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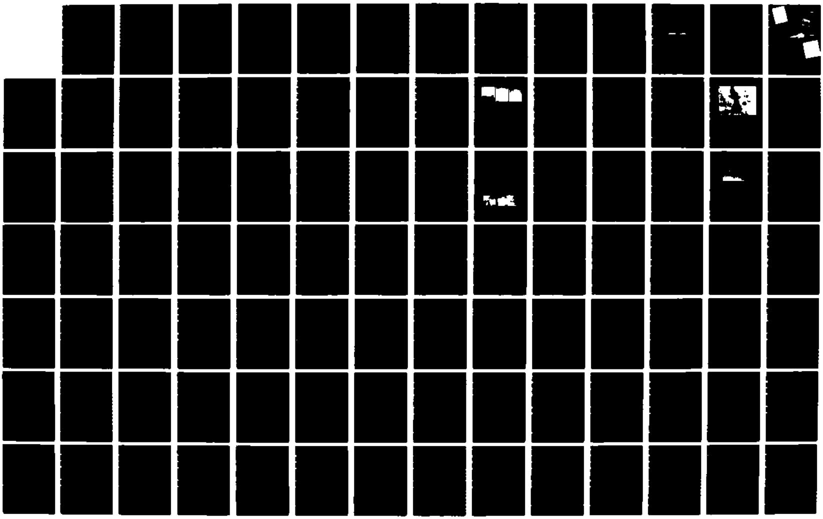

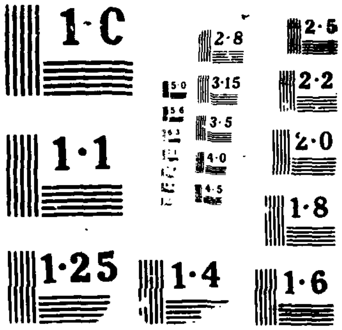
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ANNUAL TECHNICAL REPORT
MATERIALS RESEARCH LABORATORY
July 1, 1985-April 30, 1987

Brown University
Providence, Rhode Island 02912

ANNUAL TECHNICAL REPORT

MATERIALS RESEARCH LABORATORY

BROWN UNIVERSITY
PROVIDENCE, RHODE ISLAND 02912

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PREFACE

This report summarizes the research accomplishments in materials research at Brown University in 1985/87. The main thrust areas of interdisciplinary research supported by the NSF Materials Research Laboratory were concentrated in three areas:

Plasticity and Fracture (coordinated by R. J. Asaro)
Inorganic Glasses (coordinated by W. M. Risen, Jr.)
Surfaces (coordinated by P. J. Estrup).

In addition, the MRL supported the following New Initiatives:

Electron Microscopy of Layered Synthetic Microstructures (S. Nutt)
Surface Modifications of Hydrocarbons (J. W. Suggs)
Physical and Electronic Studies of Ge Passivation (J. Rosenberg)
Novel Optical Fiber Materials and Processing Methods (T. F. Morse)

MRL also provided support for research on

Materials Preparation (A. Wold)

The MRL operated six Central Facilities:

Materials Preparation Facility (directed by A. Wold)
Facility for Mechanical Testing (S. Suresh)
Electron Microscopy Facility (S. Nutt)
Optical Facility (J. Tauc and W. M. Risen, Jr.)
Electron Spectroscopy Facility (P. J. Estrup)
Microelectronics Facility (J. Rosenberg)

These Facilities provided supportive services for the MRL program and were also active in research on new techniques or new materials.

The materials research program at Brown involves investigators from the Department of Chemistry, Division of Engineering, Department of Applied Mathematics and Department of Physics. The largest single source of support was the National Science Foundation; thirteen agencies provided additional support and a significant contribution came from Brown University.

The Materials Research Laboratory was administered by a Director (J. Tauc), an Associate Director (W. M. Risen, Jr.), and an Executive Committee (R. J. Asaro, R. J. Clifton, C. Elbaum, P. J. Estrup, A. Houghton and A. V. Nurmikko).

SECTION 1

PLASTICITY AND FRACTURE

Introduction

Research in the plasticity and fracture thrust is concerned with fundamental studies of deformation and fracture in solids over size scales that range from atomistic to microstructural to macroscopic. In fact an important aim of much of the research is to provide quantitative links between the microstructural mechanisms of deformation and fracture and macroscopic behavior. Our studies are done on particular projects judged to be of most fundamental interest and, through research on the specific problems, more general frameworks for analyzing deformation and fracture processes are formulated. Most of the projects involve combined experimental-theoretical/computational study and in some cases it is the analyses that dictate the experiments. Our experimental studies are based on microstructural characterization using optical and analytic electron microscopy and special techniques developed at Brown for measuring micromechanical response under cyclic and dynamic loading. Our theoretical work is both analytical and computational. A noteworthy aspect of our computational analyses is that the detailed computations that are now possible allow for much more complete analysis of the behavior of microstructures and it is likely that the methods and models developed in this work will impact future analyses of the design and performance of microstructures.

Several studies conducted this past year have focused on microstructural and macroscopic mechanisms of large-strain plastic deformation with an emphasis on providing quantitative understanding of unstable, localized deformation mechanisms. Experimental studies in this area have included electron microscopy studies of shear band formation in polycrystals and direct observations of shear bands that form under dynamic loading conditions. The former studies were concerned with understanding how crystallographic slip is transmitted through interfaces whereas the latter work provided direct measurement of the nonuniform temperature distributions (and thermal softening) that develop as part of the dynamic shear band process. The theoretical work has included new computational studies of localized deformation in polycrystals -- this work is an example of a range of projects in *computational micromechanics* that are concerned with detailed analyses of complex deformation and fracture processes in microstructures. Experimental studies of ultra-high rate deformation of single crystals and polycrystals have also been conducted using the *pressure-shear* methods developed at Brown. The experiments have suggested that deviations from the Schmid rule play an important role in the overall slip response.

Research on the mechanics of interfaces has included computational studies of crack tip fields for cracks on interfaces. The mathematical structure of the stress and strain fields has been established by computation and the results are currently being used to model fracture processes at interfaces. The work has also been extended to include computational studies of cracks in crystalline media where the material is modelled by a large-strain, strain rate dependent theory for crystalline slip. Research has also been conducted on the mechanics of thin film interfaces. An important part of this work has been the formulation of a new continuum dislocation model for the loss of interface coherency between a strained layer and a substrate through interface dislocation generation. Such studies are pertinent for epitaxial growth of thin layers and superlattices.

