inc.

Sanders Associates

Sandia Laboratories

Standard Oil of Ohio

United States Army Research Office ✓

United States Department of Energy

→ Partial CONTENTS:

Preface	1
Section 1	
→ Plasticity of Solids.....	3
Introduction	3
Research Results.....	5
Section 2	
→ Fracture of Solids.....	13
Introduction	13
Research Results.....	15
Section 3	
→ Inorganic Glasses.....	21
Introduction	21
Research Results.....	23
Section 4	
→ Solid Surfaces.....	31
Introduction	31
Research Results.....	33
Section 5	
→ Lower Dimensionality Materials and Structures.....	37
Introduction	37
Research Results.....	39
Section 6	
→ Properties of Materials at Low Temperatures.....	41
Introduction	41
Research Results.....	43
Section 7	
→ Materials for Solar Energy Conversion.....	45
Section 8	
Other Research.....	47
Lecturers in the Materials Research Laboratory Program, 1982-83.....	53
List of Staff in the Materials Research Laboratory Program	
Applied Mathematics	59
Chemistry.....	59
Engineering	59
Materials Research Laboratory	59
Physics	59
Index of Principal Investigators.....	61

PREFACE

The Materials Research Laboratory at Brown University was engaged in 1982/83 in interdisciplinary research concentrated in four major thrust areas and three minor thrust areas. Research in each thrust area was organized by a coordinator whose names are listed below:

Plasticity of Solids.....	R. J. Clifton
Fracture of Solids.....	L. B. Freund
Inorganic Glasses.....	W. M. Risen, Jr.
Lower Dimensionality and Structures.....	P. J. Stiles
Solid Surfaces	P. J. Estrup
Properties of Materials at Low Temperatures.....	C. Elbaum
Materials for Solar Energy Conversion.....	J. J. Loferski

Following short introductions by the Thrust Area Coordinators, individual investigators present summaries of their contributions and lists of their publications. Since some of the research projects fall into more than one thrust area, cross-references are provided.

The largest single source of support for this research was the National Science Foundation Materials Research Laboratory Section. The availability and wide use of the 8 Materials Research Laboratory Central Facilities were essential for most of the research. Significant support also came from Brown University and sixteen agencies listed on page ii.

The Materials Research Laboratory was administered by a Director (G. S. Heller) and an Associate Director (W. M. Risen, Jr.) and an Advisory Committee (R. H. Cole , L. N. Cooper R. J. Clifton P. J. Estrup and J. Tauc).

SECTION 1 PLASTICITY OF SOLIDS

Introduction

Research in this area is directed toward (1) an understanding of the mechanisms and constitutive description of inelastic deformation, especially at ultrahigh strain rates, in single and multi-phase materials, (2) the development of large strain models for polycrystals based on fundamental model descriptions and experimental study of single crystals, (3) theoretical and experimental study of localized and unstable plastic flow, and (4) theoretical and experimental study of the inelastic behavior of fiber composite materials. Projects in this thrust, as well as in the Fracture of Solids thrust, described next, are chosen to be highly interdisciplinary. They typically have experimental and theoretical parts and aim to incorporate the effects of material microstructure, chemistry and micromechanics into macroscopic descriptions of plastic response. Another vital theme which is common to many of the projects and thus serves to link all the work within the thrust is material strain rate and temperature dependence. In fact, during the past year novel techniques have been developed for single crystals and polycrystals which allow fully rate dependent analyses of finite plastic flow to be performed.

Strain rate and strain rate/temperature history effects have been examined over the range of strain rates from 10^{-6} s^{-1} to 10^5 s^{-1} using a combination of stress wave loading techniques. Duffy and co-workers have continued to develop the torsional Kolsky bar technique to cover the range of strain rates from 10^{-6} s^{-1} to 10^3 s^{-1} while Clifton and co-workers have developed further plate impact methods, including the pressure-shear technique, and used them to study the strain rate range from 10^3 s^{-1} to 10^5 s^{-1} . Recent work on 4340 steels using the pressure shear technique has shown that there is a surprisingly small increase in flow stress when the strain rate is increased beyond 10^3 s^{-1} up to 10^5 s^{-1} . Preliminary interpretations are that this means that thermally activated motion of dislocations past obstacles remains the rate controlling mechanism even at strain rates as high as 10^5 s^{-1} . Recent work on strain rate and thermal history effects in bcc metals, including steels, has confirmed and further explored our earlier observations that bcc metals often display very different qualitative behavior than fcc metals. Strain rate jump and temperature decrement tests have both shown that following a jump in strain rate (e.g., by a factor of 10^{-2} s^{-1} to 10^7 s^{-1}), or a decrement in test temperature (e.g., from 20C to -80C or -190C), the resulting flow stress is often larger than what would have been if straining were at the high rate, or lower temperature from the outset. This behavior contrasts from what is usual in fcc metals and is being evaluated further by further experiment and through studies of the relevant micromechanics.

Recent work on localized shearing has included experimental and theoretical studies of shear band development during high rate torsion and during quasi-static deformation. The effects of non-uniform heating and resulting thermal softening have been studied in dynamic torsion of steels using infra-red microscopy. Work on localized shearing in ductile single crystals has been extended to bcc metals, viz., iron and niobium. As with past work on fcc metals and alloys, a goal of this new work is to document, and develop a fundamental understanding of, the effects of crystallography and micromechanics on unstable, localized plastic flow.

The constitutive theory for single crystals has been reformulated to include a full description of material rate dependence. This rate dependent theory has at least two major advantages with respect to rate independent idealizations: (1) it provides a description of the effects of rate sensitivity, and loading and strain rates, on the development of deformation patterns and (2) it renders the "slip mode" on the possible crystallographic slip systems, and thus the lattice reorientations that accompany plastic slip, unique. With this rate dependent theory a full range of material properties such as latent hardening and crystal geometry can be used in boundary value problem solutions. In addition it is now possible to make unique, well posed, predictions of lattice

rotations and deformation induced texture. Our results have shown that the formation of non-uniform lattice rotation is of great importance in determining large strain deformation patterns. Other theoretical work on shear localization is aimed at studying the role of combined material strain rate/temperature dependence on the initiation of shear bands. In particular the competing effects of material strain hardening and possible thermal softening, caused by non-uniform heating at very high strain rates, are being modelled analytically and numerically.

Our studies of single crystal plasticity are being extended to provide descriptions of large strain elastic-plastic deformation of polycrystals. The models are based on our constitutive theories for rate dependent plastic flow in single crystals. The models are being used to study the effects of microstructural mechanisms of deformation and material properties, such as strain hardening and rate sensitivity on the slip system level, on macroscopic polycrystalline response. Development of deformation textures and anisotropy along with their effects on polycrystal constitutive properties are being studied with these models. The results will then be applied to the simulation of metal forming processes as well as other deformation processes in metals that involve large strains.

Other research areas and projects in this thrust include the plasticity of polyphase and fiber composite materials. Summaries of work in these areas are included in Research Results.

Research Results

Pressure-Shear

Plate Impact Experiments

High shear-rate experiments have been conducted on thin specimens (0.2-0.4mm thick) of 4340 steel (600C temperature) sandwiched between high strength steel plates. At shear strain rates from $0.4 \times 10^5 \text{ s}^{-1}$ to $1.1 \times 10^5 \text{ s}^{-1}$ the shear stress was only 10-15% higher than obtained in dynamic torsion experiments at strain rates of 10^3 s^{-1} . In these pressure-shear experiments the flow stress did not appear to depend significantly on the hydrostatic pressure which ranged from 3.0 GPa to 4.3 GPa. The lack of a pronounced increase in flow stress with increases in strain rate beyond 10^4 s^{-1} , such as the increase observed for aluminum and copper, is viewed as indicating that the thermally activated motion of dislocations past obstacles remains the rate controlling mechanism even at strain rates greater than 10^5 s^{-1} . This view is supported by the fact that the shear stress (720 MPa) required for the highest shearing rates obtained in these experiments is less than the shear stress required for quasi-static deformation at low temperatures.

Principal Investigator: R. J. Clifton, Professor, Engineering.

Personnel: R. Klopp, Graduate Student, Engineering.

Publication:

"Dynamic Plastic Response of Metals Under Pressure-Shear Impact," R. J. Clifton, A. Gilat and C. H. Li, in *Material Behavior Under High Stress and Ultra-High Loading Rates*, (ed. by J. Mescall and V. Weiss), Plenum, 1983, pp. 1-19.

Supported by the Army Research Office and the Materials Research Laboratory/NSF.

Dislocation

Models of Plastic Flow

Precursor decay in plate impact experiments on LiF has been analyzed by using a theory for finite deformation of elastic, viscoplastic materials. Plastic flow is modeled in terms of the viscous glide of dislocations on the primary slip systems. Surface damage and the generation of dislocations at the impact

surface are included in order to assess the role of enhanced dislocation density at surfaces on precursor decay. The resulting increased density of dislocations increases the calculated precursor decay near the impact face. Nonlinear elastic effects allow the precursor amplitude to be reduced by unloading waves which overtake the precursor. The effect of these unloading waves, which originate in the region of high dislocation density near the impact face, diminishes with distance of propagation so that precursor decay beyond, say, 3mm is hardly affected. Consequently, increased dislocation density near the impact face can account for experimental observations of smaller-than-predicted precursor amplitudes, but it cannot account for the observation that the precursor amplitude continues to decrease with distance of propagation, even for thick (say > 3mm) specimens. Other mechanisms for enhanced precursor decay in the bulk of the crystal are being investigated.

Plastic flow of a polycrystalline aggregate of fcc crystals has been modeled in terms of the mobility of dislocations on the slip planes of randomly oriented grains. Geometric compatibility is maintained by requiring the rate of deformation tensor to be the same for all grains. Dislocation mobility is assumed to be governed by a linear viscous drag relation. Computer simulations of elementary macroscopic deformations such as simple shear and uniaxial extension are used to relate the macroscopic plastic response to the response of a single slip system. These results are being extended to include the case of nonlinear relationships between the flow stress and the average dislocation velocity for a single slip system.

Principal Investigator: R. J. Clifton, Professor, Engineering.

Personnel: G. Meir, Graduate Student, Engineering and W. Yang, Graduate Student, Engineering.

Publications:

"Radiation from Expanding Circular Dislocation Loops and Elastic Precursor Decay," X. Markenscoff and R. J. Clifton, *J. Applied Mechanics* 49, 1982, pp. 792-796.

"Calculation of Visco-Plastic Response of Polycrystals from Slip Theory for F.C.C. Crystals," J. P. Yang, Sc. M. thesis, Brown University. July, 1983.

Supported by the Materials Research Laboratory/NSF

and the National Science Foundation.

**Strain Rate
and Strain Rate History
Effects During Plastic Deformation**

The goal of this research is a better understanding of the mechanical response of structural metals subjected to dynamic loading. We study material behavior through experiments employing a torsional Kolsky bar apparatus in which specimens are subjected to either quasi-static or to dynamic loading well beyond the elastic limit. In addition strain rate history effects are studied through incremental strain rate tests, and temperature history effects by imposing sudden drops in a temperature during deformation. Microscopic as well as macroscopic studies of the test material are a part of this research which involves test materials ranging from alloy steels to single crystals of aluminum. This work is closely related to that of Professor R. J. Clifton on plate impact experiments, since we cover the strain rate range from 10^{-4} s^{-1} to 10^4 s^{-1} , and his experiments are in the strain rate range of 10^4 s^{-1} to over 10^5 s^{-1} . Thus our combined experiments can determine the material properties to strain rates greater than 10^5 s^{-1} .

One phase of our research involves a study of the effect of strain rate history and temperature history on flow stress in polycrystalline steel, iron and aluminum. In these experiments either a strain rate increment or a temperature decrement was imposed during torsional deformation of thin-walled tubular specimens at a strain rate of $5 \times 10^{-4} \text{ s}^{-1}$. In aluminum a drop in temperature raises the flow stress, but only to a value considerably less than obtained in a test conducted entirely at the lower temperature. We found that for mild steel under the proper temperature condition, however, that the opposite was true: the dynamic flow stress after a static pre-strain overshoots that found by straining entirely at the dynamic rate. The magnitude of the overshoot depends upon specimen temperature, becoming progressively more pronounced at lower temperatures. This phenomenon is not found in fcc and hcp metals and has a parallel in temperature history. The imposition of a sudden drop in specimen temperature from room temperature or from -80°C to -190°C during deformation of steel raises the subsequent flow stress to a value greater than found as a result of deformation entirely at the lower temperature.

Some specimens of 0.999 iron were also tested for strain rate history and temperature history effects to test the possibility that the differences found between steel and aluminum were due to impurities in the steel and the same overshoot phenomenon was found, leading to the conclusion that the behavior of iron and steel (bcc metals) is related to atomic structure and not to impurities. It was determined that a constitutive law based on a thermal activation model closely matched the experimental results for steel below room temperature. In this steel the history effects are small in comparison to strain rate or temperature sensitivity, and can be neglected in the modeling. Further investigation is needed, including microstructural examination, to explain history effects. Other current work includes an investigation into the causes of shear banding in steel specimens subjected to dynamic loading. This work has important applications in such areas as penetration and machining and frequently shear banding precedes fracture. We have developed a technique for monitoring the temperature profile within and to either side of a shear band as it forms in a thin-walled tubular specimen subjected to torsional loading. For this purpose we use a linear array of 10 infra-red radiation detectors, each of which measures temperature over an area having a 0.01 inch diameter. We have successfully applied this technique to establish the temperature profile at 6 points along the 0.1 inch gage length of 1018 CRS and 4340 steel specimens during straining at 10^{-3} s^{-1} . Both deformed bands and transformed bands have been produced in both of these steels. We are awaiting receipt of an infra-red microscope with a 10-element linear array of detectors which will allow us a closer look at the temperature profile, especially within the transformed regions.

Finally, we are continuing our study of the formation of cell-like subgrains in single crystals of pure aluminum subjected to shear deformation at strain rates in the range 4×10^{-5} to 10^{-3} s^{-1} . The shear traction is applied on planes parallel to a preferred slip system. The deformed specimens are subsequently examined in the transmission electron microscope (TEM) to track dislocation motion and cell formation resulting from the shear deformation. In the current work specimens are subjected to small increments in strain rate 10^{-2} s^{-1} , in an effort to distinguish between two differing controlling mechanisms which seem to prevail at strain rates above and below about 10^{-1} s^{-1} .

Principal Investigator: J. Duffy, Professor, Engineering.

Personnel: R. H. Hawley, Senior Research Engineer, Engineering, E. E. Crisman, Senior Research Engineer, Engineering, G. J. LaBonte, Jr., Technical Assistant, Engineering, P. Rush, Technical Assistant, Engineering, K. A. Hartley, Graduate Student, Engineering and A. A. Morrone, Graduate Student, Engineering.

Publications:

"History Effects in Polycrystalline BCC Metals and Steel Subjected to Rapid Changes in Strain Rate and Temperature," J. Klepaczko and J. Duffy, Archives of Mechanics, Warsaw, Poland, Vol. 34, No. 4, 1982, pp. 419-436.

"Strain Rate History Effects and Observations of Dislocation Substructure in Aluminum Single Crystals following Dynamic Deformation," C.Y. Chiem and J. Duffy, Materials Science and Engineering, Vol. 57, No. 2, 1983, pp. 233-247.

"Strain Rate History Effects and Dislocation Substructure at High Strain Rates," J. Duffy, Proc. 29th Sagamore Conference on Material Behavior under High Stress and Ultra High Loading Rates, presented July 1982.

"Temperature Measurements during the Formation of Shear Bands in a Structural Steel," J. Duffy, To appear in Contribution submitted to D. C. Drucker Anniversary Volume, September 1982.

"Localized Flow During Dynamic Deformation in Steel," J. Duffy, invited lecture presented at AIME meeting, Atlanta, Georgia, March 1983.

"The Dynamic Plastic Deformation of Metals: A Review," J. Duffy, Technical Report, Air Force Wright Aeronautical Laboratories: AFWAL-TR-82-4024, October, 1982.

"Incremental Strain Rate and Incremental Temperature Experiments and the Development of Constitutive Laws for BCC Metals," K. A. Hartley, M.S. Thesis, June, 1983.

Supported by the Materials Research Laboratory/NSF, the Office of Naval Research and the Army Research Office.

**Ultrasonic Studies
of Deformation Under
Stress-Pulse Loading**

We have previously described results obtained on stress-pulse loading through the use of ultrasonic measurements. In these studies a system constructed here is used to record ultrasonic attenuation and velocity changes at ~ 10 microsecond intervals, while a stress pulse of ~ 100 microsecond duration is applied. In particular, we observed that the maximum of the stress pulse is reached before that of the ultrasonic attenuation change.

In order to account for these and related results on ultrasonic velocity changes, we developed a model for time-dependent motion of dislocations under the conditions of our experiments. We have obtained qualitative agreement between the model predictions and the experiments. Additional measurements have been carried out. We have found that the results are very sensitive to flexural components of stress and the interpretation must take these into account.

Principal Investigator: C. Elbaum, Professor, Physics.

Personnel: A. Hikata, Professor (Research), Applied Mathematics.

Supported by the Materials Research Laboratory/NSF.

Quantum Rate Processes

The theory of rate processes underlies the study of the rate of transition of a system from one equilibrium configuration to another. It finds application in many fields, including creep in solids. Most work on the rates of potential barrier crossings are based on classical mechanics. However, it is recognized that quantum mechanical effects may become significant at low temperature levels and for light atoms. For example, experimental evidence for quantum-mechanical tunneling effects on the viscoelastic relaxation in poly(methyl methacrylate) has been reported.

We are continuing to study the theory of quantum rate processes in asymmetric double well potentials. The work makes use of the decomposition of stationary states into right- and left-moving states previously developed in this program. The goal is to find the analytical basis for some interesting properties of these states which were previously discovered

through numerical calculations. Work is also underway to develop computer simulation techniques for studying the behavior of such a quantum system while it is in interaction with a heat bath. It is planned to use these techniques to study the transition between rates dominated by over-the-barrier crossings at high temperature levels to those dominated by tunneling at low temperature levels.

Principal Investigator: J. H. Weiner, Professor, Engineering.

Personnel: K-F. Lau, Research Assistant, Physics.

Supported by the Materials Research Laboratory/NSF.