Research on fracture has included analyses of void initiation mechanisms and the formulation of constitutive theories for microfracturing and transformation-toughened ceramics. Constitutive theories for both ductile, microvoiding materials and more brittle, microcracking materials have been used to analyze limits to material toughness through computational study of crack propagation in such damaged materials. The computational studies of void initiation are coupled to experimental studies of debonding at interfaces between ductile metal matrices and ceramic reinforcements in metal matrix composites. Additional work is concerned with mechanisms of damage and crack propagation in ceramics and ceramic composites. Novel experimental methods have been developed to study the fracture behavior in ceramics using far-field cyclic compression for the introduction of a stable, Mode I pre-crack. The mechanics and mechanisms of crack growth under far-field cyclic compression have been investigated in notched plates of single phase and transforming ceramics where stable fracture occurs in a residual tensile zone formed at the notch-tip during cyclic deformation.

Finally we note that experimental and theoretical research has continued on dynamic fracture of metals. A plate impact experiment has been developed for simulating the loading of a semi-infinite crack by a plane tensile wave. Interpretation of the crack tip response is made through computational analysis of stress wave interaction with the crack and by comparisons of measured motions on the specimen's outer surfaces; inference is made on the mechanics of crack advance. Theoretical work has also been continued on the mechanics of dynamic propagation of microcracks as specifically related to the fundamental process of cleavage and ductile versus brittle response.

More detailed discussions of the various projects outlined above follow. Project descriptions are grouped in terms of topical area. It should be noted, however, that this grouping is done to facilitate reading whereas the projects are strongly related.

R. J. Asaro, Coordinator

Localized Plastic Deformation in Compression of Single Crystals and Polycrystals

Principal Investigator: R. J. Asaro, Professor, Division of Engineering

Personnel: S. V. Harren, Graduate Student, Division of Engineering
H. E. Deve, Graduate Student, Division of Engineering
H. Mei, Graduate Student, Division of Engineering

Sources of Support: NSF/MRL

Objectives and Approaches:

The breakdown of more or less homogeneous patterns of deformation into those characterized by localized deformation modes, in particular shear bands, appears to be an entirely natural outcome of large-strain deformation processes. Observations made to date indicate that shear localization occurs under general states of stress and strain -- although, apparently promoted by plane strain states -- and does not require softening caused by damage via *microfracture*, material strain softening, or thermal softening brought on by adiabatic heating. Such softening effects are undoubtedly important and are dominant influences in many cases. However, studies conducted over the past ten years have shown that the localization of plastic flow should also be viewed as a material constitutive instability, and thus, predictable from the constitutive laws describing the behavior of the damage free material.

Past, and very recent work, at Brown has been concerned with understanding the mciro and macromechanics of shear band formation during uniaxial and plane strain tension in single crystals. Transmission electron microscopy of the structure and crystallography of shear bands, and computational (finite element) studies using large-strain, strain rate dependent constitutive theories, showed that macroscopically localized shearing was indeed a natural outcome of crystalline slip. In particular, *geometrical softening*, caused by nonuniform lattice reorientation, was shown in the experiments (Chang and Asaro, Acta Metall. 1981; Deve et al., Acta Metall. 1987) and analysis (Asaro, 1979; Peirce, Asaro and Needleman, Acta Metall. 1982, 1983; Deve et al., Acta Metall. 1987) to be an important micromechanical influence. On the other hand, there has been considerable effort, reported in the literature, to understand the mechanics of shear localization during compression. A good deal of the phenomenology has been documented and with this information as background it seemed possible to provide more quantitative insight into the mechanisms. Our most recent work (Harren et al., 1987) has been concerned with the formation of shear bands in single crystals and polycrystals of an aluminum-3 wt. percent copper alloy tested in plane strain (channel die) compression. Transmission electron microscopy was used to study the structure and crystallography of shear bands and of such processes as the propagation of shear bands across grain boundaries. Finite element methods were used to study the formation of shear bands in both single crystals and polycrystals. The computational models of both single crystals and polycrystals used measured slip system strain hardening data, and were successful in explaining how lattice reorientations help drive the mechanisms of localization in single crystals, and in explaining the propagation of shear bands across grain boundaries in polycrystals.

Research Achievements:

Figure 1 shows an example of a single crystal subjected to plane strain (channel die) compression. The compressive strain at this point is $\epsilon = 0.37$. Macroscopic shear bands, that formed at much earlier strains, are clearly visible in the micrograph. Figure 2 shows deformed finite element meshes at two stages of loading. The crystallography and slip system strain hardening behaviors were matched to those measured on the crystal of Fig. 1. The micromechanics of the shear bands predicted by

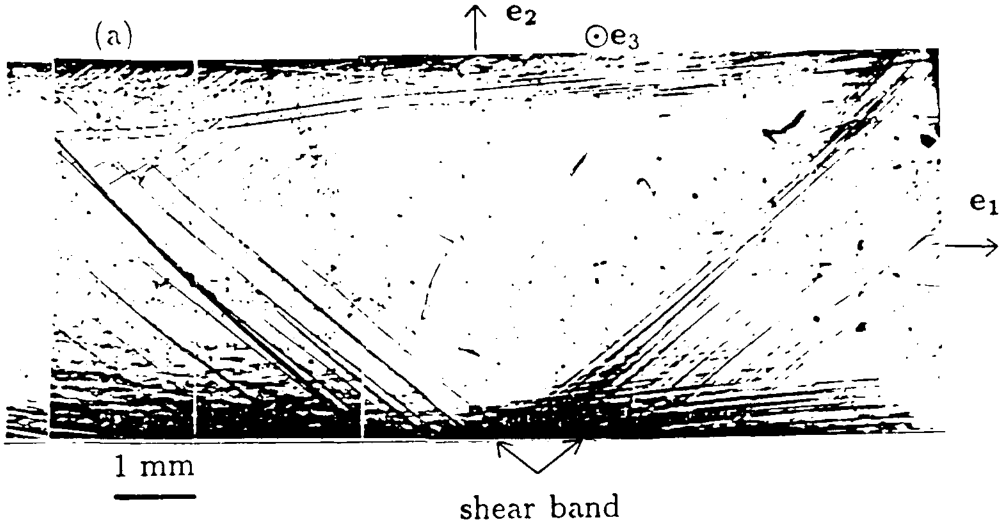


Figure 1: Optical micrograph of Eθ' at $\epsilon = 0.37$ showing macroscopic shear band traces on the lateral face.