Crystalline Plasticity

R. J. Asaro and A. Needleman have continued research in the area of large strain plasticity of crystalline solids. New experimental and theoretical work on body centered cubic single crystals is concerned with documenting the critical conditions required for localized deformation modes. These studies extend the previous work of Chang and Asaro, Lisiecki, Nelson and Asaro, Peirce, Asaro and Needleman and Goto and Asaro on necking and shear band formation in face centered cubic single crystals. The extension to body center cubic crystals is intended to provide a detailed study of the effects of material rate and temperature sensitivity both of which are much stronger in bcc metals than in the fcc metals and alloys previously studied. The constitutive models and numerical methods developed to study nonuniform deformation in rate independent crystals have been extended to include material rate dependence. A fully rate dependent constitutive theory for single crystals has been developed and solutions to full boundary value problems for crystals and bi-crystals deformed in tension have been obtained. Some of the phenomenology uncovered by these new calculations is described below. The rate dependent crystalline constitutive theory has recently been used to develop large-strain models for rate dependent polycrystals. These models are now being used to predict deformation textures in polycrystals and to study the effects of texture on constitutive response and large-strain strain hardening behavior.

Our previous experiments on single crystals of fcc metals and alloys have shown that lattice rotations

that accompany nonuniform plastic deformation play a vital role in promoting highly localized deformation modes such as shear bands. For example, our most recent work by Goto and Asaro on single crystals of precipitation hardened copper-cobalt alloys showed that the phenomenology of localized shearing in these alloys was similar to that found by Chang and Asaro in aluminum-copper alloys. Necking was found to produce a pattern of nonuniform lattice rotations that caused "geometrical softened" regions in which shear bands formed. As the shear bands developed, further lattice rotations occurred which increased the extent of geometrical softening. Our most recent finite element calculations have provided simulations of our experiments on single crystals. Calculations by Peirce, Asaro and Needleman on rate dependent crystals have also shown the vital importance of nonuniform lattice rotations and are, in fact, in very close agreement with the corresponding experiments.

The inclusion of rate dependence in the constitutive analysis was found by Peirce *et al.* to be essential in that lattice rotations are not necessarily uniquely prescribed in an idealized rate independent theory. In fact, as shown by Peirce *et al.*, even for the plane strain double slip crystal model used in their calculations, lattice rotations are not uniquely predicted for a full range of material constitutive parameters. In particular, the lattice rotations were not uniquely prescribed for the full range of latent hardening levels suggested by experiment. Rate dependence, even if it has almost no noticeable influence on strength or overall hardening behavior, imparts an inherent uniqueness to the slipping rates on each slip system thus rendering lattice rotations unique. Pierce *et al.* were thereby able to include a full range of latent hardening levels, as well as crystal geometry within the context of their double slip model, and explored a correspondingly wider range of phenomena. In addition, the effects of rate dependence itself on the development of nonuniform deformation patterns was also studied; in a few cases limits on rate dependence which essentially preclude shear bands were found.

The ability to predict lattice rotations uniquely is vital to the prediction of crystal rotation (i.e., grain rotation) in polycrystals and thereby to the prediction of deformation texture. For this reason the polycrystal models mentioned above are rate dependent. Deformation textures have been predicted for

fcc polycrystals which deform by $\{111\}\langle 110 \rangle$ slip and the effect of the anisotropy these textures produce on constitutive behavior has been explored. So far only relatively simple deformation histories have been studied but our intention is to study the effects of finite and extreme changes in strain path on strain hardening behavior. In one particular set of calculations the material rate sensitivity was chosen to be very low, e.g., consistent with experimental estimates of rate sensitivity in typical fcc alloys of copper or aluminum. After finite prestrains in axisymmetric or plane strain tension or compression the polycrystals were "unloaded" and then subjected to proportional reloading in prescribed sections of stress space. The reloadings were carried out until "yield" occurred, as defined by a critical accumulation of plastic strain—in this way a yield point was determined. This procedure produces yield surfaces as they are, in fact, measured experimentally. Our calculations have shown the formation of "corners" at stress points corresponding to the prior straining. Corners such as these as manifested in phenomenological constitutive models have been shown to promote localized deformation and for this reason, among others, our models will be used to develop more accurate, detailed constitutive laws that can be used to simulate large strain plastic flow.

Lattice misorientations either within a grain or across a grain boundary, have important effects on shear band propagation. To study these effects, LeMonds has carried out an analysis of a bi-crystal subject to plane strain tension within the rate dependent constitutive framework discussed above. The initial lattice misorientation induces strongly inhomogeneous deformations. When the latent hardening is characterized by Taylor's isotropic hardening, well defined shear bands occur and the calculations exhibit a rather abrupt transition in deformation pattern. On the other hand, when the latent is taken to be significantly greater than given by Taylor hardening, no such abrupt transition occurs and the deformation pattern evolves in a more continuous manner. Pierce *et al.* found that this high latent hardening ratio led to patchy slip which in turn gave rise to lattice misorientation that act as a kinematic barrier to shear band propagation. LeMonds' analysis shows that latent hardening has important implications for the mode of deformation within grains and, hence, for the lattice rotations and texture that evolve. This study also indicates the wide range of phenomena that can be

addressed within the rate dependent constitutive framework we have formulated using the analytical and numerical tools we have developed.

Principal Investigators: Robert J. Asaro, Professor, Engineering and Alan Needleman, Professor, Engineering.

Personnel: Herve Deve, Graduate Student, Engineering and Jeffrey LeMonds, Graduate Student, Engineering.

Publications:

"Crystal Plasticity," R. J. Asaro and A. Needleman, 50th Anniversary Issue of *J. Appl. Mech.* 50, 919 (1983).

"Micromechanics of Crystals and Polycrystals," R. J. Asaro and A. Needleman, in *Advances in Applied Mechanics* 23, 1 (1983).

Supported by the Materials Research Laboratory/NSF and the National Science Foundation.

Localization in Rate Sensitive Plastic Solids

We have extended Gurson's theory of a porous plastic solid to account for matrix material rate dependent plastic deformation. We have used this constitutive description to analyze the effect of material rate sensitivity on localization, both in the three dimensional shear band context and in the two dimensional sheet necking context. Our sheet necking analysis also illustrated effects arising from various visco-plastic constitutive descriptions on sheet necking.

Our shear band analysis illustrated the expected delay in the onset of localization due to material rate sensitivity. For a given rate sensitivity, we find a larger retarding effect on localization in plane strain tension than in axisymmetric tension. Our analysis also revealed a role of rate sensitivity in permitting the development of a stable band of excess shearing. In a previous rate-independent analysis, we found that with stress controlled nucleation of voids, a profusion of voids over a narrow range of stress could precipitate a nucleation induced localization. Positive material rate sensitivity leads to a stiffening as the shearing rate increases in the band which counteracts the weakening effect of the profuse nucleation of voids. After some excess shearing in the band, the

shearing rates inside and outside the band become nearly equal giving a stably deforming band with an excess shear accumulation.

In order to illustrate the effect of flow potential surface curvature on sheet necking, we carried out analyses using a kinematic type material model as well as a model with isotropically expanding flow potential surfaces. For this comparison, the uniaxial behavior was such that, at constant plastic strain rate, the two material descriptions give identical responses. We find a greater delay in the onset of sheet necking is predicted by the isotropic hardening model than by the kinematic hardening model, even in plane strain tension where the rate independent sheet necking predictions of these two theories coincide. The stabilizing effect of material strain rate dependence comes from the increased stiffness with increasing strain rate. Local necking induces a rapidly increasing strain rate in the incipient neck and it is the material response to this changing strain rate that affects the onset of localization. Hence it is the response of the material to a changing strain rate that governs necking behavior and identical response at constant (plastic) strain rate does not imply identical necking behavior.

Principal Investigator: A. Needleman, Professor, Engineering.

Personnel: V. Tvergaard, Visiting Professor, Engineering, M. Saje, Visiting Assistant Professor, Engineering and J. Pan, Graduate Student, Engineering.

Publications:

"Localization of Deformation in Rate Sensitive Porous Plastic Solids," J. Pan, M. Saje and A. Needleman, *International Journal of Fracture* 21, 261-278, 1983.

"Limits for Formability in Rate-Sensitive Metal Sheets," A. Needleman and V. Tvergaard, *Proceedings 4th International Conference on Mechanical Behaviour of Materials*, pp. 51-65, 1983.

Supported by the Materials Research Laboratory/NSF.

Shear Bands

The stability of simple shearing deformations of viscoplastic materials that exhibit thermal softening, strain hardening, and heat conduction has been studied by means of numerical solutions of the

governing system of nonlinear partial differential equations. Three models of material response have been considered: (a) a power law model in which the shear stress is proportional to the product of arbitrary powers of shear strain, temperature and shear strain rate; (b) an Arrhenius model in which the shear strain rate is an exponential function of an overstress divided by the absolute temperature; (c) Bodner's model which is an empirical model that exhibits a transition from weak to strong rate sensitivity of the flow stress at high strain rates. Nominally homogeneous deformations are perturbed by the presence of geometrical imperfections -- shallow grooves -- or by nonuniform initial temperature distributions. Numerical solutions are obtained to determine whether or not these perturbations cause the deformation to diverge from the homogeneous deformation that would be obtained without the perturbation. In particular, the solutions are examined for the development of shear bands of intense localized plastic deformation. For sufficiently strong strain rate sensitivity, such as a linear dependence of flow stress on strain rate, shear bands do not develop even without strain hardening. For weak strain rate sensitivity, corresponding to the response of metal alloys, shear band formation begins when thermal softening overcomes strain hardening; the rate of formation of the shear band depends on the strain rate sensitivity.

Principal Investigator: R. J. Clifton, Professor, Engineering.

Personnel: T. G. Shawki, Graduate Student, Engineering.

Publication:

"Analysis of Shear Strain Localization in Thermal Visco-Plastic Materials," T. G. Shawki, Sc.M. thesis, Brown University, June, 1983.

Supported by the Materials Research Laboratory/NSF and the Army Research Office.

Mechanics of Martensitic Transformations

We have begun a study of the effect of applied stress upon the arrangement of martensitic phases. This involved the formulation of constitutive relations. We considered a free energy function which depends upon the local change of shape and the temperature.

Properties of this function reflect the underlying symmetry of the parent and product phases, and an exchange of stability from parent to product phase at the transformation temperature. We first calculated the stable equilibria at the transformation temperature. We found a variety of stable arrangements involving the parent phase and symmetry related variants of the product phase. These consist of two or more variants arranged coherently in needle-like regions which protrude into the parent phase; they agree well with observed arrangements in alloys with mobile phase boundaries. We also considered dead loaded states at temperatures below the transformation temperature with particular attention to the question of whether the parent phase can be recovered by applying some system of dead loads. The answer to this question hinges on a delicate relation involving two vectors, a and n , used to define the transformation strain, the symmetry of the parent phase and the orientation of the loads. Curiously, our calculations indicate that the nature of the loading device has a significant effect; uniformly applied dead loads will generally produce a different arrangement of phases from an hydrostatic pressure. We plan further studies on the effect of different loading devices.

Principal Investigator: R. D. James, Assistant Professor, Engineering.

Personnel: D. Q. Nelson, Graduate Student, Engineering.

Publications:

"The Arrangement of Coherent Phases in a Loaded Body," R. D. James, Brown University Technical Report, December 1983.

"Stress-Free Joints and Polycrystals," R. D. James, Brown University Technical Report, November 1983.

Supported by the Materials Research Laboratory/NSF and the National Science Foundation.

Strength and Fracture of Two-Phase Alloys

In the area of microstructural aspects of deformation processes in two-phase alloys, we have begun an experimental study of load transfer as a strain hardening mechanism. It consists of Bauschinger effect measurements and X-ray diffraction residual stress determinations in the hard phase. A parallel

finite element analysis of deformation in two-phase alloys is being undertaken by Professor A. Needleman and graduate student, R. Beck.

Work on the fracture process in dual-phase steels continues with emphasis on the relationships between fracture, ductility and plastic deformation of the constituents. The plastic deformation of martensite is followed by micro-indentation hardness measurements. Our preliminary conclusions are that martensite deforms extensively in all alloys in the post-uniform elongation range. The degree of plastic deformation of the hard constituent, in this case, martensite, is a fundamentally important parameter of strength and fracture theories.

Principal Investigator: J. Gurland, Professor, Engineering.

Personnel: H. Stanton, Technical Assistant, Engineering, Y. L. Su, Research Assistant, Engineering and K. M. Cho, Research Assistant, Engineering.

Publications:

"Citation Classic. Commentary on Gurland, J. and Plateau, J., Trans. Am. Soc. Metals, 56 (1963) 442-454," J. Gurland, Current Contents (ET-AS), No. 8, (1983) p. 18.

"Yield, Flow and Fracture of Polycrystals," a report on 1982 Glasgow Conference, J. Gurland, European Scientific Notes, ONR, London, 36, No. 11 (1982) pp. 301-302.

Supported by the United States Department of Energy.

The Mechanical Response of Fiber Reinforced Materials

Work has continued on the dynamic plastic response of composite specimens consisting of a set of steel piano wires embedded in a matrix of lead-tin alloy. The dynamic plastic transverse deformations were produced both by impacts of a fast moving hammer in a "Hyge" shock testing machine and also by the detonation of explosive charges. The blows were applied transversely to the axes of cantilever beams and the deformations were observed by various means which included high speed cinematography and by various electronic techniques. The theory of Spencer and Shaw was tested in two respects: namely, by measuring the final plastic deformation of the cantilever tips and also the final distance

which the plastic wavefront had travelled along the cantilever during impact. Both these quantities were found to be in reasonably good agreement with the predictions of the theory. The theory is based on the simplified concept of a linear strain hardening rigid-plastic model. It was found that the agreement between theory and experiment was improved considerably when account was taken of the strain-rate dependence of the mechanical response of the lead-tin matrix material.

Principal Investigator: H. Kolsky, Professor, Applied Mathematics.

Personnel: J. Mosquera, Graduate Student, Engi-

neering and W. Carey, Technician, Applied Mathematics.

Supported by the Materials Research Laboratory/NSF and the National Science Foundation.

Summaries of Related Work

"Visco-plastic Analysis of Cracks under Quasi-static and Dynamic Conditions" - Professor C. F. Shih (Engineering) - cf. Section 2.

"Crystalline Plasticity" - Professors R. J. Asaro and A. Needleman (Engineering) - cf. Section 2.

"Analysis of Ductile Rupture" - Professor A. Needleman (Engineering) - cf. Section 2.

SECTION 2 FRACTURE OF SOLIDS

Introduction

The primary goal in the fracture thrust is to develop an interdisciplinary program with projects aimed at experimentally studying, and theoretically modelling, the effects of chemistry and microstructure on fracture. Within the thrust are participants whose main interests lie in physical and mechanical metallurgy or micro-mechanics of non-metallic materials and those whose interests are in experimental and theoretical solid mechanics and applied mathematics. A specific aim of the research in this thrust is to provide fundamental understanding of the effects of micromechanical processes on microscopic and macroscopic fracture processes. In this way the work leads not only to fundamental insights into the physics of fracture but also to an incorporation of material properties into modern fracture mechanics methodology. Specific projects during this past year have included (1) large scale numerical (finite element) solutions to quasi-statically and dynamically loaded cracks, using fully rate dependent material constitutive descriptions, (2) further development of the optical method of "caustics" to study dynamic crack propagation in metals in cases where crack tip plasticity is important, (3) studies of dynamic crack growth in anisotropic elastic-plastic materials, (4) correlations of the effects of heat treatment, processing, and microstructure with fracture toughness of steels and composite materials including cemented carbides, and (5) experimental and theoretical study of high rate fracture in fiber composite materials.

Several large strain numerical simulations of ductile rupture and crack tip elastic-plastic fields have been carried out this past year. One study, by finite element method, was concerned with studying rupture in the round bar (axisymmetric) tensile test. The constitutive law used in the calculation was developed earlier in our program and accounts for void formation on the microstructural scale. Rupture was modelled by assuming that the material fails when its stress bearing capacity falls to a critically low value. The results of this novel study show that a "zig-zag" path for fracture is preferred since, even though localized shearing occurs, the constraints due to symmetry lead to a much reduced plastic work if failure takes place by alternating shear, i.e., a "zig-zag" path. In another study of crack tip plasticity effects of material rate sensitivity were studied by developing constitutive laws and numerical procedures that account for visco-plastic material response. This study has now been extended to include inertial effects and has been applied to the problem of a circumferentially notched and pre-cracked bar subjected to stress wave loading. The geometry of the problem, along with the loading conditions, were matched to those used in our experimental studies of dynamic fracture initiation and fracture toughness. Other analyses of dynamic crack in elastic-plastic materials are described in individual project summaries that follow.

The theoretical work on dynamic fracture is coupled to an extensive range of experiments, conducted mostly on steels and on fiber composites, which are designed to elucidate the role of microstructure and fundamental material properties on macroscopic fracture. Experiments have been conducted on fracture initiation in plain carbon steels and high strength steels. Loading rates span a wide range from quasi-static to loading rates near $K_I \sim 10^6 \text{ MPa} \cdot \sqrt{\text{m}}$ --new experimental techniques have been developed that extend this range up to $10^8 \text{ MPa} \cdot \sqrt{\text{m}}$.

The optical method of caustics has been developed further to account for crack propagation in ductile materials where crack tip plastic deformation is extensive. Applications to dynamic crack growth in quenched and tempered ultra high steels have been made to date.

The material properties and constitutive laws used in our theoretical studies are obtained from parallel

experimental studies aimed directly at correlating microstructure, and processing methods, with material behavior. Two such studies involve correlating microstructures in quenched and tempered ultra-high strength steels with ductility and fracture toughness and correlating processing variables and microstructure with the fracture behavior of two phase hard composites, e.g., WC-Co cemented carbide composites. Both studies involve detailed observations of the micromechanics of fracture as they are controlled by microstructures. The work on WC-Co cemented carbides has shown that the "contiguity" of the two phases is a microstructural parameter of primary importance in controlling ductility and fracture toughness in these materials. The work on quenched and tempered steels has indicated the morphology of relatively fine carbides plays an important role in determining fracture toughness. Both these projects have led to models which relate the mechanics of micro-fracture processes to macroscopic toughness.

Additional projects are described in the Research Results.

Research Results

Analysis of Ductile Rupture

We have carried out an analysis of the round bar tensile test using a constitutive model for a porous plastic solid to account for the nucleation and growth of micro-voids. We believe this to be the first analysis of the tensile test that exhibits the failure mode so commonly observed in ductile metals. Final material failure by a loss of stress carrying capacity at some specified void volume fraction is incorporated into the model.

The results of our calculations reproduce the essential features of the cup-cone fracture process. Prior to the initiation of fracture the development of necking in the porous plastic solid is similar to that in a classical plastic solid. The kinematic constraint imposed by the axisymmetric geometry plays an important role in the development of the cup-cone fracture. In the round bar there is a tendency to shear localization, but due to axisymmetry this requires an accompanying compressive hoop strain, which tends to increase the plastic work. The increased plastic work that would be required by a straight shear fracture is avoided by the zig-zag path. The onset of fracture is associated with a sharp knee in the load deflection curve and we find that neck development virtually ceases when fracture initiates, so that our analysis indicates that the reduction in area at failure is a representative measure of the onset of macroscopic fracture in the tensile test.

Principal Investigator: A. Needleman, Professor, Engineering.

Personnel: V. Tvergaard, Visiting Professor, Engineering.

Publication:

"Analysis of the Cup-Cone Fracture in a Round Tensile Bar," V. Tvergaard and A. Needleman, *Acta Metallurgica*, in press.

Supported by the National Science Foundation.

Visco-plastic

Analysis of Cracks Under

Quasi-static and Dynamic Conditions

Recent fracture toughness measurements suggest

that loading rates and time dependent effects may be important at room temperature for certain technologically important structural steels, examples being A533B and 304 stainless steels. To understand some aspects of these effects, analyses based on an over-stress viscoplastic constitutive relation were carried out. In the small-scale-yielding analyses, the load level is controlled by the elastic stress intensity factor K , while the loading rate is controlled by the time rate of change of K . For loading rates in the quasi-static range (between 10^{-4} to 10^{+2} MPa $\sqrt{m/s}$) the near-tip fields are observed to depend on the loading-rate and the period of sustained loading. Similar dependence of the near-tip fields on loading rates is also noted in contained and large scale plasticity regimes where the J -integral is the appropriate crack-tip parameter. These results coupled with a critical stress or critical crack opening displacement criterion suggest that the value of K , or the nonlinear fracture mechanics parameter J , at crack initiation is loading-rate dependent. Further analyses which include dynamic or inertia effects in the momentum equations are being pursued. Energy integrals have been formulated for the accurate determination of the near-tip fields characterized by K or J under dynamic conditions. These integrals involve the integration of stress, displacement gradients, and particle velocity and acceleration over a finite domain and are especially appropriate within the context of finite element analysis. This approach has been employed to study the externally notched round bar subject to a tensile pulse - a configuration employed by Costin, Duffy and Freund to measure the dynamic fracture toughness. The analyses show that the dynamic fracture toughness in the elastic-plastic regime can indeed be estimated from the certain remote measurements proposed by Costin *et al.*

Principal Investigator: C. F. Shih, Associate Professor, Engineering.

Personnel: T. Nakamura, Graduate Student, Engineering.

Publications:

"Energy Integrals for Dynamic Crack Analysis," T. Nakamura, C. F. Shih and L. B. Freund, in preparation.

"Analysis of Dynamically Loaded Circumferentially Notched Round Bars Using Energy Integrals," T. Nakamura, C. F. Shih and L. B. Freund, in preparation.

"On the Time and Loading Rate Dependence of Crack-Tip Fields at Room Temperature - Viscoplastic Analysis of Tensile Small-Scale Yielding," M. M. Little, E. Krempl and C. F. Shih, in Elastic-Plastic Fracture, Second Symposium, Vol. 1 - Inelastic Crack Analysis, ASTM STP 803.

"Viscoplastic Analysis of a Compact Tension Specimen in Mode I Loading," M. M. Little, E. Krempl and C. F. Shih, to appear in Engineering Fracture Mechanics.

Supported by the Materials Research Laboratory/NSF and the National Bureau of Standards

Transverse Shear Effects for Through-Cracks in an Elastic Plate

The state of stress in a thin elastic plate which contains through-cracks has been studied with a view toward assessing the influence of transverse shear on the crack tip stress and deformation fields. Based on the assumption that the through-the-thickness extensional strain is uniform in the thickness direction, a crack tip boundary layer solution has been obtained for the tensile opening mode of deformation (mode I). As anticipated, the generalized plane stress solution prevails everywhere in the plane of the plate except near boundaries. Near points on any smooth boundary, including the crack faces away from the tips, the plane stress solution is only slightly perturbed. Near crack tips, however, a complicated boundary layer is developed. A standard separation of variables approach to the analysis of the boundary layer fails, but an exact solution has been found in the form of a real integral. When evaluated, the solution shows a finite lateral contraction at the crack tip (in contrast to the generalized plane stress result), and the inner solution merges smoothly with the plane stress solution at distances from the tip of one-half to three-fourths of the plate thickness, depending on the value of Poisson's ratio. The connection between the inner and outer stress intensity factors has been verified by application of Rice's path-independent J-integral.

Principal Investigator: L. B. Freund, Professor, Engineering.

Personnel: W. Yang, Graduate Student, Engineering.

Publication:

"Transverse Shear Effects for Through-Cracks in an Elastic Plate," W. Yang and L. B. Freund, Brown University Technical Report, November 1983.

Supported by the National Science Foundation.

The Optical Method of Caustics in Plastic Fracture Mechanics

The shadow spot method, or the optical method of caustics, has been established as a valuable experimental procedure in fracture mechanics for measuring elastic stress intensity factors in planar fracture specimens. It has been observed, however, that if the crack tip deformation fields in specimens of ductile materials can be characterized by means of a single plastic intensity factor, analogous to the stress intensity factor in elastic fracture mechanics, then the shadow spot method has potential for use in measuring this plastic intensity factor. The value of the J-integral has been adopted as the plastic strain intensity factor, and the lateral contraction of a planar specimen of power-law hardening material is calculated in terms of J on the basis of the so-called HRR asymptotic field of elastic-plastic fracture mechanics. For any given value of the hardening parameter, n , the theoretical caustic curve which would be generated by geometrical reflection of normally incident parallel light from points of the deformed specimen surface lying well within the crack tip plastic zone is determined. It has been found that the value of J is proportional to the maximum transverse diameter of the shadow spot to the power $(3n + 2)/n$. The result provides a basis for direct measurement of fracture characterizing parameters in ductile metals and other ductile materials.

Principal Investigator: L. B. Freund, Professor, Engineering.

Personnel: A. J. Rosakis, Graduate Student, Engineering and C. C. Ma, Graduate Student, Engineering.

Publications:

"Optical Determination of the Intensity of Crack Tip Deformation in a Power-Law Hardening Material," L. B. Freund, A. J. Rosakis and C. C. Ma, in Material Behavior Under High Stress and Ultrahigh

Loading Rates, (ed. by J. Mescall and V. Weiss) Plenum, pp. 265-272, 1983.

"Analysis of the Optical Shadow Spot Method for a Tensile Crack in a Power-Law Hardening Material," A. J. Rosakis, C. C. Ma and L. B. Freund, *Journal of Applied Mechanics*, Vol. 50, December 1983.

Supported by the Materials Research Laboratory/NSF and the National Science Foundation.

Analysis of Dynamic Crack Growth in Elastic-Plastic Materials

The study of the effects of inertia during elastic-plastic crack growth has been continued. In previous work in this area, steady-state antiplane shear crack growth had been analyzed for both rate-independent and rate-dependent materials. During this year, the crack growth models were generalized to allow for anisotropic plastic response of the materials. The main conclusions on the importance of inertia in the process are unaltered, but the magnitude of the effect depends on the degree of anisotropy. The main effort was devoted to a numerical study of dynamic crack growth in an elastic-ideally plastic material under plane strain conditions, with particular interest in the influence of inertia on the stress and deformation fields near the crack tip. The material was characterized by the Mises yield condition and J_2 flow theory of plasticity. The shape of the zone of active plastic flow near the crack tip and the variation of stress and strain distributions within this zone were calculated. It was found that material inertia has a significant effect on material response for particles near the moving tip, and the possibility of elastic unloading at points adjacent to the crack path as the crack tip passes is suggested by the numerical results. To simulate fracture propagation in a material which separates by means of a locally ductile mechanism, a critical crack tip opening angle growth criterion is imposed on the solution in order to determine the relationship which must exist between a remotely applied stress intensity factor and the crack tip speed to satisfy the growth criterion. The calculated relationship between dynamic fracture toughness and crack tip speed is compared to experimental data on 4340 steel obtained previously. The measured and calculated toughness-speed relationships were quite similar, providing strong evidence that material inertia on the microscale is a major factor in material

resistance to fracture at high rates.

Principal Investigator: L. B. Freund, Professor, Engineering.

Personnel: P. S. Lam, Research Associate, Engineering.

Publications:

"The Influence of Inertia on Elastic-Plastic Antiplane Shear Crack Growth," L. B. Freund, *Proceedings of the Ninth U. S. National Congress of Applied Mechanics*, pp. 121-126, 1982.

"Some Theoretical Results on the Dependence of Dynamic Stress Intensity Factor on Crack Tip Speed," L. B. Freund, *Proceedings of the NSF/ARO Workshop on Dynamic Fracture*, ed. W. G. Knauss, to appear.

"Elastic-Plastic Finite Element Analysis of Steady State Dynamic Crack Growth in Plane Strain Tension," P. S. Lam and L. B. Freund, *Brown University Technical Report*, October 1983.

Supported by the Materials Research Laboratory/NSF and the National Science Foundation.

Microstructure and Fracture Toughness of Cemented Carbides

The results previously obtained by R. Deshmukh (Brown University Ph.D. 1982) were further evaluated in a theoretical study of the effect of grain growth on contiguity in two-phase structures. In multiphase structures contiguity is an important parameter, particularly in the case of cemented carbides, where a number of properties are related to the contiguity of the carbide phase. Contiguity is also measured to study the sintering mechanism in WC-Co alloys. Previous studies have indicated that the reduction in the contiguity of WC during sintering is a direct result of the disappearance of WC-WC boundaries. However, the effects of geometrical changes in the microstructure which normally occur during sintering have not been investigated. In this work a mathematical model is proposed which relates contiguity to changes of grain diameter. The model predicts that contiguity will decrease as growth of second phase particles takes place. These results were applied to the microstructure of liquid-phase sintered WC-25 wt% Co alloys to account partially for the observed change in contiguity with

time.

Principal Investigator: J. Gurland, Professor, Engineering.

Publication:

"Science of Hard Materials," Proceedings of the International Conference on the Science of Hard Materials, Jackson, Wyoming, 1981, (ed. R. K. Viswanadham, D. J. Rowcliffe and J. Gurland), Plenum Publishing Corporation, New York, NY (1983).

Supported by the Materials Research Laboratory/NSF.

**Failure of
Fiber-Reinforced Materials**

Cracks in plates of fiberglass-epoxy composite have been studied theoretically. The material is composed of two orthogonal families of strong fibers. When a straight crack is running parallel to one family of fibers, the double cantilever model can be used. For dynamic propagation, the idealization of fiber inextensibility leads to a one-dimensional wave equation for the displacement. The fracture criterion furnishes a boundary condition to be satisfied at the crack tip, whose position is unknown. Freund (SIAM-AMS Proc. 12, 21-37 (1979)) has used an energy release rate criterion to solve some specific problems of this sort. Using instead the critical stress criterion, we have shown how to determine the crack length as a function of time for an arbitrary history of the opening displacement at the edge of the plate (1).

In connection with the double cantilever model, work on static deflection of beams has been carried out. For materials composed of fibers parallel and perpendicular to the beam axis, small fiber extensibility tends to lessen the flexural deflection and, by comparison, emphasize the shearing deflection, which is usually neglected in classical beam theory. The Timoshenko shearing correction is based on a displacement field that does not satisfy the boundary conditions. By treating the axial fibers as extensible but the cross-wise fibers as inextensible, we have derived a beam theory that accounts for shearing deflections in a self-consistent way. Except in regions close to the ends of the beam, the deflection is like that given by the Timoshenko theory, but with a different shear correction factor. Experimental work to test this theory is being carried out by

others.

(1) "Crack Speeds in an Ideal Fiber-Reinforced Material," A. C. Pipkin, Q. Appl. Math., forthcoming.

Principal Investigator: Allen C. Pipkin, Professor, Applied Mathematics.

Personnel: Wen-Biao Wang, Research Assistant, Applied Mathematics.

Supported by the Materials Research Laboratory/NSF and the National Science Foundation.

**Fracture of
Fiber-Reinforced Composites
and Elastic Properties of Woven Fabrics**

Work has continued on the study of the propagation of running cracks in test specimens of cross-ply fiberglass composites which consist of rectangular nets of glass fibers embedded in an epoxy matrix (Scotchply 1002). Efforts have been made to refine the simple theory which is based on the model of an ideal fiber-reinforced elastic solid (1) to account for some of the anomalous experimental results observed in this work. The main anomaly observed was that the theory based on the simple model predicts that the fracture path cannot turn through a right angle at any point in its path which is beyond the mid point of the specimen. It has been shown that if the finite extensibility of the material in the fiber direction is taken into account this restriction is lifted and we have found that on the basis of such a theory much better quantitative agreement with experimental results can be achieved.

Some experiments have also been carried out on the elastic properties of woven fabrics to determine how well their response conforms to theoretical predictions. The particular geometry which was investigated was the longitudinal extension modulus of woven linen when it is stretched at 45° to the rectangular fiber directions. The experimental results have been shown to conform well with the theoretical predictions, the effective extensional modulus being very high when the breadth to length ratio is greater than unity, and then falling off to a very much lower value when this ratio is great compared to unity. Under these conditions, fibers no longer are held at both their ends by the grips of the testing machine

and shear deformation become possible.

(1) G. Sun, H. Kolsky and A. C. Pipkin, *Eng. Fract. Mech.* 17, pp. 349-360 (1983).

Principal Investigator: H. Kolsky, Professor, Applied Mathematics.

Personnel: G. Sun, Visiting Scholar, Applied Mathematics, M. Z. Hu, Visiting Scholar, Applied Mathematics, J. Mosquera, Graduate Student, Engineering and W. Carey, Technician, Applied Mathematics.

Supported by the Materials Research Laboratory/NSF.

Oxidation and Fracture Characteristics of Reaction Bonded Silicon Nitride (RBSN)

The application of high strength ceramic materials for high temperature components in gas turbine engines not only requires that these normally brittle materials exhibit high strength, toughness and creep resistance at elevated operating temperatures, but also that they stand up to the hot corrosive and erosive atmospheres within the turbine engines. This requires that the RBSN be as completely reacted and as free of internal flaws (unreacted silicon and porosity) as possible. It also requires that any oxidation of unreacted silicon within the volume of the material and any surface flaws in the RBSN be sealed by the surface treatment to prevent these flaws from acting as fracture initiation sites in service.

The nitridation of silicon compacts containing small amounts of fully reacted silicon nitride powder has been proven to lead to enhanced microstructural control resulting in greater density and fracture toughness. In particular, control over the amount and dispersion of unreacted silicon and α/β ratio in the resulting RBSN was improved considerably. A better understanding of the controlling reaction mechanisms and the role of the 'seed' particles was developed and applied to produce more fully reacted bodies with improved properties.

Various techniques of coating RBSN to reduce high temperature oxidation were developed. Different nitride-based coatings were investigated to determine the relative protection afforded to the underlying RBSN. The role of the coating at low oxidation

temperatures (1000C) is to prevent extensive internal oxidation of the RBSN. Sealing off the short circuit paths in an attempt to isolate the interconnecting porosity considerably reduced the surface area available for oxidation. The role of the coating at higher oxidation temperatures (1200C) is to prevent the conversion of the surface silicon nitride to cristobalite and silica. Therefore, the most successful coatings employed for high temperature protection were those which exhibited the greatest oxidation stability but at the same time had coefficients of thermal expansion to prevent failure by spalling. At 1000C thicker coatings will result in more extensive coverage of the surface pores and thus lead to lower rates of oxidation, whereas at higher temperatures the oxidation rates appeared to be less dependent on coating thickness. In most cases the oxidation of the underlying material was substantially reduced and in some instances completely eliminated.

Principal Investigator: Marc H. Richman, Professor, Engineering.

Personnel: Otto J. Gregory, Graduate Student, Engineering and J. Fogarty, Senior Technical Assistant, Engineering.

Publications:

"Strength and Fracture Toughness of Reaction Bonded Si_3N_4 ," S. C. Danforth and M. H. Richman, *Bulletin of the American Ceramics Society*, 62, 501 (1983).

"Microstructure of RBSN Prepared with Si_3N_4 Additions," O. J. Gregory and M. H. Richman, accepted for publication in *METALLOGRAPHY*.

"The Role of Si_3N_4 Additions in the Reaction Bonding of Silicon Compacts," O. J. Gregory and M. H. Richman, accepted for publication in *J. Mat. Sci.*

"Thermal Oxidation of Sputter-Coated RBSN," O. J. Gregory and M. H. Richman, accepted for publication in *J. Am. Ceram. Soc.*

Supported by the Materials Research Laboratory/NSF.

Summaries of Related Work

"Localization in Rate Sensitive Plastic Solids" - Professor A. Needleman (Engineering) - cf. Section 1.

"Strength and Fracture of Two-Phase Alloys" - Professor J. Gurland (Engineering) - cf. Section 1.

"Strain Rate and Strain Rate History Effects During Plastic Deformation" - Professor J. Duffy (Engineering) - cf. Section 1.

SECTION 3 INORGANIC GLASSES

Introduction

The Inorganic Glasses Group focuses its research on understanding the structures, relaxation phenomena, and electronic states and properties of the three main types of inorganic glasses: ionic and non-ionic oxide glasses, including fast ionic conductors; amorphous semiconductors; and amorphous metals. Fundamental issues concerning the amorphous state are being addressed by studying each of these types of materials and by developing new theoretical and new experimental methods for their investigation.

Among the significant advances achieved in this year and reported briefly in this section are the following. The techniques developed by Tauc for studying relaxation processes of photogenerated carriers using photoinduced absorption were applied to α -Si in which the defect concentration was varied. The results were interpreted in terms of photocarrier trapping in defect states. The carrier transport to these states is dominated by multiple trapping at high temperatures and tunneling at low temperatures. The high temperature data cannot be explained by a model based on geminate recombination. Maris' work on phonon transport in glasses, which provides new insight into processes related to localization as well as transport is reported. Bray, Cole and Risen report studies and development of methods to investigate the structure and behavior of fast ionic conducting (FIC) glasses. This includes particular attention to the central issues of the transport processes. Understanding the underlying structures of these ionic oxide glasses is the key to progress in using them for FIC, optical, or other materials applications, and Bray and Risen report NMR, IR and Raman studies of borate, silicate and related glasses. Their work also has addressed the question of identifying the interactions of particular importance in the glass transformation region, as they are reflected in the structures determined, in order to relate these structures and glass formation interactions to the properties of the glasses.