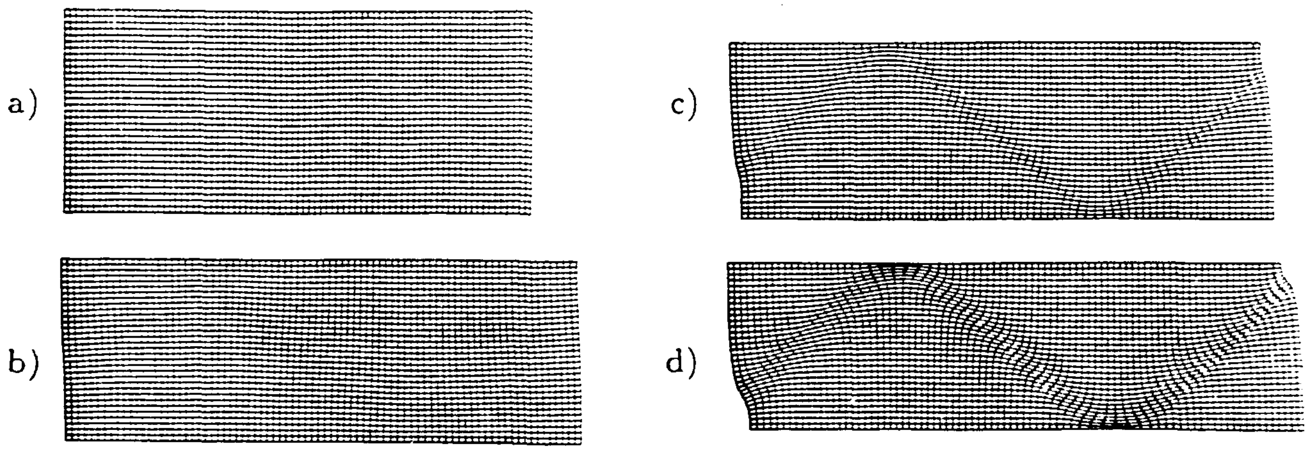


Figure 2: Deformed finite element meshes for the single crystal. The strain levels shown are (a) $\epsilon^m = -0.096$, (b) $\epsilon^m = -0.199$, (c) $\epsilon^m = -0.236$ and (d) $\epsilon^m = -0.288$.

the calculations are in close agreement with what was found experimentally. For example, Fig. 3 shows contours of a) maximum principle logarithmic strain, b) glide strain on one slip system, c) slide strain on the second (conjugate) slip system, and d) lattice rotation in degrees. Figure 3d indicates that abrupt lattice rotations occur across shear band boundaries; these lattice reorientations produce a *geometrical softening* which helps "drive" the shear band. Our transmission electron microscopy has shown that these rotations occur in essentially the manner predicted by the calculations.

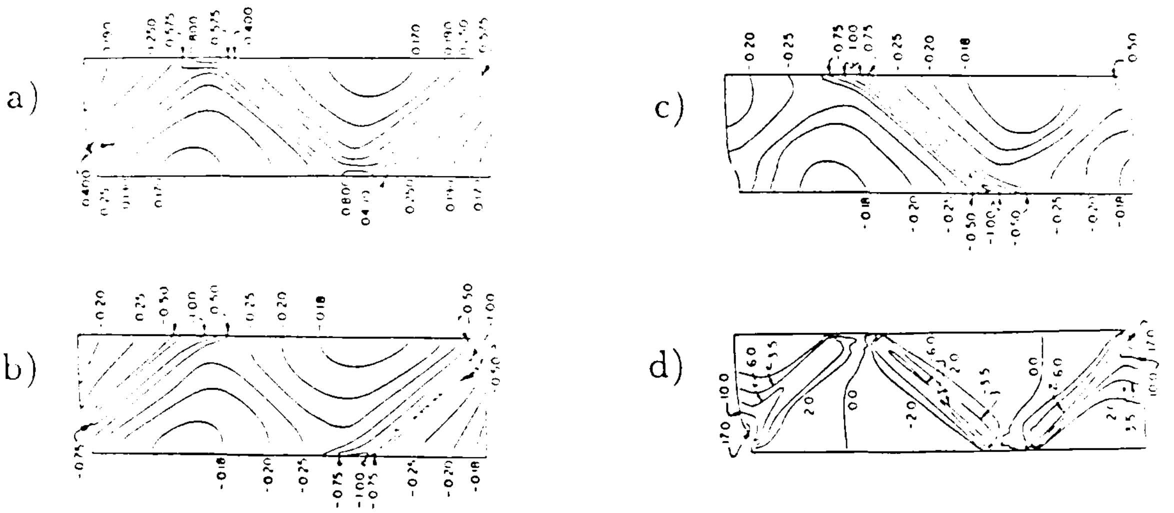


Figure 3: Contour plots of (a) maximum principal logarithmic strain, (b) glide strain γ_1, (c) glide strain γ_2 and (d) lattice reorientation in degrees. These correspond to the mesh shown in Fig. 2d. Note that the contour levels shown are measured with respect to $\epsilon^m = 0$.

Figure 4 shows a transmission electron micrograph of a shear band propagating through a grain boundary. The substructural features of shear bands of this type are quite complicated and are described, in detail, by Harren et al., 1987. One interesting aspect of the micromechanics of shear band *transmission* through grain boundaries is, what can be described as, a localized reorientation of the crystal lattice on both sides of the boundary so as to bring the dominant (i.e. most plastically active) slip systems toward alignment. This process occurs, in fact, as a natural part of even the macroscopically uniform deformation process.

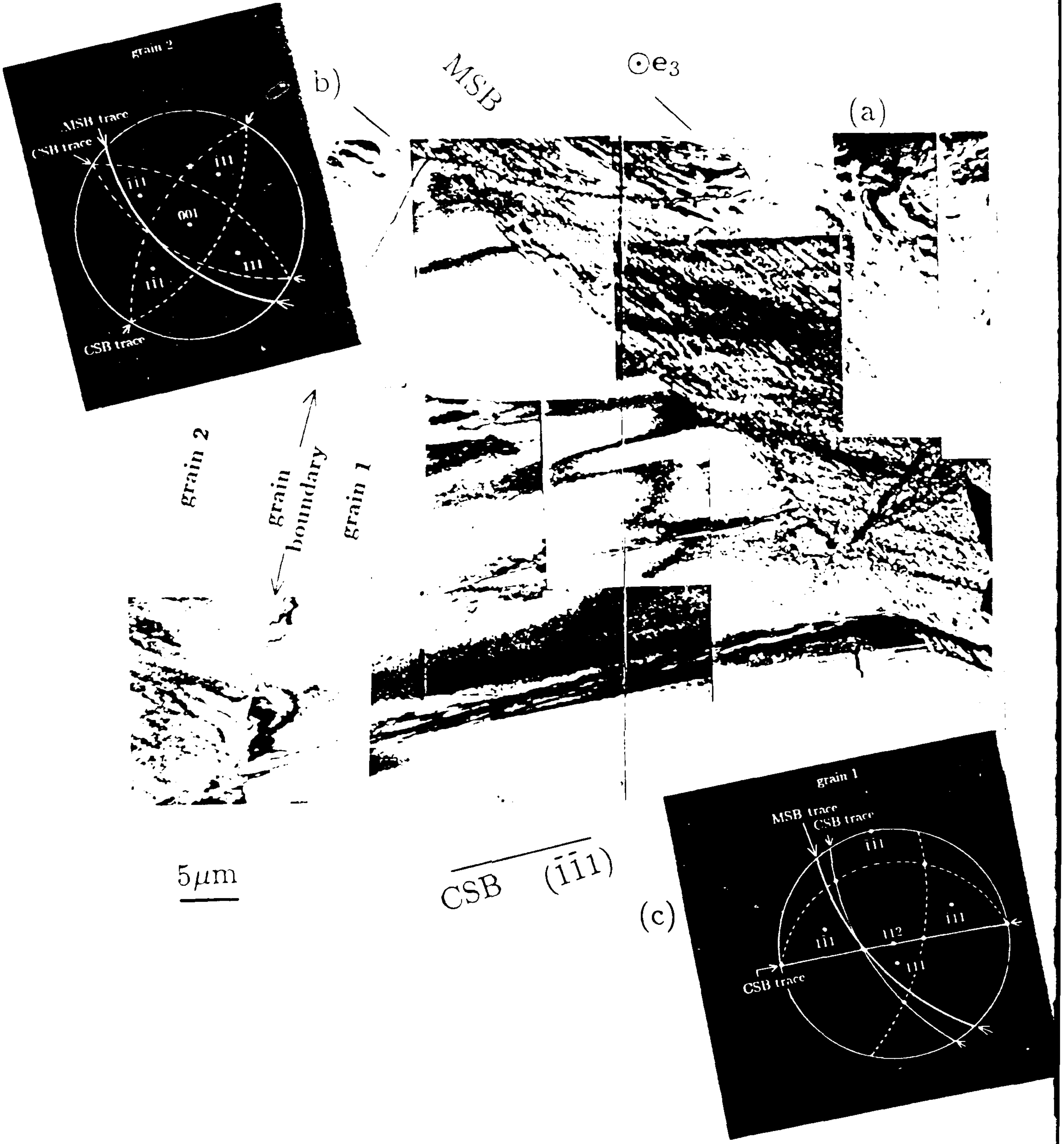


Figure 4: (a) Bright field electron micrograph of the polycrystal at $\epsilon = 0.43$. The plane of observation is normal to the transverse direction. (b) Crystallographic orientation of grain 2. The orientations, on the transverse face, of the CSB traces and MSB traces are indicated by the arrows, whereas, the {111} planes are represented by zone circles. (c) Same as (b) but for grain 1.

Figures 5a-5c show three deformed finite element grids of a polycrystal deformed in plane strain compression. These are analogous to the computations described in the section, "Development of Physically Based Constitutive Models for Crystal [illegible]" for tension and shear. Figure 6 illustrates the phenomena of lattice alignment described above. In this figure the orientation of the most active slip system on each finite element is plotted. Initially there was nearly a 36° misorientation between the lattices of grains 20 and 15, but it is clear from Fig. 6 that the traces of the dominant slip systems have reoriented more into alignment as the shear band propagates through the boundary. The computations also illustrate how localized plastic deformation initiates at grain boundary triple points as a natural outcome of the anisotropic properties of each grain. Note how in Figs. 5a-5c that macroscopic shear bands propagate across grain boundaries with little change in orientation as a result of this lattice alignment.

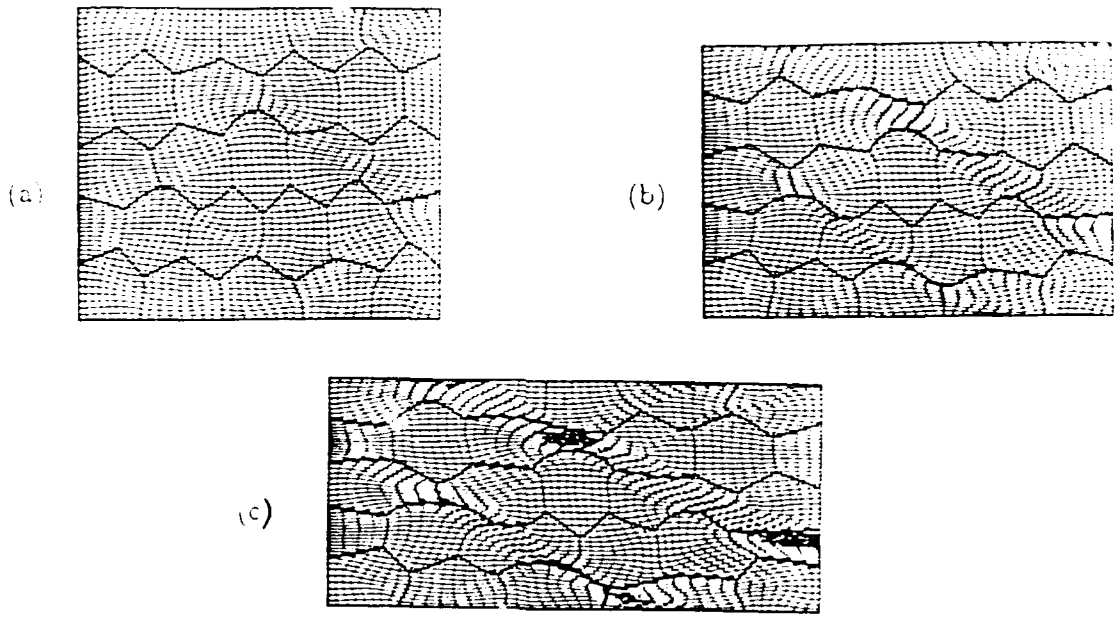


Figure 5: Deformed polycrystal finite element mesh as a function of strain. The strain levels are (a) $\epsilon = 0.381$, (b) $\epsilon = 0.511$ and (c) $\epsilon = 0.693$.

The experimental portion, in particular the electron microscopic observations, of this research is continuing to gain more insight into the mechanisms of slip transmission through interfaces. The computational aspects of our work have now been extended to three dimensions where a specific aim is to explicitly account for the influence of interfaces in triggering nonuniform and localized plastic deformation.