The problem of understanding glass formation in general and spin glasses in particular is being addressed by Houghton and Kosterlitz

Their most recent studies on disordered systems and spin glasses, which have produced results based on both the infinite range S-K spin glass model and the random axis model of magnetism, are reported here. Experimental studies of metallic glasses at low temperature also are reported here. This work by Elbaum has progressed to the stage at which it is possible to address the effects of annealing on the complex interactions responsible for ultrasonic behavior.

Research Results

Time Resolved Spectroscopy of Amorphous Semiconductors

The techniques for studying relaxation processes of photogenerated carriers using photoinduced absorption were applied to amorphous silicon and amorphous hydrogenated silicon in which the defect concentration was varied. The first work on this problem was picosecond studies of a -Si: H doped with P or B (or both) published in Phys. Rev. Lett. 48, 1132 (1982). In 1982/83, the work was extended to non-hydrogenated amorphous Si in which the defect concentration was varied by using different methods of preparation. a -Si: H: P and electron irradiated a -Si: H. The results were interpreted in terms of photocarrier trapping in defect states. The carrier transport into these states is dominated by multiple trapping at high temperatures and tunneling at low temperatures. This model explains the dependence of the trapping time on temperature and on the density of the states in the gap associated with defects. An important conclusion from this work is that the high-temperature data cannot be explained by a model based on geminate recombination.

The studies on doped samples (a-Si: H:P, a -Si: H:B) and electron irradiated samples were extended into long-time domain (10^{-4} to 10^{-2} sec.) in which the decay of the photoinduced absorption is due to carrier recombination. The recombination decay is a power law indicating that dispersive processes are involved. The dispersion parameter was determined as a function of temperature, doping level, and defect concentration produced by irradiation. The results are a contribution to an understanding of the recombination process in amorphous tetrahedral semiconductors, in particular of the role of tunneling.

Principal Investigator: J. Tauc, Professor, Engineering and Physics.

Personnel: Z. Vardeny, Research Associate, Engineering, J. Strait, Research Assistant, Physics, D. Pfost, Research Assistant, Physics.

Publications:

"Picosecond trapping of carriers in amorphous silicon," Vardeny, Z., Strait, J. and Tauc, J., Appl. Phys. Lett. 42, 580 (1983).

"Photoinduced absorption study of recombination in amorphous Si: H doped with P or B." Pfost, D. and Tauc, J., Sol. State Communications, 48, 195 (1983).

"Time resolved spectroscopy of electronic relaxation processes," Tauc, J., in *Hydrogenated Amorphous Silicon*, ed. J. I. Pankove (Academic Press, NY) (to be published).

Supported by the Materials Research Laboratory/NSF.

Phonon Transport in Dielectric Glasses

We have developed a new computer algorithm to find the phonon density of states and normal mode vibrational patterns for disordered systems. The method is applicable to systems of any dimensionality, and can handle fairly large numbers of particles ($\sim 10^4$). We have used this algorithm to study the localization length for Anderson-localized phonons. This length has been determined for a simple 2-dimensional model of a glass. Numerical results have been obtained for varying amounts of disorder, and as a function of phonon frequency.

Principal Investigator: H. J. Maris, Professor, Physics.

Personnel: M. L. Williams, Graduate Student, Physics.

Supported by the Materials Research Laboratory/NSF.

NMR Study of Fast Ion Conducting Glasses

Ionic motion in fast ion conducting (FIC) glasses in the $\text{Li}_2\text{O-LiCl-B}_2\text{O}_3$ glass system has been studied using NMR techniques. Li^+ NMR spectra indicate the presence of two distinct Li nuclei, mobile and stationary. Spectra have been analyzed to obtain the fraction of mobile ions, F , as a function of temperature. The results have been analyzed with two models. The first method of analysis assumes that the rapid rise of F with increasing temperature corresponds to a transition to the FIC state. Activation energies are calculated assuming that $f \propto e^{-E_A/kT}$. The activation energies obtained appear to be much more sensitive to compositional changes than those obtained from conductivity measurements. The results indicate that addition of LiCl (while keeping total Li content constant) lowers the activation

energy, and then a single Cl provides several sites for Li nuclei to occupy. The second model attributes the observed spectra to a distribution of activation energies. A Gaussian distribution provides a good fit to the data, although it produces mean activation energies which are slightly greater than those obtained by conductivity experiments. The distribution is observed to narrow and move to lower activation energies with increasing Cl content. This again indicates that the Cl ions provide a large number of sites with low dissociation energy for the Li nuclei.

Principal Investigator: P. J. Bray, Professor, Physics.

Personnel: David Hintenlang, Graduate Student, Physics.

Publications:

"NMR Studies of Structure and Ion Motion in Glasses," P. J. Bray, M. L. Lui, D. E. Hintenlang, *Wissenschaftliche Zeitschrift*, 2 International Otto-Schott Colloquium, Jena 1982, p. 409 (1983).

"Recent NMR Studies of Oxide, Fluoride, and Super-ionic Conducting Glasses," P. J. Bray, D. E. Hintenlang, M. L. Lui, R. V. Mulkern, *Glastechnische Berichte*, XIII International Glass Conference, July 1983, Hamburg, p. 892 (1983).

"NMR Studies of Fluoride and Fast Ion Conducting Glasses," P. J. Bray, D. E. Hintenlang, R. V. Mulkern, S. G. Greenbaum, D. C. Tran, and M. Drexhage, *J. Non-Crystalline Solids* 56: 27 (1983).

Supported by the Materials Research Laboratory/NSF.

Spectroscopic Study of Structures in the

Li₂O-LiF-B₂O₃

Fast Ion Conducting Glass System.

One of the key problems in the area of fast ionic conducting (FIC) glasses has to do with the role of added alkali halide. If the halide becomes incorporated in the glass network, the network will be modified and its spectrum reflect this modification. If it does not, the thermodynamic implications are serious and the kinetic factors are forced to dominate in an unexpected manner. The LiF - Li₂O - B₂O₃ is an especially important system to study in this regard because it contains FIC compositions, but the studies to date have shown no halide incorporation. The

previously reported studies were done at compositions at which key spectral features of the network were not present. In this study, initial Li₂O - B₂O₃ compositions were selected so that the Raman bands due to unmodified B₃O₃ rings and moieties containing rings modified by formation of tetrahedral boron were present. With these compositions as the base glasses, addition of LiF was made under controlled conditions and the spectra measured. It was found that additional network conversion was effected by the LiF added, so the alkali halide must modify the network by incorporation. The implications of this work, the determination of cation motion in FIC systems, and investigation of related systems are under investigation.

Principal Investigator: William M. Risen, Jr., Professor, Chemistry.

Personnel: David E. Turcotte, Research Assistant, Chemistry and Efstratios I. Kamitsos, Research Associate, MRL, Chemistry.

Publication:

"A Spectroscopic Study of the Role of LiF in the LiF - Li₂O - B₂O₃ Glass System," D. Turcotte, E. I. Kamitsos, and W. M. Risen, Jr., *Solid State Comm.* (in preparation).

Supported by the Materials Research Laboratory/NSF.

The Structural Environment of Four Coordinated Borons in Alkali Borate Glasses

The environment of four-coordinated borons is being investigated using NMR techniques. Three techniques are currently being used:

(a) The narrow response from four-coordinated borons in the ¹¹B NMR spectrum is being studied very carefully at low magnetic fields and resonance frequencies. Since the ¹¹B quadrupolar interaction

varies as Q_{cc}^2/ν_0 where Q_{cc} is the quadrupole coupling constant and ν_0 is the resonance frequency in the absence of quadrupole effects, the interaction is larger at low frequencies. Analysis of the characteristic asymmetric line shape generated by the second-order interaction will yield a value of Q_{cc} . If successful, this procedure will permit the "fingerprinting" of the various BO₄ configurations in

glasses in the same way BO_3 groups have been "fingerprinted" in the past.

(b) The portion of the ^{10}B NMR spectra for the glasses will be analyzed to extract Qcc and (possibly) the asymmetry parameter η which measures the departure of the electric field gradient tensor from axial symmetry.

(c) A special study of glasses with different ratios of ^6Li to ^7Li will yield information on the strength of the dipolar interaction in ^{11}B NMR due to the nearby arrangement of the lithium ions. The variation of the dipolar broadening with changes in the $^6\text{Li}/^7\text{Li}$ ratio can be used to determine the boron-lithium separation distance.

Through these studies more information will be gained on whether the extent of short-range order in alkali borate glasses extends beyond nearest neighbors. Particular attention is being placed on glasses in the diborate composition range where other studies have indicated that structures similar to the lithium diborate crystal may exist.

Principal Investigator: P. J. Bray, Professor, Physics.

Personnel: S. J. Gravina, Graduate Student, Physics.

Supported by the National Science Foundation.

A Structural Study of Lithium Borosilicate Glasses

A ^{11}B NMR study of the boron coordinations in the lithium borosilicate glass system has yielded information on the compositional dependence of N_4 , the fraction of boron atoms in BO_4 units, N_{3S} , the fraction of boron atoms in symmetric BO_3 units, and N_{3A} , the fraction of boron atoms in asymmetric BO_3 units. Initially, N_4 increases linearly with increasing lithium oxide content in the glass. In this region the boron coordination in the glass is independent of the SiO_2 content. This behavior continues until the ratio of lithium oxide content to boron oxide content is higher than a critical value R_2 , which increases linearly with the SiO_2 content of the glass. Beyond R_2 , N_4 decreases while N_{3A} increases with higher lithium oxide content. In this region the presence of SiO_2 favors the formation of BO_4 units.

This behavior of boron coordinations in the lithium borosilicate glass system is qualitatively similar to that in the sodium borosilicate glass system. However, there are significant quantitative differences showing that the microstructures in the two glass systems are different. This is in contrast to the binary alkali borate glass systems where the substitution of one alkali oxide for another does not affect the boron coordinations in the glass.

Principal Investigator: P. J. Bray, Professor, Physics.

Personnel: Ming L. Lui, Graduate Student, Physics.

Supported by Owens-Corning Fiberglass, Inc.

NMR Study of Heavy Metal Fluoride Glasses

An F^{19} NMR study of heavy metal fluoride glasses has been undertaken to examine the dependence of fluorine motion on glass composition. The results indicate that the addition of the glass stabilizing agents LaF_3 and AlF_3 to the binary system $\text{ZrF}_4\text{-BaF}_2$ raises the activation energy of fluorine motion by 30 to 60%. These results are consistent with the observed changes in microhardness as a function of composition. Both indicate a tightening of the glass structure with the addition of stabilizing agents.

Optical dispersion measurements by previous workers indicated that lithium and sodium play markedly different structural roles upon the addition of up to 20 molar % of the appropriate alkali halide to the glass network. Of the glasses studied by NMR, those containing 20 mol % LiF had by far the highest activation energy of 0.75 e.v./ion while a similar glass with 20 mol % NaF had an activation energy of only 0.35 e.v./ion. The result supports the contention that sodium and lithium enter the glass network differently.

Principal Investigator: P. J. Bray, Professor, Physics.

Personnel: R. V. Mulkern, Graduate Student, Physics.

Publications:

"Recent NMR Studies of Oxide, Fluoride, and

Superionic Conducting Glasses," P. J. Bray, D. E. Hintenlang, M. L. Lui, R. V. Mulhern, *Glastechnische Berichte*, XIII International Glass Conference, July 1983 Hamburg, p. 892 (1983).

"NMR Studies of Fluoride and Fast Ion Conducting Glasses," P. J. Bray, D. E. Hintenlang, R. V. Mulhern, S. G. Greenbaum, D. C. Tran, and M. Drexhage, *Journal of Non-Crystalline Solids*, Vol. 56, p. 27 (1983).

Supported by the National Science Foundation.

NMR Studies of Glasses Based on Boron Sulfide

Fast ion conducting (FIC) glasses based on B_2S_3 have recently been fabricated. NMR studies have been performed to examine the microstructure of glassy B_2S_3 and binary glasses in the Li_2S - B_2S_3 system. ^{41}B NMR spectra of g - B_2S_3 revealed only 3-coordinated boron and no motional narrowing of the NMR spectra at temperatures up to 500K, in contrast to an NMR study performed by other workers.

We have observed that, without proper out-gassing of the glass melt, residual H_2S may form some four-coordinated boron, and large quantities of residual gases may allow the motional narrowing of the spectra that was previously observed.

Binary glasses were made over the range of possible glass formation by splat quenching the glass melt. Addition of Li_2S was observed to create some four-coordinated boron. The fraction of four-coordinated boron, N_4 , obtained as a function of composition, is qualitatively similar to that obtained in the analogous oxide glasses, but quantitatively different. Li spectra in these glasses consist of extremely narrow lines at room temperature, indicating very rapid motion of Li ions at these temperatures.

Principal Investigator: P. J. Bray, Professor, Physics.

Personnel: David Hintenlang, Graduate Student, Physics.

Supported by the Materials Research Laboratory/NSF.

Protons in Natural Glasses

The different structural arrangements for protons within natural glasses can be determined using NMR. The protons within the glass can incorporate themselves in three ways: 1) hydroxyl groups, 2) molecular water, 3) hydronium ions.

The hydroxyl group consists of a single hydrogen atom bonded to an oxygen atom. Since the oxygen nucleus possesses no magnetic moment, it will not contribute any dipolar broadening or splitting to the proton NMR response. The observed proton NMR spectrum is a single line. However, it is possible for a neighboring alkali ion (if present) to interact with the proton and broaden the resonance appreciably.

Molecular water (H_2O) can exist within the glass system with individual molecules sitting interstitially in the glass network. Molecular water can be modeled as a "Pake doublet". The Pake doublet is characterized by 2 resonant peaks symmetrically located around the proton resonance frequency.

Hydronium can be modeled as a three-spin system. This also will lead to a characteristic resonant line shape with two symmetrically-located peaks and a third peak at the proton resonance frequency.

At sufficiently low temperatures, these characteristic line shapes are distinct. However, at higher temperatures they all collapse into a narrow line due to thermal motion which averages out the interactions.

The narrow proton line in several natural glasses has been observed at room temperature. The expected continuation of this study will be to perform NMR studies at lower temperatures in order to "freeze-out" the different structural arrangements, and obtain quantitative measures for the amount of each structure present in the glasses.

Principal Investigator: P. J. Bray, Professor, Physics.

Personnel: Edward J. Holupka, Graduate Student, Physics.

Publication:

"Proton Resonance in Natural Glasses," P. J. Bray and E. J. Holupka, *Journal of Non-Crystalline Solids*. Accepted for publication.

Supported by Sandia Laboratories.

**Glass Formation
and Transition in
Alkali Pentasilicate Glasses**

The far infrared and Raman spectra of alkali pentasilicates and series of analogous mixed alkali pentasilicates were studied as a function of preparation condition and composition to investigate the relationship between the interactions of importance in glass formation and in glass transitions. In recent work we observed cation-network vibrational features of several of the glasses, as prepared, and showed that certain of the Raman bands reflect disorder in the network due to the sort of network angle distributions that result from the presence of dissimilar cations. In this study the behavior of the cation-network bands upon annealing, in both single and mixed alkali glasses, was found to show that the cation-site interaction is optimized in the glass formation process, and does not change in either frequency or breadth with annealing. Moreover, it was found that the force field for this interaction in the glasses varies linearly with their glass transition temperature. However, the band widths of vibrations reflecting network disorder decrease with annealing, consistent with the interpretation that the cation-site nearest neighbor structure is optimized initially and that the annealable structure involves connecting network portions. These results lead to two postulates: that the cation-site band breadth is due to a wide distribution of vibrational couplings to the network rather than to a range of cation-site structures; and, that the same cation-site interaction is key to both glass formation and glass transition. Research to test these postulates, investigate their consequences, and form a more complete picture of ionic oxide glasses is now underway.

Principal Investigator: William M. Risen, Jr., Professor, Chemistry.

Personnel: Efstratios I. Kamitsos, Research Associate, Chemistry.

Publication:

"Vibrational Spectra of Single and Mixed Alkali Silicate Glasses," E. I. Kamitsos and W. M. Risen, Jr., *J. Noncryst. Solids*, accepted for publication (1983).

Supported by the Material Research Laboratory/NSF.

**Time Domain Spectroscopy
of Glass and Polymers**

Exploratory measurements were made on a series of mixed alkali oxide-silicate glasses, of composition $x\text{Cs}_2\text{O}$, $(1-x)\text{Na}_2\text{O}, 5\text{SiO}_2$, in collaboration with the research group of W. M. Risen, Jr. These showed losses in the 0.1-10GHz region which were not much greater than fused quartz (silica) for the sodium glass ($x=0$), significantly so for the cesium glass ($x=1$) and indications of decreased losses at intermediate compositions. The results need to be refined by a powerful technique developed here to correct for small residuals, but suggest that the systems do exhibit a mixed alkali effect at microwave frequencies, not unlike that for d.c. conductance, which may make them useful as dielectric materials with very low loss.

As a preliminary to studies of fast ionic conducting glasses, which are of interest for use as solid electrolytes, design work was done to develop suitable cells for measurement of samples which can be readily produced, with procedures of correcting unavoidable imperfections in both.

A series of measurements with J. Perl (visiting from IIT) has shown that solutions of water with 1-propanol exhibit a single principal Debye relaxation rather than two for uncoupled motions of the two kinds of dipolar molecules. A faster relaxation was also found, centered at 4GHz independent of composition over most of the range and also indicative of local but cooperative motions in hydrogen bonded complexes rather than 'one molecule' diffusion like reorientations.

Principal Investigator: R. H. Cole, Professor, Chemistry.

Personnel: Paul Winsor IV, Research Associate, Chemistry and Jeffery Perl, Graduate Student, Visitor for six weeks from Illinois Institute of Technology.

Publications:

"Bridge Sampling Methods for Admittance Measurements from 500kHz to 5GHz," R. H. Cole, *IEEE Trans. Instrumentation and Measurement* IM-32, 42

(1983).

"Dielectric and NMR Relaxation of Poly (methyl vinyl ketone) in Dilute Solution," S. Mashimo, P. Winsor, and R. H. Cole; K. Matsuo and W. H. Stockmayer, *J. Phys. Chem.*, 16,965 (1983).

Supported by the Materials Research Laboratory/NSF and National Science Foundation.

Theoretical Studies of Spin Glasses

We have been investigating the random axis model of magnetism as a model of a class of disordered systems which display spin glass order at low temperatures. The experimental importance of this model is that it is believed to describe certain rare earth alloys and its theoretical importance is that it is soluble for arbitrary dimension in the limit of the number of spin components $N = \infty$. In this limit, the model has a high temperature paramagnetic phase and a low temperature spin glass phase for $2 < d < 4$. Above four dimensions there is also a ferromagnetic phase. However, this limit is unphysical and the existence of a spin glass for $d > 2$ may be an artifact of the $N = \infty$ limit. We have been investigating the stability of the spin glass phase in the replica formalism for finite N by $1/N$ expansions.

In the $N = \infty$ limit, the spin glass phase is replica symmetric which is believed to mean that the phase is ergodic so that equilibrium statistical mechanics is applicable. When we look at the stability of this phase against Gaussian fluctuations we find that the stability matrix has at least one eigenvalue of the wrong sign which means that the spin glass phase is one of broken replica symmetry. The calculations are technically complicated but we are convinced that our results are correct. These results imply that the spin glass phase is non-ergodic and suffers from all the diseases of the more conventional band-disordered spin glass. This throws doubt on the existence of a separate low temperature phase for $d > 4$, but investigations into the nature of this phase are for the future.

Principal Investigator: J. M. Kosterlitz, Professor, Physics.

Personnel: Anil Khurana, Research Associate, Physics and Anu Jagannathan, Research Assistant, Physics.

Supported by the Materials Research Laboratory/NSF.

Disordered Systems and Spin Glasses

We have studied the dynamics of the infinite-range Sherrington-Kirkpatrick spin-glass model for which relaxation times diverge when N , the number of spins, tends to infinity. Calculations on a large but finite system are very difficult, so we mimic a large finite system in equilibrium by working with $N = \infty$ and imposing, by hand, a canonical distribution at an initial time. For short times, where no barrier hopping has occurred we find that the Edwards-Anderson order parameter, q_{EA} , is identical to that obtained from an analysis of the mean-field equations of Thouless, Anderson, and Palmer and, with further assumptions, gives $q(x=1)$ in Parisi's theory, in agreement with earlier work. For times longer than the longest relaxation time (of the finite system), true equilibrium is reached and our theory agrees with previous statistical-mechanics calculations using the replica trick. There is no violation of the fluctuation-dissipation theorem. A simple physical interpretation of the Parisi variable x is given. Rather than interpret x as a time as had been suggested, it was shown that $dx(q)/dq$ is the probability that the overlap of the site magnetization, between different phases than the system can exist in, is q .

Principal Investigator: Anthony Houghton, Professor, Physics.

Personnel: F. Seco, Research Assistant, Physics.

Publications:

"Role of Initial Conditions in Spin Glass Dynamics and Significance of Parisi's $q(x)$," A. Houghton, S. Jain and A. P. Young, *J. Phys. C16*, L375 (1983).

"Role of Initial Conditions in the Mean Field Theory of Spin Glass Dynamics," A. Houghton, S. Jain and A. P. Young, *Phys. Rev. B28*, 2630 (1983).

Supported by the Materials Research Laboratory/NSF.

Ultrasonic Studies of Metallic Glasses

We have previously reported a series of ultrasonic observations on two families of metallic glasses

(PdSiCu, PdNiP) at low temperatures (below ~ 1 K). The results showed that in these materials ultrasonic attenuation as a function of amplitude, frequency and temperature does not behave in accordance with predictions of the two-level system (TLS) tunneling theory. We have since then found that two stages exist in the amplitude dependence of ultrasonic attenuation in metallic glasses at low temperatures. One of these stages (the "first") occurs at relatively low amplitudes and has the frequency and temperature dependence predicted by the TLS tunneling theory. At higher amplitudes this is followed by the stage which we previously observed and discussed. This ("second") stage is characterized by an amplitude dependence which can be several powers of ten larger than the "first" stage and has the frequency and temperature dependence described earlier. As an extension of these studies we have been conducting experiments on the effects of "relaxing" the glass on the above properties. This involves systematic annealing treatments, within the temperature range of the glass' stability, for various periods of time, followed by ultrasonic studies at low temperatures.

Principal Investigator: C. Elbaum, Professor, Physics.

Personnel: A. Hikata, Professor (Research), Applied Mathematics and G. Cibazar, Graduate Student, Physics.

Supported by the Materials Research Laboratory/NSF and the National Science Foundation.

NMR Study of the Mixed - Alkali Effect in Aluminas

Pulsed NMR studies have been performed on K- β alumina and Na (0.5) - K (0.5) β alumina in an investigation of the mixed-alkali effect. The spin-lattice relaxation time, T_1 , was measured for ^{27}Al nuclei. The relaxation of ^{27}Al nuclei is governed by the fluctuating electric field gradients produced by the mobile cations, and can therefore be used as a probe of ionic motion. K- β alumina exhibits a minimum in T_1 at about 333K, while the mixed-alkali effect manifests itself by shifting the minima of Na (0.5) - K (0.5) β -alumina to a higher temperature, 500K. The activation energies obtained on the low side of the minima are, however, identical for both samples. It is felt that this is because NMR is detecting the local motion of the cations in regions associated with interstitial O^{2-} . If this analysis is correct, the reported data indicate that the mixed alkali effect in β -alumina is induced by a change of vibrational frequencies of mixed-alkali pairs due to polarization differences of the different cations.

Principal Investigator: P. J. Bray, Professor, Physics.

Personnel: David Hintenlang, Graduate Student, Physics.

Supported by the Materials Research Laboratory/NSF.

SECTION 4 SOLID SURFACES

Introduction

The general objective of the surface research program is to develop improved microscopic models of the fundamental physical properties of solid surfaces, and a better understanding of the relationship of these properties to the chemical interactions occurring at the interface. Thus, studies have been made of the crystallographic and electronic surface structure which have served as a basis for investigations of dynamic phenomena such as inelastic scattering, adsorption and desorption. The program has involved collaborations between physicists and chemists, and has included both experimental and theoretical studies.

Results obtained by individual investigators are reported in the following section. Among them is the finding, by Diebold, that optically pumped sodium atoms can be used as a highly sensitive probe of atom-surface scattering. Greene has succeeded in diffracting helium atom beams from solid surfaces and is extending the experiments to other noble gases. At the same time, Cole has investigated theoretically the interaction of such atoms with solid substrates. Greene has also measured alkali metal desorption rates and thereby explored effects of surface phase transitions on chemical dynamics. Parallel studies by Estrup have shown that reconstructive transitions can dominate the kinetics of adsorbate dissociation and desorption. These investigations rely on detailed experimental and theoretical work, due to Estrup and Ying, on the phase transitions that take place at molybdenum and tungsten surfaces. As an aid in the study of the electronic structure of these and other surfaces, work has been undertaken by Stiles and Estrup to enhance the sensitivity of optical surface spectroscopy by electoreflectance techniques.

Research Results

The Scattering and Ionization of Atoms at Surfaces

Further studies of the rates of desorption of Li, Na, K, and Cs atoms from the (111) and (100) surfaces of silicon at low coverages extend work reported earlier. The different rates for surfaces stable and metastable in the temperature range 800-1000K are interpreted as resulting from phase changes at $1120 \pm 40\text{K}$ (111) and $980 \pm 20\text{K}$ (100). The measurements are fitted by a model that has the stable surface consisting of terraces separated by widely spaced edges or steps where most of the adsorbed atoms are concentrated and interact. On the terraces as well as the whole metastable surface, there is rapid two-dimensional diffusion and the atoms move independently. Similar experiments on surfaces of pyrolytic graphite and SiC show different behavior in that there is no interaction between the adsorbed atoms and adsorption appears to occur on two, or sometimes three, kinds of sites with different binding energies.

Beams of He, Ne, Ar and Kr scattered from the (100) surface of LiF show structure that in the case of He is well-resolved into individual diffraction peaks. Improvement in the resolution and signal-to-noise ratio for the scattering of the other gases is needed. This is expected to result from a new method using a pulsed nozzle and two chopper disks to produce beams with a very narrow ($\sim 1\%$) range of velocities. Design and construction of the apparatus needed are proceeding well.

Principal Investigator: E. F. Greene, Professor, Chemistry.

Personnel: A. LeGrand, Graduate Student, Physics and D. (Locotos) Stewart, Graduate Student, Chemistry.

Publications:

"Silicon (111) and (100) Surfaces and Their Interactions With Cs, K, Na, and Li; Phase Changes and Kinetics of Desorption Studied by Surface Ionization," E. F. Greene, J. T. Keeley and M. A. Pickering, *Surface Science* (submitted).

"Influence of Surface Phase Transitions on Desorption Kinetics: Compensation Effect," P. J. Estrup, E. F. Greene, A. M. Horlacher and M. A. Pickering,

Bull. Am. Phys. Soc. 28, No. 3, 336 (1983).

Supported by the Materials Research Laboratory/NSF, the Department of Energy and the National Science Foundation.

Optically Pumped Atoms as a Scattering Probe

Hyperfine state changes of Na atoms induced by scattering off LiF surfaces have been studied using an optical pumping technique. In this method, a tunable high resolution visible dye laser is used to select a single ground ($F=1$) hyperfine state of collimated Na atoms which are subsequently scattered off a well-characterized LiF surface. The same laser is used to probe the scattered fluorescence intensity via a modulation/locking detection system, yielding a measure of the amount of state selection remaining in the scattered beam. Preliminary results lend strong support to the conclusion that the scattering event induces significant hyperfine state changes in the sodium; a high percentage of incident state selection is seen to be lost after the scattering event. This implies a magnetic interaction near the surface which scrambles the hyperfine states during the collision. Further detailed theoretical and experimental studies will soon be under way.

Principal Investigator: Gerald J. Diebold, Assistant Professor, Chemistry.

Personnel: Paul R. Muessig, Research Assistant, Chemistry.

Supported by the Materials Research Laboratory/NSF.

Experimental Studies of Chemisorption

The kinetics of dissociation and desorption of simple molecules adsorbed on transition metal surfaces are being investigated. The rate of these processes, under isothermal or temperature-programmed conditions, is measured through the changes observed in the photoelectron (XPS and UPS) spectrum from the surface and the mass-spectrum from the gas phase. Results have been obtained for chemisorbed CO and C_2H_2 on Mo(100) and Mo(110). The activation energy for CO dissociation is found to be strongly dependent on crystal orientation, being 0.60 eV for the (100) face and 0.85 eV for the (110) face.

Co-adsorbed carbon decreases, and co-adsorbed oxygen increases, the activation energy for dissociation, while both co-adsorbates decrease the desorption energy (for β -CO). The data are consistent with a model in which metal back-donation to the CO π^* antibonding orbital weakens the C-O bond. The results for C_2H_2 dissociation indicate that the C-C bond scission obeys first order kinetics, with activation energy 1.4 eV on clean Mo(110), a value which is decreased significantly by co-adsorption of either C or O. The effect of co-adsorbed sulfur is currently under study.

Principal Investigator: P. J. Estrup, Professor, Physics and Chemistry.

Personnel: J. Erickson, Graduate Student, Physics.

Supported by the Materials Research Laboratory/NSF.

Surface Reconstruction and Surface Phase Transitions

Studies of surface reconstruction on molybdenum and tungsten, and of the associated phase transitions, have continued. Recent efforts have been focused on the nature and origin of structural transformations induced by temperature changes and by the presence of adsorbed species. Detailed results have been obtained for the H/W(100) system, for which the phase diagram has been extended to temperatures above 400K and a new region of incommensurate phases has been discovered. By combining LEED observations with accurate adsorption-desorption measurements, the enthalpy and entropy changes for the reconstruction have been determined for the first time. The results indicate that the reconstruction involves a pronounced stiffening of the substrate lattice, corresponding to an increase in the effective surface Debye temperature from about 200K to about 300K.

Principal Investigator: P. J. Estrup, Professor, Physics and Chemistry.

Personnel: L. D. Roelofs, Research Associate, MRL, A. M. Horlacher, Graduate Student, Chemistry and J. W. Chung, Graduate Student, Physics.

Publications:

"Two-Dimensional Phases in Chemisorption Systems," L. D. Roelofs and P. J. Estrup, *Surface Sci.*

125, 51 (1983).

"Compatibility of FIM and LEED Observations for the W(100) Reconstruction," P. J. Estrup, L. D. Roelofs and S. C. Ying, *Surface Sci.* 123, L703 (1982).

"Desorption of Hydrogen from Tungsten (100)," A. M. Horlacher, R. A. Barker and P. J. Estrup, *Surface Sci.* (in press).

Supported by the Materials Research Laboratory/NSF and the National Science Foundation.

Structural Phase

Transition on W and Mo Surfaces

Two model Hamiltonians: The ϕ^4 model and the X-Y model with cubic anisotropy, have the appropriate symmetry for a description of the various phase transitions seen on W and Mo(001) surfaces. They have been studied extensively with the help of self-consistent phonon theory, Migdal renormalization group analysis, and Monte-Carlo simulation. We have accomplished two major goals in the past year. First, the subsurface layer degrees of freedom as well as the adsorbate variables have been integrated to provide an explicit temperature and coverage dependent effective two-dimensional Hamiltonian. This model Hamiltonian, besides useful as a starting point for detailed study of the phase diagram, shows clearly how incommensurate phase arises from competition of two length scales from interlayer and intralayer couplings.

Secondly, the Monte Carlo simulations demonstrate that the finite size effect for the X-Y model is far greater than the ϕ^4 model. This is due to the fact that in the X-Y model, the short range order persists a long way above the transition temperature T_c . This result provides an immediate explanation for the puzzling long tail in the LEED data for W(001) and Mo(001).

Principal Investigator: S. C. Ying, Professor, Physics.

Personnel: G. Y. Hu, Research Assistant, Physics.

Publications:

"Monte-Carlo and Renormalization-Group Studies of Surface Structural Phase Transitions," L.D. Roelofs, G. Y. Hu and S. C. Ying, *Phys. Rev. B* 11, (1983).

"Model for the Surface Reconstruction Phase

Transition of Clean and Hydrogen Adsorbed W(001) and Approximate Solution," L. D. Roelofs, S. C. Ying and G. Y. Hu, A.V.S. Symposium, Boston, (1983).
 "Effective Two-Dimensional Lattice Dynamic Hamiltonian for Surface Structural Phase Transition," S. C. Ying and G. Y. Hu, A.V.S. Symposium, Boston, (1983).

Supported by the Materials Research Laboratory/NSF.

Surface

Reflectance Spectroscopy

Electroreflectance techniques are being developed to enhance the surface sensitivity of this optical method. A large AC electric field is applied to the surface under investigation with the aid of a removable transparent electrode. This field, which is normal to the surface, modulates the optical properties of the surface region while the bulk contribution to the reflectivity remains unchanged. An *in situ* tungsten filament provides the incident light and permits a simple and convenient optical system. The difference in electroreflectance spectra from clean and adsorbate-covered surfaces is used to obtain information about the interface region. In the visible region the spectra provide data about changes in the joint density of electronic states. In the infra-red, absorption peaks due to adsorbed species are identified by means of the Stark effect. Experiments are underway which combine the electroreflectance technique with standard methods such as LEED, AES and ESD in studies of semiconductor (Ge) and metal (Mo and W) surfaces.

Principal Investigators: P. J. Estrup, Professor, Physics and Chemistry and P. J. Stiles, Professor, Physics.

Personnel: B. D. Parker, Graduate Student, Physics and J. Prybyla, Graduate Student, Chemistry.

Supported by the Materials Research Laboratory/NSF.

Molecular

Interactions in Physisorption

Theoretical studies have been carried out concerning the nature of the fundamental interactions occurring between physisorbed species, and between the adsorbed species and the substrate. Explicit calculations have been done for a system consisting of noble gas atoms adsorbed on a graphite surface. In addition, a theory has been developed to describe deviations from two-dimensionality of an adsorbed film.

Principal Investigator: M. W. Cole, Visiting Professor, Physics and Chemistry.

Publications:

"The Interaction Between Noble Gases and the Basal Plane Surface of Graphite," M. W. Cole and J. R. Klein, *Surf. Sci.* 124, 547 (1983).

"Substrate Mediated Dispersion Interaction Between Adsorbed Atoms and Molecules," Suzanne Rauber, J. R. Klein, M. W. Cole and L. W. Bruch, *Surf. Sci.* 123, p. 173 (1982).

"Substrate Screening of the Interaction Between Adsorbed Atoms and Molecules," Suzanne Rauber, J. R. Klein and M. W. Cole, *Physical Review B* 27, 1314 (1983).

"Deviation From Two-Dimensionality in Classical Adsorbed Films," P. A. Monson, M. W. Cole, Flavio Toigo, William A. Steele, *Surf. Sci.* 122, p. 401 (1982).

Supported by the Materials Research Laboratory/NSF and the National Science Foundation.

Summaries of Related Work

Electronic Properties of Semiconducting Surface Space Charge Layers - Professor J. J. Quinn (Physics) - cf. Section 5.

Electronic Properties of Two-Dimensional Systems - Professor P. J. Stiles (Physics) - cf. Section 5.

SECTION 5 LOWER DIMENSIONALITY MATERIALS AND STRUCTURES

Introduction

A number of different three dimensional structures studied in materials science have in common the interesting feature that, in the appropriate temperature range, their behavior is characteristic of a system with lower dimensionality. Surface space charge layers at semiconductor interfaces are a prime example. The motion of carriers normal to the interface is quantized by the interface potential. At low temperature the energy separation between the quantized levels is large compared to thermal energies. The carriers are unable to make transitions to higher quantized levels, but are completely free to move along the interface; thus they behave as a two dimensional electron gas.

The goal of the lower dimensional materials and structures group is to understand the elementary excitations, the thermodynamic, transport, and optical properties of a number of different systems whose behavior is dominated by this lower dimensional character.

The space charge layer at semiconductor interfaces, already mentioned, are just one example. Thin metallic films or wires, both normal and superconducting, are another. Liquid crystal films and thin magnetic films are additional examples. In all of these systems there is some characteristic length which controls the behavior of the sample. If this characteristic length is large compared to one (or more) of the sample dimensions, the sample behavior is characteristic of a lower dimensional system. For example, in normal metal films the conductivity is controlled by the electron mean free path. If this mean free path is very large compared to the film thickness, the conductivity will be characteristic of a two dimensional system. The same is true in ordered phases if the coherence length, or range of the order parameter, for the condensed phase exceeds the sample thickness. The lower dimensional materials and structures group tries to take advantage of these similarities between quite different materials in understanding their physical behavior.