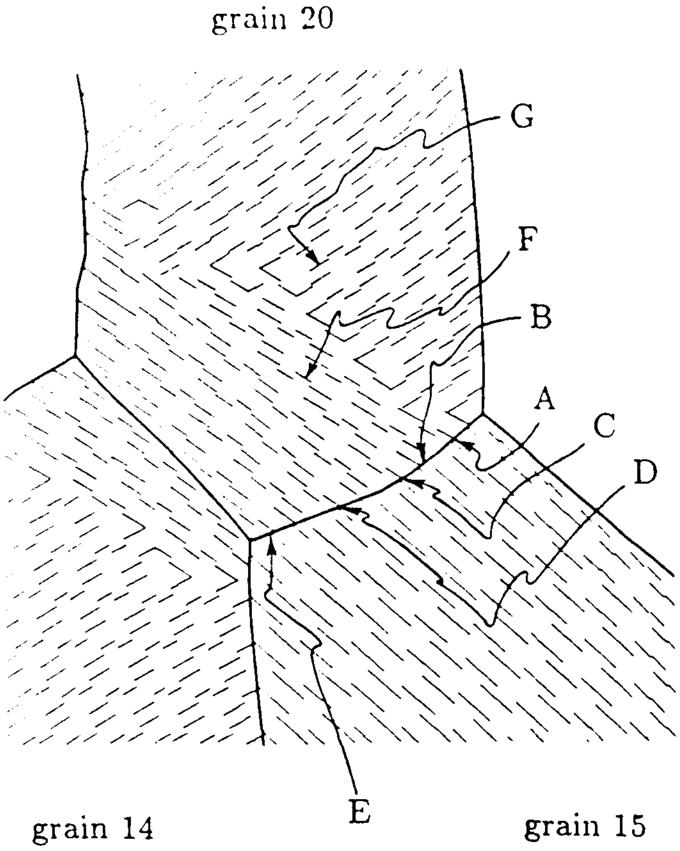


Figure 6: Current lattice orientations at $\epsilon = 0.217$. Shown is the impingement of grain 15's "grain level" shearing mode upon the 15-20 grain boundary.

<u>Publications</u>:

H.E. Deve, S.V. Harren, R.J. Asaro and C. McCullough, "Micro and Macroscopic Aspects of Shear Band Formationin Internally Nitrided Single Crystals of Fe-Ti-Nn Alloys," *Acta Metall.*, (1987) in press.

S.V. Harren, H.E. Deve and R.J. Asaro, "Shear Band Formation in Plane Strain Compression," submitted to *Acta Metall.*

Development of Physically Based Constitutive Models for Crystalline Materials

Principal Investigator: R. J. Asaro, Professor, Division of Engineering

Personnel: S. Harren, Graduate Student, Division of Engineering
H. Mei, Graduate Student, Division of Engineering

Sources of Support: NSF/MRL

Objectives and Approaches:

In order to predict behavior in large strain deformation processes, especially those associated with ductile fracture or localized deformation phenomena, it is essential for the descriptions of material behavior to accurately represent the underlying microstructural deformation mechanisms. Material features such as strength, strain rate and temperature sensitivity, stress and strain path dependence of strain hardening, along with anisotropy, are known to strongly influence the stability of plastic deformation and thus the qualitative patterns of deformation that develop at finite strains. Research at Brown during the past several years has been aimed at developing physically based constitutive theories that incorporate those properties just mentioned and which can be used in analyses of phenomena studied experimentally. The formulation of such theories, along with their incorporation into novel numerical calculations of strain deformation processes has led to a quantitative understanding of a range of complex deformation processes, and in particular of processes that involve the development of failure modes.

Earlier interest in understanding the process of shear band development in ductile single crystals has led to the development of large strain, strain rate dependent constitutive laws that were used to perform the first full boundary value problem analyses of necking and shear localization in crystalline solids. These laws are based on full nonlinear kinematical descriptions of both the deformation and rotation of the material and of the crystal lattice. In this way important phenomena such as nonuniform reorientation of the crystal are predicted and full account is taken of the effects of anisotropic material response. These single crystal constitutive laws have been used to develop large strain, rate dependent models for polycrystalline deformation. These new constitutive theories are used to predict the development of deformation induced crystallographic textures and the influence of texture on strain hardening response. They are also used to study how strain hardening and strain rate sensitivity on the microscale are translated to macroscopic behavior. Our studies of stress path dependent strain hardening have shown that material rate sensitivity strongly influences (usually retards) plastic straining following abrupt departures in stress direction. The details of this behavior are especially important for the analysis of unstable deformation which, in turn, sets limits for ductility and toughness.

Most recently we have conducted full numerical solutions of the deformation of polycrystals with the aims including 1) an evaluation of the effects of nonuniform deformation on polycrystalline consituttive behavior and texture development and 2) a comparison between the predictions of the fall solutions and those of our physical models.

Research Achievements:

Figures 7a-7d show examples of deformed finite element meshes for the case of a polycrystal deformed in plane strain tension. The polycrystal model was based on the idealized two dimensional crystallography proposed by Asaro (Acta Metall. 1979) except that three slip systems oriented at 60° to each other were accounted for. Initially the grains had the shape of regular hexagons and were of random orientation; the grains are indicated by the heavier lines. For the simulations of tension and shear periodic boundary conditions were applied which produced orthotropic symmetry. Strain rate dependent plastic shearing on the slip system level was described by a power law flow law of the form

$$\dot{\gamma}^{(\alpha)} = \dot{a}^{(\alpha)} \operatorname{sign}(\tau^{(\alpha)}) \left\{ \left| \frac{\tau^{(\alpha)}}{g^{(\alpha)}} \right| \right\}^{1/m}$$

where $\tau^{(\alpha)}$ = resolved shear stress on the αth slip system and $g^{(\alpha)}$ is an internal variable describing the current slip system strength; $\dot{a}^{(\alpha)}$ is a reference strain rate which can be interpreted such that if a *constant strain* experiment were conducted at the rate $\dot{\gamma}^{(\alpha)} = \dot{a}^{(\alpha)}$ then $\tau^{(\alpha)} = g^{(\alpha)}$ would be the measured shear stress-shear strain response. For the calculated results shown below the strain hardening function was taken to have the form

$$g^{(\alpha)} = g_0 + h_\infty \gamma_a + (g_\infty - g_0) \tanh \left\{ \left(\frac{h_0 - h_\infty}{g_\infty - g_0} \right) \gamma_a \right\}$$

where

$$\gamma_a \equiv \int_0^t \sum_\alpha |\dot{\gamma}^{(\alpha)}| \, dt$$

is the accumulated slip strain. To account for latent hardening, $\dot{g}^{(\alpha)}$ is taken to have the form