Research Results

Electronic Properties of Semiconducting Surface Space Charge Layers

We extended our study of collective modes and optical absorption in semiconducting surface space charge layers to superlattice structures.

In earlier work, K. S. Yi and J. J. Quinn investigated the subband structure, the elementary excitations and the optical properties of space charge layers at anisotropic semiconductor surfaces, like the Si-(111) and Si-(110) surfaces. This work made definitive predictions on the number and position of resonance in the optical absorption spectrum, how the resonances depended upon the angle of incidence, the polarization and frequency of the incident radiation, and on the thickness of the insulating layer and the gate electrode. These predictions coupled with careful optical studies should clear up completely the question of valley degeneracy in Si-(111) and Si-(110) surface inversion layers.

Two extensions of the Yi-Quinn work are immediately suggested. One is to use the non-local theory of surface response to study the problem of surface reflectance spectroscopy. Pioneering experimental work in this area has been carried out by Estrup and Stiles and their collaborators in the surface-thrust of the Brown MRL. Our theoretical work should help in the understanding of their results, since an ordered chemisorbed layer has many properties similar to those of a surface space charge layer. This work is in an early stage of development. The second extension is to the study of collective modes and optical properties of semiconductor superlattice structures. These materials can be thought of as a periodic array of space charge layers. Some important results in this area have already been obtained by Tselis, Gonzalez de la Cruz and Quinn. Among these results are the dispersion of intrasubband and intersubband plasma modes in semiconductor superlattices. Currently, work on surface plasma modes and their coupling to surface and bulk phonons in superlattices is being studied.

Principal Investigator: John J. Quinn, Professor, Physics.

Personnel: Gerardo Gonzalez de la Cruz, a visiting postdoctoral fellow from the Institute Polytechnic, Mexico.

Publications:

"Linear Response of a Surface Space Charge Layer on an Anisotropic Semiconductor," J. J. Quinn and K. S. Yi, *Phys. Rev. B* **27**, 1184 (1983).

"Optical Absorption and Collective Modes of Surface Space Layers on Anisotropic Semiconductors," J. J. Quinn and K. S. Yi, *Phys. Rev. B* **27**, 2396 (1983).

"Helicon Modes in Semiconducting Superlattice Structures," J. J. Quinn, A. Tselis and G. Gonzalez de la Cruz, *Solid State Comm.*

"Collective Modes of Type II Semiconductor Superlattices," J. J. Quinn, A. Tselis and G. Gonzalez de la Cruz, *Proc. EP2DS V Conf.*, Oxford, p. 497 (1983), to appear in *Surface Sci.*

Supported by the Materials Research Laboratory/NSF and the National Science Foundation

Electronic Properties of Two-Dimensional Systems

The unique behavior of the quasi two-dimensional system has focused a great deal of research effort on these lower dimensional systems. Their unique behavior has been revealed more fully with the observation of the quantum Hall effect. We have been studying the magnetoconductivity of these systems at low temperatures, where the effect of temperature is not dominating. We are studying the oscillations in the magnetic moment known as the de Haas-van Alphen effect, the magnetocapacitance as a function of frequency and resistance, the thermopower with and without a magnetic field and an entirely new effect known as the quantized resistance, in a hope of elucidating the role of the density of states in the quantized Hall effect. It is not that these effects are not interesting in their own behalf (they give important information on the system in their own right), it is just the ease of combining them in a description. The four effects give varying aspects of the density of states, its dependence on energy, frequency, magnetic field, its energy derivative, the state of localization and others. Each of the effects gives results that are convoluted in a different way. It is hoped that we will continue to unravel their behavior. We have had success in all of the effects.

Principal Investigator: Phillip J. Stiles, Professor, Physics.

Personnel: H. Closs, Graduate Student, Physics, B. B. Goldberg, Graduate Student, Physics, R. P. Smith, Graduate Student, Physics, D. Syphers, Graduate Student, Physics, R. Zeller, Graduate Student, Engineering and L-C. Zhao, Graduate Student, Applied Mathematics.

Publications:

"Quantum Hall Studies in Si MOSFETS for ν Less Than One," D. A. Syphers, J. S. Brooks and P. J. Stiles, *Solid State Comm.* 46, 243 (1983).

"Quantized Magnetoresistance in Two-Dimensional Electron Systems," F. F. Fang and P. J. Stiles, *Phys. Rev. B* 27, 6487 (1983).

"Shubnikov-de Haas Oscillations in Si Inversion Layers," K. C. Woo and P. J. Stiles, *Phys. Rev. B*, 28(12) 7101 (1983).

"de Haas-van Alphen Effect in a Si Inversion Layer," F. F. Fang and P. J. Stiles, *Phys. Rev. B*, 28(12) 6996 (1983).

"The Complex Capacitance of Si Inversion Layers in the Quantized Resistance Regime," B. B. Goldberg, D. A. Syphers, L-C. Zhao and P. J. Stiles, *Proc. Vth Intl. Conf. on Electronic Properties of Two-Dimensional Systems* (1983, Oxford) to be published in *Surface Science*.

"Thermoelectric Effects in Silicon MOSFETS in High Magnetic Fields," R. P. Smith, H. Closs and P. J. Stiles, *Proc. Vth Intl. Conf. as above*.

"Multiple Connect Quantized Resistance Regions," D. S. Syphers, F. F. Fang and P. J. Stiles, *Proc. Vth Intl. Conf. as above*.

"de Haas-van Alphen Effect in a Single Two Dimensional Layer," *Proc. Vth Intl. Conf. as above*.

"The Oxidation of Ge Surfaces at Pressures Much Greater than One Atmosphere," E. E. Crisman, Y. M. Ercil, J. J. Loferski and P. J. Stiles, *J. Electrochem. Soc.* 129, 1845 (1982).

Supported by the Materials Research Laboratory/NSF

and the Office of Naval Research.

***Thin Liquid
Crystal Films***

We have continued our theoretical studies of the smectic C-A transition in thin liquid crystal films by studying the behavior of the orientational order correlation function. We have calculated this function at high temperatures in a formalism that allows us to match our result approximately to that obtained from the renormalization group at lower temperatures. Thus, we have obtained for the first time a theoretical prediction for the approximate behavior of this function at all temperatures. Ultimately we hope to compare our result with experimental measurements.

Principal Investigator: R. A. Pelcovits, Assistant Professor, Physics.

Personnel: S. W. Heinekamp, Research Assistant, Physics.

Publication:

"Spin-spin Correlation Function in the Two-Dimensional XY Model," S. W. Heinekamp and R. A. Pelcovits, submitted to *Phys. Rev. B*.

Supported by the Materials Research Laboratory/NSF.

Summaries of Related Work

Surface Reflectance Spectrometry - Professor P. J. Estrup (Physics and Chemistry) and Professor P. J. Stiles (Physics) - cf. Section 4.

Molecular Interactions in Physisorption - Professor M. W. Cole (Physics and Chemistry) - cf. Section 4.

Surface Reconstruction and Surface Phase Transitions - Professor P. J. Estrup (Physics and Chemistry) - cf. Section 4.

Structural Phase Transition on W and Mo Surfaces - Professor S. C. Ying (Physics) - cf. Section 4.

SECTION 6

PROPERTIES OF MATERIALS AT LOW TEMPERATURES

Introduction

The general motivation for this work is that certain interesting properties and phenomena exist only in this regime and some other properties of materials, which are of interest at all temperatures, can be investigated most effectively at low temperatures. The specific issues reported on in this section cover: (a) Plastic deformation of solid helium, a quantum solid in which tunneling motion of defects is expected to play an important role in the deformation process. (b) The solidification of helium in small pores, which concerns the nucleation of solid in a supercooled liquid and determination of the solid-liquid interfacial energy together with its temperature dependence. (c) Propagation of waves in fluid-filled porous media, with special emphasis on the role of the fluid's viscosity, which is determined by using helium as the fluid and changing its state from normal to superfluid by changing the temperature. (d) The low temperature recombination mechanisms of atomic hydrogen and deuterium in the presence of various surfaces.

Research Results

Plastic Deformation and Ultrasonic Attenuation in Solid Helium-Four

In the period covered by this report we have investigated two areas: (a) The transmission of ultrasonic waves between bulk solid helium and a very thin layer of liquid helium; (b) The transmission and reflection of waves at the interface between bulk solid and liquid helium. In these studies we used frequencies of 5 to 15 MHz, i.e., well below the values at which the anomalous Kapitza transmission sets in. We have observed, nonetheless, departures in our results from the predictions of the classical acoustic mismatch theory. These departures are being studied in detail as a function of temperature and crystal orientation.

Principal Investigator: C. Elbaum, Professor, Physics.

Personnel: A. Hikata, Professor (Research), Applied Mathematics, J. Beamish, Research Associate, Materials Research Laboratory and M. Manning, Graduate Student, Physics.

Supported by the Materials Research Laboratory/NSF.

Solidification and Superfluidity of Helium in Restricted Geometries

Earlier experiments have indicated that for helium contained in restricted geometries (packed powders of various particle sizes, porous Vycor glass, etc.) the superfluid transition temperature is lowered and solidification requires substantial overpressures above the bulk freezing pressure. We have studied these phenomena through a novel approach, namely the propagation of ultrasonic waves. In particular, we have measured the transverse sound velocity in porous Vycor glass containing Helium-four at pressures up to about 85 bars, in the temperature range $0.3\text{K} \leq T \leq 4.2\text{K}$. From changes in the sound velocity we have determined that overpressures required to initiate freezing ranged from 18 bars at 1.3K to 30.7 bars at 2.38K, and we have obtained the melting curve in the pressure-temperature phase diagram for Helium-filled porous Vycor. From these overpressures we have, in turn, obtained values for

the interfacial free energy between liquid and solid Helium over the range of temperature studied. It is noted that within the accuracy of our determinations this interfacial free energy is independent of temperature between 1.3 and 2.38K, thus indicating that the entropy contribution is very small.

Principal Investigator: C. Elbaum, Professor, Physics.

Personnel: A. Hikata, Professor (Research), Applied Mathematics and J. Beamish, Research Associate, Materials Research Laboratory.

Publication:

"Solidification and Superfluidity of ^4He in Porous Vycor Glass," J. R. Beamish, A. Hikata, L. Tell and C. Elbaum, *Phys. Rev. Lett.* 50, 6 (1983).

Supported by the Materials Research Laboratory/NSF and the National Science Foundation.

Wave Propagation in Fluid-Filled Porous Media; Helium in Vycor

We have used Helium-four filled porous Vycor (a porous silica glass with a network of interconnected pores about 30Å in radius) as a system to which the Biot theory of sound propagation in fluid-filled porous media can be applied. The unique properties of superfluid helium permit the limiting, zero viscosity, features of the Biot theory to be explored in a manner not accessible with ordinary (classical) fluids. In this context, we have measured longitudinal and transverse sound velocity behavior in liquid Helium-four filled porous Vycor, as a function of temperature and pressure. We compared our results with Biot's theory of sound propagation in fluid-filled media and found this theory to apply well to the present case. In particular: (a) Biot's expression for the effective elastic moduli gave good agreement with the measured pressure dependence of the longitudinal sound velocity. (b) The transition from the low-to-high-frequency limits of the Biot theory was achieved through the superfluid transition, and the resulting decoupling effect was found also to be consistent with the Biot theory. (c) From the temperature dependence of the sound velocities, the superfluid fraction in Vycor was found to have a temperature dependence (near T_λ) of the form $\rho_s(T) \propto (1 - T/T_\lambda)^\xi$. The exponent ξ was essentially

equal to the bulk value $\xi = 2/3$.

Principal Investigator: C. Elbaum, Professor, Physics.

Personnel: A. Hikata, Professor (Research), Applied Mathematics and J. Beamish, Research Associate, Materials Research Laboratory.

Publication:

"Sound Velocity in Helium-Filled Porous Vycor Glass," J. R. Beamish, A. Hikata and C. Elbaum, Phys. Rev. B, 27, 9 (1983).

Supported by the Materials Research Laboratory/NSF and the National Science Foundation.

Low Temperature Relaxation and Recombination Processes for Atomic Hydrogen and Atomic Deuterium

The relaxation and recombination mechanisms for atomic hydrogen and deuterium have been examined in a 9 GHz ESR spectrometer at temperatures between 0.5 and 0.7K. The electronic relaxation time is weakly dependent on density and temperature and is felt to be dominated by atomic hydrogen

hitting a wall covered with a helium film and flipping its spin via an interaction with paramagnetic impurities on the underlying substrate. From a measurement of the low temperature flux of atomic deuterium and the known sensitivity of the ESR spectrometer, the assumption that recombination is dominated by the surface leads to a wall recombination coefficient of greater than $5 \times 10^{-11} \text{ cm}^3/\text{sec}$. This value when used in conjunction with the measured bonding energy for atomic D on a helium surface, implies that the recombination cross length is several orders of magnitude larger for atomic D than for atomic H.

Principal Investigator: George Seidel, Professor, Physics.

Personnel: Rulon Mayer, Research Assistant, Physics.

Supported by the National Science Foundation.

Summary of Related Work

Electronic Properties of Semiconducting Surface Space Charge Layers - Professor J. J. Quinn (Physics) - cf. Section 5.

SECTION 7 MATERIALS FOR SOLAR ENERGY CONVERSION

Research Results

Investigation of Photovoltaic Solar Cells

This program has focused on the preparation and characterization of thin films of compound semiconductors (CuInSe_2 , CdS , GaAs) and insulators (SiO_2). Films of all of these materials have been deposited by rf-sputtering. Films, one of them CdS , have been deposited by evaporation in vacuum from a resistance heated crucible and by chemical vapor transport in pure hydrogen. Films of two of them (CuInSe_2 and CdS) have been deposited by chemical spray pyrolysis. In addition, work continues on germanium thermophotovoltaic devices.

We have continued improvements in the analysis of thin films by energy dispersive analysis of X-rays (EDAX), wave dispersive analysis of X-rays (WDX) and cathodoluminescence in the MRL Central Facility for Electron Microscopy. Mr. C. J. Li of the Semiconductor Research Institute, Chinese Academy of Sciences, Beijing, China, took up this program after Dr. T. Warminski returned to Warsaw, Poland.

We used EDAX to characterize the interface between a 4 percent Si 96 percent Ge single crystal layer deposited on a GaAs crystal by CVD by a group at the CNRS in France. This particular Si-Ge alloy was selected because it should have the same lattice constant as GaAs . We expect that the junction formed between a wide bandgap semiconductor (GaAs) and a small band gap semiconductor (Ge) will act as an electrostatic barrier (minority carrier mirror) to the flow of light generated minority carriers in the small band gap material. Such junctions would be incorporated in heterostructure devices of the type $\text{p-GaAs/p-Ge/n-GaAs}$. If the p-Ge and n-Ge regions are thin compared to a minority carrier diffusion length in the materials, the reverse saturation current will be reduced below the value it would have in the conventional structure: ohmic contact/ p-Ge/n-Ge ohmic contact. The EDAX analysis of the interface showed that Ge was present in the GaAs and that Ga and As were present in the Ge . In both cases the concentrations were high enough to control

the conductivities and conductivity types of such junctions. This characterization casts doubt on the appropriateness of CVD for preparation of such structures; the time-temperature combinations needed to deposit Si and Ge on GaAs lead to interdiffusion of their constituent elements.

We also studied the interface between a CuInSe_2 crystal and a CdS layer deposited over it by chemical vapor transport in pure hydrogen. Again EDAX analysis along lines perpendicular to the plane of the interface showed significant interdiffusion of the elements, Cd into the CuInSe_2 and Cu and In into the CdS . The substrate temperatures during CdS deposition were between 400°C and 600°C . Extrapolation of the results obtained at these temperatures to deposition at 200°C , the CuInSe_2 temperature while CdS layers are deposited over it by evaporation of sputtering, indicate that interdiffusion may occur even at the "low" temperature.

Our studies of CuInSe_2 films produced by chemical spray pyrolysis have included the first successful depositions onto metallic surfaces. Deposition on insulating substrates has been demonstrated by the Brown group and others as long as five years ago. However, very little was reported about its deposition on conducting substrates. Films of stoichiometric composition (as shown by EDAX) and of the desired chalcopyrite structure (as shown by X-ray diffraction) could be obtained with the proper choice of deposition parameters. The films were p-type and had resistivities suitable for solar cells (10^{-2} to 10^3 ohm cm). Photovoltaic cells were prepared from these films by depositing evaporated low resistivity (10^{-1} to 10^{-2} ohm cm) films of CdS over them; the photovoltaic parameters of the best of these devices were: open circuit voltage 0.130 V; short circuit current, 2.3 mA/cm² and fill factor, 0.27 , efficiency, less than 1 percent. Open circuit voltages up to 0.43 V have been observed in some of these devices.

We spent some time developing a method for depositing thick (~ 20 micron) stoichiometric films of SiO_2 over sapphire substrates for acoustic-electric device application. It was found that extremely slow rf-sputtering deposition rates (a few angstroms per

minute) were required to produce homogeneous high quality films of SiO_2 . Similar deposition rates were used to produce thick layers of GaAs on sapphire. Based on our experience with these two materials, we are in the process of determining whether films of other semiconductors like CuInSe_2 deposited very slowly may have better properties for PV cells than films deposited at "conventional" rates of about 1000 Å/minute.

Principal Investigator: Joseph J. Loferski, Professor, Engineering and Barton Roessler, Professor, Engineering.

Personnel: Gordon Kenshole, Visiting Senior Research Associate, Engineering; C. J. Li, Visiting Research Associate, Engineering; E. E. Crisman, Senior Research Engineer, Engineering; R. Beaulieu, Technical Assistant, Engineering; W. Oates, Technical Assistant, Engineering; P. Sarro, Postdoctoral Fellow, Engineering; R. Arya, Graduate Student, Engineering; C. Case, Graduate Student, Engineering; E. Vera, Research Associate, Physics; G. Landis, Graduate Student, Physics; T. Russell, Graduate Student, Engineering and C. Toro, Graduate Student, Engineering.

Publications:

"Theoretical and Experimental Studies of Tandem or Cascade Solar Cells: A Review," J. J. Loferski, Proceedings of the Sixteenth IEEE Photovoltaic Specialist Conference, San Diego, California, (September 1982).

"Photovoltaic and Structural Properties of $\text{CuInSe}_2/\text{CdS}$ Solar Cells," J. J. Loferski, R. R. Arya, T. Warminski and R. Beaulieu, Solar Energy

Materials, 8. (1983) 471-481.

"Diffusion of Copper and Other Effects in the Chemical Vapor Deposition of Cadmium Sulfide on Single Crystal Copper Indium Selenide Substrates," G. Kenshole, C. J. Li, C. R. Toro and J. J. Loferski, Proceedings of the Fifth European Communities Photovoltaic Solar Energy Conference, Athens, Greece, (October 1983).

"Preparation and Properties of CuInSe_2 Thin Films Deposited on Conducting Substrates by Chemical Spray Pyrolysis for Photovoltaic Cells," P. M. Sarro, R. R. Arya, R. Beaulieu, T. Warminski and J. J. Loferski, Proceedings of the Fifth European Communities Photovoltaic Solar Energy Conference, Athens, Greece, (October 1983).

"Prospects for Large Scale Terrestrial Solar Energy Conversion through Photovoltaic Solar Cells," J. J. Loferski, to be published.

"Tandem Cell Structures," J. J. Loferski, Proceedings of the 2nd ROC Solar Cell Workshop, Taiwan (June 1983).

Supported by the Materials Research Laboratory/NSF, the U. S. Department of Energy, the Naval Research Laboratory, Standard Oil of Ohio, the Mobil Oil Foundation, Sanders Associates and the Jet Propulsion Laboratory.

Summaries of Related Work

The Low Temperature Synthesis and Properties of Co_9S_8 , Ni_3S_2 and Fe_7S_8 " - Professor A. Wold (Chemistry) - cf. Section 8.

Photoelectronic Properties of ReS_2 and ReS_2 Single Crystals - Professor A. Wold (Chemistry) - cf. Section 8.

SECTION 8 OTHER RESEARCH

Research Results

The Low Temperature Synthesis and Properties of Co₉S₈, Ni₃S₂, and Fe₇S₈

The treatment of the sulfate salts of cobalt, nickel and iron, with a controlled mixture of H₂ and H₂S at low temperatures yielded Co₉S₈, Ni₃S₂, and Fe₇S₈. The sulfides prepared here were characterized by X-ray diffraction, magnetic susceptibility and thermogravimetric analysis. The method of preparation was found to yield single phase materials which were free of ferromagnetic impurities. Co₉S₈ and Ni₃S₂ exhibited temperature independent magnetic susceptibility which is consistent with Pauli paramagnetism.

The field dependent magnetic susceptibility measurements for Fe₇S₈ were sensitive to the thermal history of the sample. Annealed samples showed strong field dependent behavior (i.e. large spontaneous magnetization), whereas quenched samples did not. Slow-cooled samples exhibited less field dependent behavior than the annealed samples which indicated less ordering of the vacancies. These observations are consistent with the Bertaut model for vacancy ordering in ferromagnetic Fe₇S₈.

Photoelectronic Properties of ReS₂ and ReSe₂ Single Crystals

Large single crystals of ReS₂ and ReSe₂ were grown by chemical vapor transport, and several of their properties were investigated. Both were found to be n-type semiconductors with resistivities in the range of 1-10 ohm-cm. Photoelectrochemical measurements in aqueous solutions of I₃⁻/I⁻ resulted in high photocurrent densities, with ReSe₂ being the more efficient photoelectrode. Analysis of their optical absorption spectra resulted in lowest-energy indirect optical band gaps of 1.32(5) eV for ReS₂ and 1.17(5) eV for ReSe₂. Photoelectrochemical spectral response measurements resulted in a measured lowest-energy indirect optical band gap of 1.4 eV for ReS₂ which is in close agreement with that

measured from optical absorption.

The photoelectrochemical properties of ReS₂ and ReSe₂ were observed to follow some trends found in other transition metal chalcogenides. In general, the diselenides have smaller band gaps and more negative flat-band potentials than the corresponding disulfides. It has also been observed that both the metal and the anion have an effect on the positions of the valence band and the conduction band. Thus, the transition metal dichalcogenides exhibit a fairly wide range of photoelectrochemical characteristics.

Preparation and Characterization of Cd_{1-x}Mn_xSe (x ≤ 0.25) Single Crystals

In this section, we are reporting on the growth and characterization of single crystals of the general composition Cd_{1-x}Mn_xSe. These materials were grown as part of a joint program with the National Magnet Laboratory at M.I.T. The crystals were grown from the melt, using the Bridgman technique.

The as-grown crystals possessed a relatively high range of inhomogeneity with respect to manganese distribution from top to bottom of the boules. An equilibrium state could, however, be attained by a subsequent five-day annealing of the growth tube in the constant temperature zone of a wound-core transport furnace at 600C to yield samples with high resistivity. The crystals thus formed were cut into discs and subjected to various treatments and measurements. The addition of excess cadmium and trace quantities of gallium or indium to slices of the crystal, and annealing in evacuated silica tubes at various temperatures, increased the conductivity as well as the number of carriers. The maximum number of carriers obtained was $2 \times 10^{19} \text{ cm}^{-3}$.

X-ray diffraction patterns of the crystals grown to date (x ≤ 0.25) indicated the formation of single-phase products which could be indexed on the basis of a hexagonal unit cell.

Magnetic measurements on sections cut along the growth axis of the unannealed crystal indicated

inhomogeneity with respect to manganese distribution, extending from top to bottom of the crystal. Such non-uniformities were indicated by differences of as much as $0.6\mu_B/\text{Mn(II)}$ between top and bottom sections of the crystal boule. However, annealing of these crystals in the growth tube at 600C resulted in the redistribution of manganese throughout the boule. The measured effective moments corresponded closely to the theoretical values of $5.9\mu_B$, as expected for a localized spin-only moment d^5 system.

Optical transmissions were measured using a tungsten iodide lamp and a calibrated silicon diode. Spectral transmission data were obtained using a monochromator (Oriel Model 7240). Very high transparency is observed in the longer wavelengths as the energy of the incident photons becomes small compared to the optical transition gap, which is 1.74 eV for cadmium selenide.

The electrical measurements were made using the van de Pauw technique. As-grown, annealed crystals indicated resistivities greater than $10^6 \Omega\text{-cm}$. Burmeister *et al.* (1) and Hung *et al.* (2) have shown that the resistivity of cadmium selenide is related to cadmium or selenium pressure, and decreases with cadmium vapor. This is consistent with the high resistivities observed for the manganese-doped samples grown in the presence of excess selenium. However, annealing under cadmium pressure at 800C increases markedly the conductivity and the number of carriers.

References: (1) M. Hung, N. Ohasi, K. Igaki, *Jap. J. Appl. Phys.* 8 (6), 652 (1969). (2) R. A. Burmeister, Jr., and D. A. Stevenson, *Phys. Stat. Sol.* 24, 683 (1967).

Principal Investigator: A. Wold, Professor, Chemistry.

Personnel: K. Dwight, Professor (Research), Chemistry, R. Kershaw, Senior Research Engineer, Chemistry, D. Ridgley, Research Associate, Chemistry, W. Croft, Visiting Professor, Chemistry, Y. Qian, Research Associate, Chemistry, R. Brusasco, Graduate Student, Chemistry, L. Carreiro, Graduate Student, Chemistry, D. D'Ambra, Graduate Student, Chemistry, J. Foise, Graduate Student, Chemistry, J. Fournier, Graduate Student, Chemistry, M. Gray, Graduate Student, Chemistry, D. Pasquariello, Graduate Student, Chemistry.

Publications:

"Magnetic and Electrical Properties of Rhodium(III)Oxide(III)," H. Leiva, R. Kershaw, K. Dwight and A. Wold, *Mat. Res. Bull.* 17, 1539 (1982).

"Preferential Neutralization in Low Energy Helium Ion Scattering from the Second Layer of MoS_2 Basal Plane Surfaces," S. M. Davis, J. C. Carver and A. Wold, *Surface Science* 124, L12 (1983).

"Preparation and Characterization of $\text{Cd}_{0.95}\text{Mn}_{0.05}\text{Se}$ Single Crystals," B. Khazai, R. Kershaw, K. Dwight and A. Wold, *Mat. Res. Bull.* 18, 217 (1983).

"The Dependence of Magnetic Properties on Structure in the System $\text{Fe}_2\text{Ge}_x\text{Si}_{1-x}\text{O}_4$," M. Tellefsen, R. Kershaw, K. Dwight and A. Wold, *J. Solid State Chem.* 46, 328 (1983).

"The Adsorption and Binding of Thiophene, Butene and H_2S on the Basal Plane of MoS_2 Single Crystals," M. Salmeron, G. A. Somorjai, A. Wold, R. Chianelli and K. S. Liang, *Chemical Physical Letters* 90, (2), 105 (1982).

"Magnetic Polaron Contributions to Donor Bound Exciton in $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$," C. A. Huber, A. V. Nurmikko, M. Gal and A. Wold, *Solid State Communications* 46, (1), 41 (1983).

"Preparation and Properties of the Systems $\text{Fe}_{2-x}\text{Cr}_x\text{WO}_6$, $\text{Fe}_{2-x}\text{Rh}_x\text{WO}_6$, and $\text{Cr}_{2-x}\text{Rh}_x\text{WO}_6$," H. Leiva, R. Kershaw, K. Dwight and A. Wold, *J. Solid State Chem.* 47, 293 (1983).

"Preparation and Properties of Substituted Iron Tungstates," K. Sieber, H. Leiva, K. Kourtakis, R. Kershaw, K. Dwight and A. Wold, *J. Solid State Chem.* 47, 361 (1983).

"Hydrogen Reduction Studies of Members of the System $\text{MgFe}_{2-x}\text{Cr}_x\text{O}_4$," Y. Qian, R. Kershaw, K. Dwight and A. Wold, *Mat. Res. Bull.* 18, 543 (1983).

"Photoelectronic Properties of Cu_3PS_4 and $\text{Cu}_3\text{PS}_2\text{Se}$ Single Crystals," J. V. Marzik, A. K. Hsieh, K. Dwight and A. Wold, *J. Solid State Chem.* 49, 43 (1983).

"Growth and Characterization of n- WS_2 and Niobium-Doped p- SW_2 Single Crystals," J. Baglio, E. Kamieniecki, N. DeCola, C. Struck, J. Marzik, K. Dwight and A. Wold, *J. Solid State Chem.* 49, 166 (1983).

"Dependence of Magnetic Properties on Structure in the Systems NiMoO_4 and CoMoO_4 ," K. Sieber, R. Kershaw, K. Dwight and A. Wold, *Inorg. Chem.* 22, 2667 (1983).

Supported by the National Science Foundation, the Office of Naval Research, the U. S. Army Research Office, Exxon Research Laboratories and the General Telephone Laboratories.

Tie Molecule Behavior in Semi-Crystalline Polymers

An important microstructural feature of many semi-crystalline polymers is the existence of parallel crystalline lamellae separated by amorphous regions. The latter, it is believed, contain many long-chain molecules which connect adjacent lamellae. These are referred to as tie molecules and it has been conjectured that they play a role in crack initiation and propagation in these materials.

In an effort to gain insight into their thermomechanical behavior, we have been conducting computer simulations of idealized models of tie molecules. Previous work in this program considered the behavior of a single tie molecule. These simulations showed that at large extensions the tie molecule exerted tensile forces on the attached lamellae and that these are in accord with the expected behavior of an entropic spring. However, for small interlamellar spacing, the atoms of the tie molecule exerted a pressure on the lamellae, as would be expected from a gas, and at an equilibrium spacing, these forces balanced each other.

We have now extended this work in order to study the effect of interaction between tie molecules and have carried out extensive computer simulation of two tie molecules which connect the same pair of lamellae and which interact with each other. The results of these simulations show that the interaction between the tie molecules has surprisingly little effect upon their force-length-temperature relation.

Principal Investigator: J. H. Weiner, Professor, Engineering.

Personnel: D. Berman, Graduate Student, Engineering.

Publication:

"Relative Importance of Internal Pressure and Excluded-Volume Effects in Resolution of Network Collapse Problem," J. H. Weiner and T. W. Stevens, *Macromolecules* 16, 672 (1983).

Supported by the Materials Research Laboratory/NSF and the Gas Research Institute.

N-Orbital Hubbard Model for Metal Insulator Transitions

Work on understanding and developing a consistent approximation for the Hubbard model¹ for metal-insulator transitions was continued. The insight gained² from studying the model on an infinite-dimensional hypercubic lattice led to a planar approximation. As a first step towards solving the model in this approximation, the enumerative problem for planar diagrams with quartic vertices was worked out. Work is underway on calculating the Green functions in this approximation. The zero dimensional case (i.e., no electron hopping) is being considered with a view to studying the one particle spectrum as a function of temperature and interaction strength.

¹Hubbard, J., *Proc. Roy. Soc. A* 281, 401(1964).

²Wegner, F., unpublished.

Principal Investigator: A. Khurana, Research Associate, Materials Research Laboratory.

Publication:

"Planar Diagrams - Some Enumerative Results," A. Khurana, submitted to *Commun. Math. Phys.*

Supported by the Materials Research Laboratory/NSF.

X-Ray Topographic Studies of Germanium

X-ray topographic studies have continued on crystal imperfections in germanium. A series of single crystal specimens was obtained from the various commercial growers and subjected to extensive X-ray topographic mapping. Large variations were observed in both number density and character of the dislocations in the topographs of different specimens. The differences appear to correlate directly with the source of the specimens: i.e., single specimens from different batches of the same supplier display similar X-ray topographs. With the collaboration of Dr. M. C. Narasimhan, a journal article is being prepared which will summarize the results of this study.

With additional support from the Naval Research Laboratory, we are extending this study to single crystal germanium used for thermal-photovoltaic devices. In particular, we plan to compare the topographic maps of dislocations and imperfections with electron beam induced current (EBIC) maps of the device output. It is anticipated that this comparison will contribute greatly to the understanding of the relative electrical activity of the various crystal imperfections, particularly in the vicinity of the device p/n junction region. Stereo pairs will be used to relate the imperfections with the junction position.

In collaboration with P. J. Stiles of the Physics Department, we have undertaken preliminary X-ray studies of thick nitride and oxide layers on single crystal germanium. By the process of high pressure oxidation and one atmosphere nitridation of the ensuing oxides, thick (~5000Å) layers of these compounds have been prepared on germanium crystal surfaces. X-ray diffraction of commercial powders of GeO_2 , GeO and $\beta\text{-Ge}_3\text{N}_4$ correlated with far infrared transmission of both pressed powder and single crystal specimens, indicate that the oxide is forming as an amorphous layer but that the subsequent nitrogen treatment converts the amorphous oxide to a crystalline nitride or oxynitride. Thicker layers are now being prepared on single crystals to provide specimens for X-ray diffraction studies and associated lattice parameter measurements.

Principal Investigator: Barton Roessler, Professor, Engineering.

Personnel: M. C. Narasimhan, Visiting Lecturer, Engineering, E. E. Crisman, Senior Research Engineer, Engineering; W. Oates, Technical Assistant, Engineering.

Publication:

"The Nitridation of Thick Germanium Oxide Films on Single Crystal Germanium," E. E. Crisman, O. Gregory and P. J. Stiles, J. Electrochem. Soc. (in publication).

Supported by the Materials Research Laboratory/NSF.

Picosecond Spectroscopy of Semiconductors

Photomodulation techniques on picosecond timescale have been employed to study the kinetics of excitons

and electron-hole plasmas in several crystalline semiconductors of potential importance in electro-optical devices. This work is a continuation effort by us to provide direct measurement of energy relaxation and lifetime processes in varying material environment.

During this year we have examined the influence of magnetic ions on properties of free and impurity bound excitons in semimagnetic semiconductors (SMSC) such as $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$. Here we have directly benefited from the sophisticated materials facility of Professor Aaron Wold at Brown whose laboratory has been the origin of several high quality crystals for us.

As one consequence of the exchange interaction in SMSC's of the Mn-ions with Bloch derived states near the band extrema, we have found that an exciton localized at an impurity site can have its energy profoundly modified by the magnetic interaction of the ions within its Bohr orbital volume. In particular, the optical spectra associated with spontaneous or induced radiative recombination with such interband excitations will show anomalous energy shifts and linewidth broadening behavior as a function of temperature. At a sufficiently low temperature, a spontaneous local magnetic ordering can occur where an energy gain from such an ordering is on the order of 15 meV in $\text{n-Cd}_{0.90}\text{Mn}_{0.10}\text{Se}$. By applying short pulse laser techniques, the formation and decay of such magnetically coupled excitons have been directly studied. For example, the initial capture of a free exciton at an impurity has been measured to occur in about 10 psec at 10K, intermediate by mixed crystal disorder effects. Furthermore, the evolution of the magnetically ordered state about the bound exciton at 2K has been determined to take place in approximately 400 psec.

Principal Investigator: A. V. Nurmikko, Professor, Engineering.

Personnel: J. H. Harris, Graduate Student, Physics.

Publications:

"Interface Recombination and Carrier Confinement at a $\text{GaAs}/(\text{Ga},\text{In})\text{P}$ Heterojunction as Studied by Picosecond Population Modulation Spectroscopy," J. H. Harris, S. Sugai and A. V. Nurmikko, Appl. Phys. Lett. 40, 885 (1982).

"Strong Electron-Phonon Interaction Effects in

Modulated Transient Reflectance Spectra of $\text{Ga}_{.50}\text{In}_{.50}\text{P}$," S. Sugai, J. H. Harris and A. V. Nurmikko, Solid State Comm. 43, 913 (1982).

"Magnetic Polaron Contribution to Donor Bound Exciton in $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$," C. A. Huber, A. V. Nurmikko, M. Gal and A. Wold, Solid State Comm. 46, 41 (1983).

"Picosecond Kinetics of the Donor Bound Exciton in $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$," J. H. Harris and A. V. Nurmikko, Physics. Rev., B28, 1181 (1983).

"Strong Photoinduced Infrared Absorption in GaP," C. A. Huber and A. V. Nurmikko, J. Appl. Phys. 54, 326 (1983).

"Magnetic Polaron Contribution to Donor Bound Exciton in $(\text{Cd,Mn})\text{Se}$," C. A. Huber, A. V. Nurmikko, M. Gal and A. Wold, Solid State Comm. 46, 41 (1983).

"Formation of the Bound Magnetic Polaron in $(\text{Cd,Mn})\text{Se}$," J. H. Harris and A. V. Nurmikko, Phys. Rev. Lett. 51, 1472 (1983).

"Photoluminescence in the Semimagnetic $(\text{Zn,Mn})\text{Te}$," M. Gal, Y. Hefetz, J. Ajo and A. V. Nurmikko, Phys. Rev. B28, 4500 (1983).