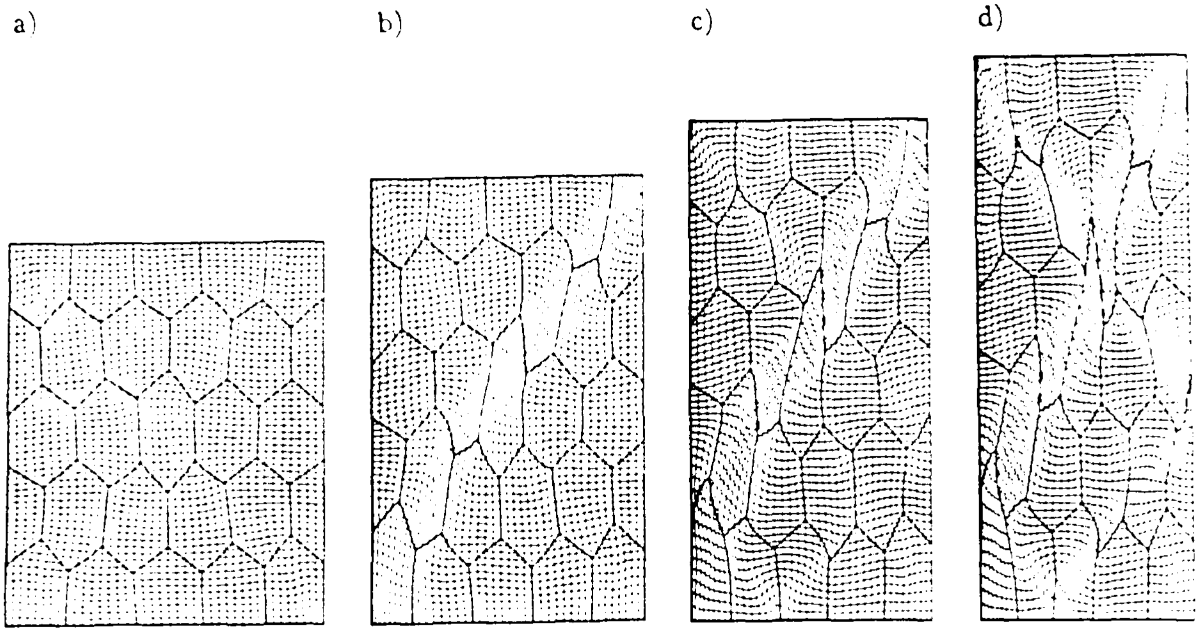
$$\dot{g}^{(\alpha)} = h_{\alpha\beta}(\gamma_a) |\dot{\gamma}^{(\beta)}|$$

with

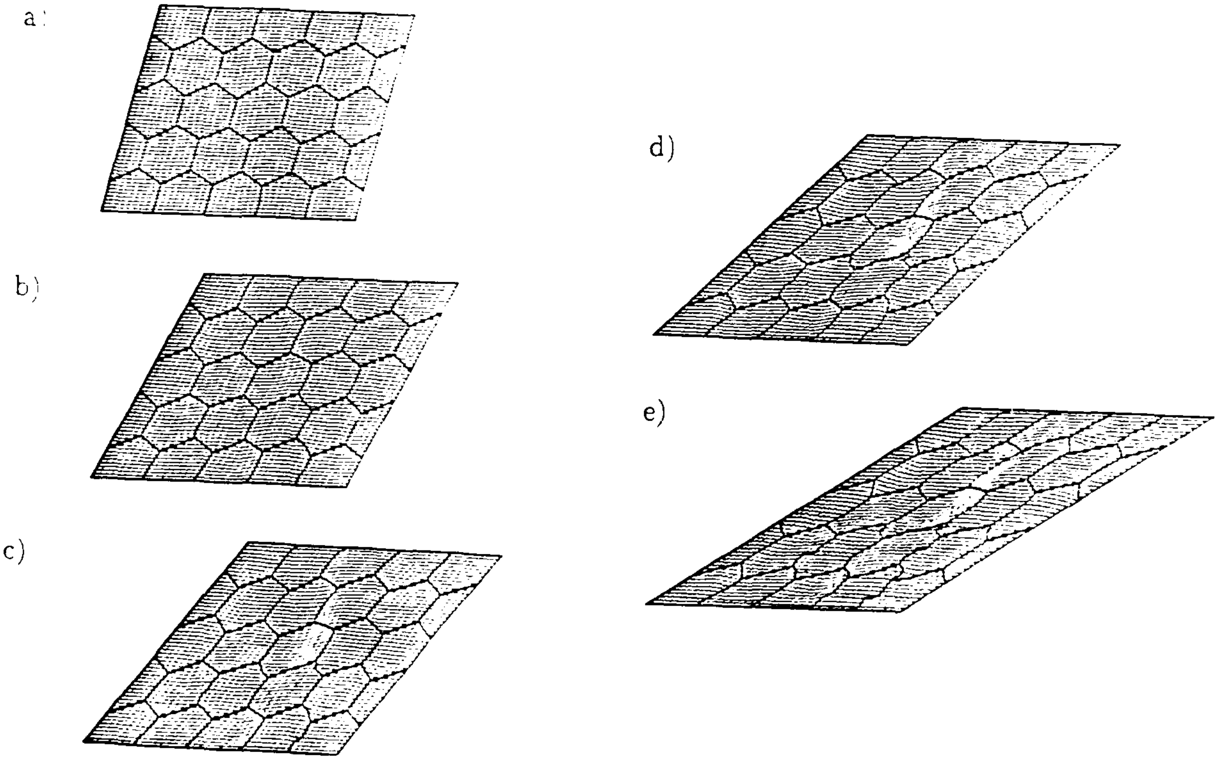
$$h_{\alpha\beta}(\gamma_a) = g'(\gamma_a) q_{\alpha\beta} \ .$$

$q_{\alpha\beta}$ are latent hardening ratios. Figures 7a-7d illustrate how nonuniform modes of deformation begin to develop at nominal strain levels of only 0.2; at a stage where the tensile strain has increased to 0.4 clearly discernable shear bands have developed. Shear bands continue to sharpen and propagate through grain boundaries with little change in their macroscopic orientation. Additional bands become visible at latter stages as may be observed in Fig. 7d.

Similar nonuniform behavior occurs for the cases of compression and shear. Figures 8a-8e show deformed finite element grids for the case of simple shear. As was observed for the case of tension, nonuniform deformations are clearly visible at shear strains of $\gamma = 0.25$ and localized modes are visible at strains of $\gamma = 0.75$ although they actually begin at much lower strains.



Figures 7a-7d: Deformed finite element meshes from the tension calculations. The strain levels are: (a) e=0.20, (b) e=0.40, (c) e=0.60 and (d) e=0.80.