Supported by the Materials Research Laboratory/NSF, the Air Force Office of Scientific Research, and the Department of Energy.

Summary of Related Work

Oxidation and Fracture Characteristics of Reaction Bonded Silicon Nitride (RBSM) - Professor M. H. Richman (Engineering)- cf. Section 2.

LECTURES IN THE MATERIALS RESEARCH LABORATORY PROGRAM, 1982-83

October 1, 1982

Chemistry Colloquium: Dr. James Skinner, Columbia University, **ROLE OF SOLITONS AND OTHER DEFECTS IN POLYMER RELAXATION.**

October 7, 1982

Condensed Matter Seminar: Dr. S. Luryi, Bell Laboratories, Murray Hill, NJ, **QUANTUM PERCOLATION AND QUANTIZATION OF HALL RESISTANCE IN SEMICONDUCTING INVERSION LAYERS.**

October 15, 1982

Chemistry Colloquium: Dr. Richard Gonsales, University of Rhode Island, **CATALYTIC AND INFRARED STUDIES OVER WELL-CHARACTERIZED Pt/Ru SUPPORTED BY METALLIC CLUSTERS.**

October 18, 1982

Physics Colloquium: Professor David Nelson, Harvard University, **HEXOTIC PHASES OF MATTER.**

October 22, 1982

Chemistry Colloquium: Dr. William Jackson, Howard University, **LASER STUDIES OF THE DYNAMICS OF PRE-DISSOCIATION IN SMALL MOLECULES.**

October 28, 1982

Theoretical Seminar: Dr. H. Levine, Schlumberger-Doll Research Center and Brown University, **EFFECTIVE POTENTIALS VIA MONTE CARLO SIMULATION.**

October 28, 1982

Condensed Matter Seminar: Dr. J. Jose, Northeastern University, **ELECTRONIC ENERGY SPECTRUM IN APERIODIC POTENTIALS.**

October 29, 1982

Chemistry Colloquium: Dr. R. Sarma, SUNY (Albany), **PLASTICITY OF THE DNA DOUBLE HELIX: AN NMR STUDY.**

November 1, 1982

Joint Physics-Chemistry Colloquium: Professor John McTague, Brookhaven National Laboratory, **TREASURE FROM TRASH: SYNCHROTRON RADIATION FOR CONDENSED MATTER AND SURFACES.**

November 4, 1982

Condensed Matter Seminar: Dr. John Hegarty, Bell Laboratory, Murray Hill, NJ, **EXCITON DYNAMICS IN TWO-DIMENSIONAL GaAs QUANTUM WELLS.**

November 5, 1982

Solid Mechanics Seminar: Professor James Rhodes, University of Strathclyde, Glasgow, Scotland, **BUCKLING BEHAVIOR OF THIN WALLED STRUCTURES.**

November 12, 1982

Chemistry Colloquium: Dr. Jan Tobochnik, Worcester Polytechnic Institute, **THE TWO-DIMENSIONAL MELTING CONTROVERSY.**

November 18, 1982

Condensed Matter Seminar: Dr. S. Safran, Exxon Labs, **THEORY OF DOMAIN GROWTH OF**

Annual Technical Report

SURFACE SUPERLATTICES.

November 19, 1982

Chemistry Colloquium: Dr. William Chupka, Yale University, LASER MULTIPHOTON STUDIES OF IONIZATION ASSOCIATION PROCESSES OF GASEOUS MOLECULES.

November 29, 1982

Physics Colloquium: Professor Hallock, University of Massachusetts at Amherst, NEW EXPERIMENTS WITH HELIUM-4 FILMS.

December 2, 1982

Solid Mechanics Seminar: Professor Piotr Perzyna, Institute of Fundamental Technological Research, Polish Academy of Sciences, Warsaw, Poland, ON CONSTITUTIVE MODELLING FOR PLASTIC FLOW, INSTABILITY AND FRACTURE.

December 3, 1982

Solid State Seminar: Dr. L. Pietronero, Harvard University/Brown Boveri, ELECTRONIC AND TRANSPORT PROPERTIES OF GRAPHITE INTERCALATION COMPOUNDS AND CARBON POLYMERS.

December 9, 1982

Condensed Matter Seminar: Professor Mildred Dresselhaus, MIT, THE PHYSICS OF INTERCALATED GRAPHITE.

December 13, 1982

Physics Colloquium: Professor Cornelius T. Moynihan, Rensselaer Polytechnic Institute, HEAVY METAL FLUORIDE GLASSES - A NEW CLASS OF INFRARED TRANSMITTING MATERIALS.

December 17, 1982

Chemistry Colloquium: Dr. Myung Jhon, Carnegie Mellon, MOLECULAR THEORY OF POLYMER CONFORMATIONS - LAMINAR AND/OR TURBULENT FLOW.

December 20, 1982

Solid Mechanics Seminar: Professor Nicolas Triantafyllidis, Department of Aerospace Engineering, University of Michigan, THIN ELASTIC RODS UNDER LARGE DISPLACEMENTS AND ROTATIONS.

January 6, 1983

Condensed Matter Theory Seminar: Professor D. Adler, MIT, ELECTRONIC STRUCTURE AND PHOTOINDUCED EFFECTS IN AMORPHOUS SEMICONDUCTORS.

January 7, 1983

Chemistry Colloquium: Dr. Michael McBride, Yale University, ROLE OF LOCAL STRESS IN ORGANIC SOLID STATE REACTIONS.

February 9, 1983

Solid Mechanics Seminar: Professor Roger Fosdick, Department of Aerospace and Mechanics, University of Minnesota, Minneapolis, THE STRUCTURE AND STABILITY OF GIBBSIAN STATES.

February 17, 1983

Condensed Matter Seminar: Dr. G. Prinz, Naval Research Laboratory, FE-SEMICONDUCTOR HETEROSTRUCTURES AND SUPERLATTICES.

February 21, 1983

Solid Mechanics Seminar: Dr. Jean L. Raphanel, CNRS, Institute National Polytechnique de Grenoble,

Grenoble, France, THE ESTIMATION OF LARGE DEFLECTIONS OF A PORTAL FRAME UNDER ASYMMETRIC PULSE LOADING.

February 23, 1983

Condensed Matter Physics Discussion Group: Dr. Alex Tselis, Brown University, ELEMENTARY EXCITATIONS IN SEMICONDUCTOR SUPERLATTICES.

February 28, 1983

Physics Colloquium: Professor Peter Wolff, National Magnet Lab/MIT, NONLINEAR OPTIC STUDIES OF ELECTRON DYNAMICS IN SEMICONDUCTORS.

March 2, 1983

Condensed Matter Physics Discussion Group: Professor D. J. Dunstan, University of Linz, Austria, DISTANT PAIR RECOMBINATION KINETICS.

March 3, 1983

Condensed Matter Seminar: Dr. Sherman Susman, Argonne National Lab, PHYSICS AND CHEMISTRY OF LITHIUM/ALUMINUM. IS IT REALLY A FAST ION CONDUCTOR?

March 9, 1983

Solid Mechanics Seminar: Professor Sol Bodner, Technion-Israel Institute of Technology, Haifa, Israel, DYNAMIC PERFORATION OF VISCOPLASTIC PLATES BY PROJECTILES.

March 9, 1983

Condensed Matter Physics Discussion Group: Dr. Carmen Huber, Brown University, BOUND EXCITONS AND MAGNETIC POLARON EFFECT IN SEMIMAGNETIC SEMICONDUCTORS.

March 10, 1983

Condensed Matter Seminar: Professor D. Guidotti, Brown University, SECOND HARMONIC GENERATION IN CENTRO-SYMMETRIC SEMICONDUCTORS. A NEW FROM OF SILICON?

March 17, 1983

Condensed Matter Seminar: Professor H. van Driel, University of Toronto, LASER-INDUCED PERIODIC SURFACE STRUCTURE ON SOLIDS AND LIQUIDS.

March 23, 1983

Solid Mechanics Seminar: Dr. Richard King, National Bureau of Standards, Washington, D.C., CRACK ARREST AT A HIGH TOUGHNESS INTERFACE.

March 28, 1983

Solid Mechanics Seminar: Professor R. T. Shield, Department of Theoretical & Applied Mechanics, University of Illinois at Urbana-Champaign, LARGE DEFORMATIONS WITH SMALL ELASTIC STRAINS.

March 31, 1983

Condensed Matter Seminar: Professor H. Gerritsen, Brown University, CdTe IN AN ELECTROCHEMICAL LIGHT STORAGE DEVICE.

April 11, 1983

Physics Colloquium: Professor G. Barnes, Iowa State University and Cornell University, NMR APPLIED TO HYDROGEN IN METALS: SOME REMARKABLE NEW FINDINGS.

April 13, 1983

Condensed Matter Physics Discussion Group: Professor H. Maris, Brown University, LIQUID HYDROGEN BELOW 14K.

April 14, 1983

Thermodynamics, Fluid Mechanics and Chemical Processes Group: Professor C.-M. Ho, Department of Aerospace Engineering, University of Southern California, UNSTEADY BEHAVIOR OF A FREE SHEAR LAYER.

April 18, 1983

Solid Mechanics Seminar: Dr. Pauli Pederson, Technical University of Denmark, Lyngby, Denmark, SENSITIVITY ANALYSIS.

April 19, 1983

Solid Mechanics Seminar: Professor Philip G. Hodge, Jr., University of Minnesota, SIMPLE EXAMPLES OF COMPLEX PHENOMENA IN PLASTICITY.

April 20, 1983

Condensed Matter Physics Discussion Group: Gregory T. Cibuzar, Brown University, METALLIC GLASSES.

April 20, 1983

Special Condensed Matter Seminar: Dr. J. P. Franck, University of Alberta, OBSERVATIONS OF GRAIN BOUNDARIES AND GRAIN BOUNDARY MELTING IN F_{CC} AND H_{CP} 4He .

April 21, 1983

Condensed Matter Seminar: Professor Richard Stratt, Brown University, COOPERATIVE INTRA-MOLECULAR MOTIONS IN CONDENSED MATTER PHYSICS.

April 22, 1983

Chemistry Colloquium: Dr. Eugene Helfand, Bell Labs, RELAXATION PROCESSES IN POLYMERS: KINETICS OF CONFORMATIONAL TRANSITIONS.

April 27, 1983

Condensed Matter Physics Discussion Group: Mr. Gen-Yu Hu, Brown University, MONTE-CARLO SIMULATIONS OF STRUCTURAL PHASE TRANSITIONS.

April 28, 1983

Dr. L. L. Chang, IBM Research Center, RECENT DEVELOPMENTS IN SEMICONDUCTOR SUPERLATTICES.

April 29, 1983

Thermodynamics, Fluid Mechanics and Chemical Processes Group: Professor George Springer, Department of Mechanical Engineering, University of Michigan, THE CURING OF EPOXY MATRIX COMPOSITES.

May 2, 1983

Solid Mechanics Seminar: Professor Rodney J. Clifton, Brown University, NUMERICAL SIMULATION OF HYDRAULIC FRACTURING.

May 3, 1983

Physics Colloquium: Professor A. Leggett, Cornell University, QUANTUM MECHANICS AT A MACROSCOPIC LEVEL.

May 4, 1983

Condensed Matter Physics Discussion Group: Dr. A. Khurana, Brown University, A PLANAR APPROXIMATION TO THE METAL-INSULATOR TRANSITION?

May 5, 1983

Condensed Matter Seminar: Professor M. Azbel, IBM and Tel Aviv University, CONDUCTANCE OF ONE-DIMENSIONAL RANDOM SYSTEMS.

May 5, 1983

Theoretical Seminar: Professor R. Brower, Harvard and UC at Santa Cruz, DIFFUSIVE GEOMETRY FOR DENDRITIC INSTABILITY.

May 9, 1983

Physics Colloquium: Professor E. Brezin, Harvard and Saclay, PHASE TRANSITIONS IN SYSTEMS WITH WALLS, FINITE SIZES, INTERFACES.

May 11, 1983

Chemistry Colloquium: Dr. F. Wudl, University of California, Santa Barbara, FROM ORGANIC METALS TO SUPER CONDUCTORS, OR MANAGING CONDUCTION ELECTRONS IN ORGANIC SOLIDS.

May 12, 1983

Condensed Matter Seminar: Professor A. V. Nurmikko, Brown University, EXCITON KINETICS IN SEMIMAGNETIC SEMICONDUCTORS.

May 16, 1983

Special Condensed Matter Seminar: Professor J. Stuke, University of Marburg, West Germany, PARAMAGNETIC STATES IN DOPED AND AMORPHOUS SILICON AND GERMANIUM.

May 17, 1983

Solid Mechanics Seminar: Dr. Pabitra N. Sen, Schlumberger-Doll Research, Ridgefield, CT, DIELECTRIC ENHANCEMENT DUE TO GEOMETRICAL AND ELECTRO-CHEMICAL EFFECTS.

May 19, 1983

Theoretical Seminar: Dr. Peter Orland, Imperial College of Science and Technology, London, ACTION FOR A CHROMOELECTRIC SUPERCONDUCTOR.

June 14, 1983

Solid State Discussion Group: Dr. Stephen B. Libby, Brown University, ELECTRON DELOCALIZATION BY A MAGNETIC FIELD IN TWO-DIMENSIONS.

June 21, 1983

Solid State Discussion Group: Miss J. Louise Tell, Brown University, PHASE TRANSITIONS OF HYDROGEN ADSORBED IN POROUS GLASS.

June 28, 1983

Solid State Discussion Group: Professor Charles Elbaum, Brown University, LIQUID AND SOLID HELIUM.

LIST OF STAFF IN THE MATERIALS RESEARCH LABORATORY PROGRAM

APPLIED MATHEMATICS

Professors A. Hikata (Research), H. Kolsky, A. C. Pipkin; Visiting Scholars M. Z. Hu, G. Sun; Technician W. Carey; Research Assistant W-B. Wang; Graduate Student L-C. Zhao.

CHEMISTRY

Professors R. H. Cole, K. Dwight (Research), P. J. Estrup (Physics), E. F. Greene, W. M. Risen, Jr., A. Wold; Assistant Professor G. J. Diebold; Visiting Professors W. Croft, M. W. Cole (Physics), Senior Research Engineer R. Kershaw; Research Associates E. I. Kamitsos, Y. Qian, D. Ridgley, P. Winsor IV; Research Assistants P. R. Muessig, D. E. Turcotte; Graduate Students R. Brusasco, L. Carreiro, D. D'Ambra, J. Foise, J. Fournier, M. Gray, A. M. Horlacher, D. Pasquariello, J. Perl, J. Prybyla, D. (Locotos) Stewart.

ENGINEERING

Professors R.J. Asaro, R. J. Clifton, J. Duffy, L. B. Freund, J. Gurland, G. S. Heller, J. J. Loferski, A. Needleman, A. V. Nurmikko, M. H. Richman, B. Roessler, J. Tauc (Physics), J. H. Weiner; Associate Professor C. F. Shih; Assistant Professor R. D. James; Visiting Professor V. Tvergaard; Visiting Assistant Professor M. Saje; Visiting Lecturer D. Narashimhan Postdoctoral Fellow P. Sarro; Visiting Senior Research Associate G. Kenshole; Visiting Research Associates C. J. Li; Senior Research Engineers E. E. Crisman, R. H. Hawley; Research Associates P. S. Lam, Z. Vardeny; Research Assistants K. M. Cho, Y. L. Su; Senior Technical Assistant J. W. Fogarty; Technical Assistants R. Beaulieu, G. J. LaBonte, Jr., W. Oates, P. Rush, H. Stanton; Graduate Students R. Arya, D. Berman, C. Case, H. Deve, O. J. Gregory, K. A. Hartley, R. Klopp, J. LeMonds, C. C. Ma, G. Meir, A. A. Morrone, J. Mosquera, T. Nakamura, D. Q. Nelson, J. Pan, A. J. Rosakis, T. Russell, T. G. Shawki, C. Toro, W. Yang, R. Zeller.

MATERIALS RESEARCH LABORATORY

Research Associates J. Beamish, E. I. Kamitsos, A. Khurana, L. D. Roelofs.

PHYSICS

Professors P. J. Bray, C. Elbaum, P. J. Estrup (Chemistry), A. Houghton, J. M. Kosterlitz, H. J. Maris, J. J. Quinn, G. Seidel, P. J. Stiles, J. Tauc (Engineering), S. C. Ying; Assistant Professor R. A. Pelcovits; Visiting Professor M. W. Cole (Chemistry); Visiting Postdoctoral Fellow G. Gonzalez de la Cruz; Research Associates A. Khurana, E. Vera; Research Assistants S. W. Heinekamp, G. Y. Hu, A. Jagannathan, K-F. Lau, R. Mayer, D. Pfof, F. Seco, J. Strait; Graduate Students J-W. Chung, G. Cibuzar, H. Closs, J. Erickson, B. B. Goldberg, S. J. Gravina, J. H. Harris, D. Hintenlang, E. J. Holupka, A. LeGrand, G. Landis, M. L. Lui, M. Manning, R. V. Mulkern, B. D. Parker, J. Prybyla, R. P. Smith, D. Syphers, M. L. Williams.

Principal Investigators

Asaro R. J.	8-9, 12
Bray P. J.	21, 24-26, 29
Clifton R. J.	1, 3, 5-6, 10
Cole M. W.	31, 35, 40
Cole R. H.	1, 21, 27-28
Cooper L. N.	1
Diebold G. J.	31, 33
Duffy J.	3, 7, 15, 19
Elbaum C.	1, 7, 21, 29, 43-44
Estrup P. J.	1, 31, 33-35, 39-40
Freund L. B.	1, 15-18
Greene E. F.	31, 33
Gurland J.	11, 18-19
Heller G. S.	1
Houghton A.	21, 28
James R. D.	11
Khurana A.	28, 49
Kolsky H.	12, 19
Kosterlitz J. M.	21, 28
Loferski J. J.	1, 40, 46
Maris H. J.	21, 23
Needleman A.	8-12, 15, 19
Nurmikko A. V.	48, 50-51
Pelcovits R. A.	40
Pipkin A. C.	18-19
Quinn J. J.	35, 39, 44
Richman M. H.	19, 51
Risen Jr., W. M.	1, 21, 24, 27
Roessler B.	46, 50
Seidel G.	44
Shih C. F.	12, 15-16
Stiles P. J.	1, 31, 35, 39-40, 50
Tauc J.	1, 23

Weiner J. H.	8, 49
Wold A.	46, 48, 50-51
Ying S. C.	31, 34-35, 40

DATE
ILME