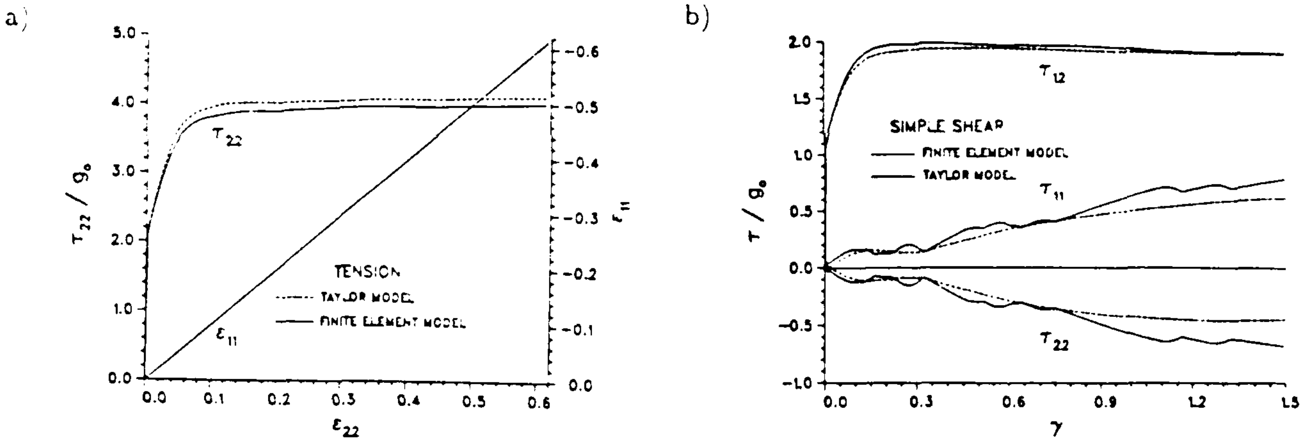
Figures 8a-8e: Deformed finite element meshes from the simple shear calculations. The strain levels are: (a) γ=0.25, (b) γ=0.51, (c) γ=0.75, (d) γ=1.00 and (e) γ=1.50.

Figures 9a and 9b illustrate part of the constitutive response predicted by the finite element models, along with the comparable predictions obtained using the rate dependent "Taylor-like" model of Asaro and Needleman (Acta Metall. 1985). Simulations using our polycrystal model were made using the same grain distributions, and boundary conditions, as were used in the finite element models.

Figure 9a shows the tensile stress-tensile strain response and Fig. 9b shows the shear stress-shear strain response. In both cases it is seen that the Taylor model initially overestimates the material's stiffness but at small, but finite strains, the overall stress strain responses are quite close. In the case of shear both models predict a *textural softening*.

The shearing histories that were imposed in both the finite element and Taylor modelcalculations were constrained to be simple shearing histories. Under such conditions it is experimentally observed that normal stresses tend to develop; these are also shown in Fig. 9b. The maxima and minima observed in the Taylor model predictions are due to the finite number of grains involved in the simulation and the fact that they rotate into *texturally harder* and *softer* orientations.

We are intending to continue this type of computational modelling in order to guide the development of three dimensional models like our rate dependent Taylor like model. To this end, and in collaboration with Professor M. Ortiz, we have extended the finite element analyses to three dimensions.



Figures 9a, 9b: **(a) Global stress-strain responses, under tension, of the Taylor and finite element polycrystal models. (b) Same as (a) except for simple shear.**

Publications:

S.V. Harren and R.J. Asaro, "Nonuniform and Localized Deformations in Polycrystals and Aspects of the Validity of the Taylor Model," submitted to *Journal of the Mechanics and Physics of Solids*.

Adiabatic Shear Bands

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

Personnel: A. Molinari, Visiting Assistant Professor, Division of Engineering

Sources of Support: ARO and MRL

Objectives and Approaches:

The objective of this research is to obtain simple analytical formulae for determining whether or not shear strain localization will occur and, if so, the critical nominal strain at which the localization becomes catastrophic. From numerical solutions of the fully nonlinear system of equations governing simple shearing deformations of thermoviscoplastic materials one can conclude that inertia, heat conduction and elasticity are relatively unimportant in shear band formation for the specimen sizes and strain rates that are used in torsional Kolsky bar experiments. Thus, these effects are neglected to obtain a simplified system of equations for which localization analysis can be done in essentially closed form.

Research Achievements:

Critical conditions for shear localization in simple shearing of thermoviscoplastic materials have been obtained in closed form for simple, representative models of material response. Explicit results obtained for the idealized, but fully nonlinear problem show the roles of strain-rate sensitivity, thermal softening, strain hardening, and initial imperfection on the localization behavior. Application of the analysis to shear band formation in torsional Kolsky bar experiments on two steels indicates that the principal features of the behavior observed in the experiments are predicted by the analysis.

Publications:

A. Molinari and R. J. Clifton, "Analytical Characterization of Shear Localization in Thermoviscoplastic Materials," (to appear in the Journal of Applied Mechanics).

Adiabatic Shear Bands

Principal Investigator: J. Duffy, Professor, Division of Engineering

Personnel: K.A. Hartley, Graduate Student, Division of Engineering, now Staff Member, Bell Telephone Laboratories
A. Marchand, Research Associate, Division of Engineering
G.J. LaBonte, Technical Assistant, Division of Engineering
R.H. Hawley, Research Engineer, Division of Engineering

Sources of Support: MRL, ARO, ONR

Objectives and Approaches:

Adiabatic shear band formation is a major damage mechanism in ductile steels since it usually represents catastrophic failure. The purpose of this research is to obtain a better understanding of the formation process of adiabatic shear bands in steels submitted to dynamic loading. Thin-walled tubular specimens were tested in pure shear by means of a torsional Kolsky bar at strain rates high enough to produce shear banding. Since this method provides only average values of strain and strain rate, the experiments were performed using high speed photography to measure the local strain within the shear band during its formation. In addition, infrared radiation techniques were employed to measure the surface temperature. The tests were conducted with different steels producing either a very narrow transformed band (AISI 4340 VAR and HY-100 steel) or a much wider deformed band (1018 CRS, 1020 HRS 1215 Steel).

Research Achievements:

It appears from our results that the plastic deformation process can be divided into three stages as shown in Figures 10 and 11. In the first stage of deformation, the shear strain is homogeneous: it does not vary either in the axial or in the circumferential directions. With further straining, and starting near the maximum stress, a second stage is entered into in which the strain is inhomogeneous: the strain distribution varies in the axial but not in the circumferential direction. The third stage initiates with the rapid drop in the load carrying capacity of the specimen, during which the amount of local strain increases into an ever-narrower shear band, and the strain varies strongly in the circumferential direction. The maximum value of the localized deformation before fracture seems to be about 600% within a band width of 100 μm for 1018 CRS, about 900% with a 10 μm width for 4340 VAR, while it is about 1500% with a corresponding width of 20 μm for HY-100 steel (1-4). For the last of these steels, short exposure photographs taken during the last stage of deformation indicate that very different magnitudes of localized strain occur at different locations on the circumference. This implies that the shear band may be propagating around the specimen. With an observed spot width on the specimen's surface of 35 μm, the maximum recorded temperature rise inside the shear band and before fracture was 410°C in 4340 VAR, 490°C in HY-100, and 575°C in 1018 CRS (1-3). However, for steels with a narrow shear band, i.e. the 4340 VAR and the HY-100 steels, experiments with a narrower observed spot (about 7 to 10 μm) will be needed to measure temperature accurately.

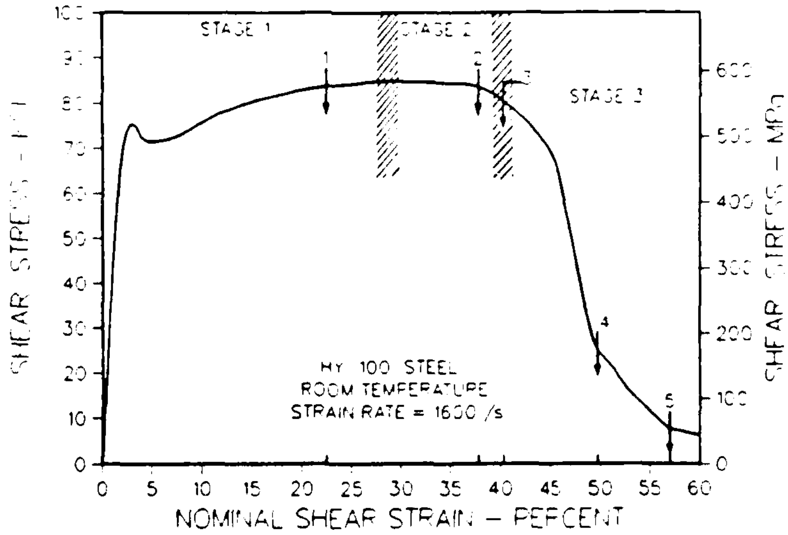


Figure 10: A typical stress-strain curve showing the strain values at which the photographs in Figure 11 are taken.

Homogeneous Deformation Stage 1

Inhomogeneous Deformation Stage 2

Shear Band Stage 3

Figure 11: Photographs of the grid patterns obtained in three separate tests at a nominal strain rate of 1600/s and illustrating (a) a homogeneous deformation, (b) an inhomogeneous shear strain distribution, and (c) a shear band.

Publications

A. Marchand and J. Duffy, "An Experimental Study of the Formation Process of Adiabatic Shear Bands in a Structural Steel," Brown University Report, ONR Contract N00014-85-K-0597, April 1987.

K.A. Hartley, J. Duffy and R.H. Hawley, "Measurement of the Temperature Profile during Shear Band Formation in Steels Deforming at High Strain Rates," Brown University Report No. DAAG-29-85-K-0003/2, March 1986. To be published in the *Journal of Mechanics and Physics of Solids*.

S.L. Semiatin, J.J. Jonas, T.G. Shawki and J. Duffy, "Effect of Material Imperfections on Flow Localization in Torsion," *Scripta Metallurgica*, 21, pp. 669-674 (1987).

K.A. Hartley, "Temperature Profile Measurement During Shear Band Formation in Steels at High Strain Rates," Ph.D. Thesis, August 1985.

H. Yaguchi, K.A. Hartley, R.H. Hawley and J. Duffy, "The Effect of MnS Inclusions in AISI 1215 Free-Machining Steels on Shear Band Formation under High Strain Rate Torsional Testing," 25th Annual CIM Conference of Metallurgists, Toronto, Canada, August 17-20, 1986, pp. III-68 to III-82.

Dynamic Fracture Initiation of Metals and Metal Matrix Composites

Principal Investigators: J. Duffy, Professor, Division of Engineering
R.J. Asaro, Professor, Division of Engineering
C.F. Shih, Professor, Division of Engineering
L.B. Freund, Professor, Division of Engineering
S. Suresh, Associate Professor, Division of Engineering

Personnel: A. Marchand, Research Associate, Division of Engineering
R.H. Hawley, Research Engineer, Division of Engineering
S. Lee, Graduate Student, Division of Engineering
T.A. Christman, Graduate Student, Division of Engineering
H. Couque, Graduate Student, Division of Engineering, now Staff Member Southwest Research Institute

Sources of Support: MRL, ARO, ONR

Objectives and Approaches:

To answer the need for an experimental technique that would provide a value for the dynamic plane strain fracture toughness of a material, a dynamic fracture initiation test has been developed by Duffy and co-workers. In this test, a specimen in the shape of a notched round bar with a fatigue induced crack at the notch root is subjected to a dynamic tensile loading pulse of sufficient magnitude to fracture the specimen during the initial rise of the loading pulse, Fig. 12. The accuracy of this procedure was examined in the light of a recent finite element analysis using a mesh in the r-z plane as shown in Fig. 13. This fracture technique is employed in the study of the dynamic fracture behavior of AISI 1020 steel and of a 2124-T6 aluminum alloy reinforced with 13·2 v/o SiC whiskers. For the 1020 steel, an investigation was conducted into the effects of temperature, loading rate, and various microstructural parameters. For the composite, dynamic behavior is compared with quasi-static behavior and with the behavior of the reinforced 2124-T6 aluminum alloy.

Research Achievements:

A finite element analysis of the dynamic plane strain fracture toughness experimental technique showed that the dynamic fracture toughness can be determined to good accuracy from the experimentally obtained P-δ record, as long as the ratio of the crack depth to bar radius exceeds 0.7. Dynamic fracture toughness at stress intensity rates of $K_{Ic} \sim 2\times10^6$ MPa $\sqrt{m}$ s^{-1} and quasi-static fracture toughness at $K_{Ic} \sim 1$ MPa $\sqrt{m}$ s^{-1} were measured and correlated with the microstructures in 1020 steel. The fracture tests were conducted over the range of test temperatures from -150°C to 150°C in which fractures were observed to be purely by cleavage to a fully fibrous mechanism. As can be seen from Fig. 14, under high rate conditions the transition from a cleavage to a fibrous type of fracture initiation occurs at a higher temperature over a narrow temperature range. Statically, two of the microstructures showed a higher fracture toughness in the range -60°C to 0°C than at room temperature. This phenomenon was studied in some detail through an additional series of tests and shown to model by a relation in which K_{Ic} is proportional to $\sqrt{\text{strength}}$.

The results of a series of experiments on the dynamic behavior of a metal-matrix composite show that, in general, fracture toughness in the reinforced material is sensitive to loading rate but that the stress-strain behavior does not change with deformation rate in the range from quasi-static strain rate to 3000/s. A scanning electron micrograph of the fatigue area of dynamic tests of reinforced material is shown in Fig. 15. Preliminary observations seem to indicate no significant differences in the failure mechanisms between dynamic and static tests at room temperature, in spite of the higher dynamic value of K_I. Further detailed analyses of the failure mechanisms are currently in progress.

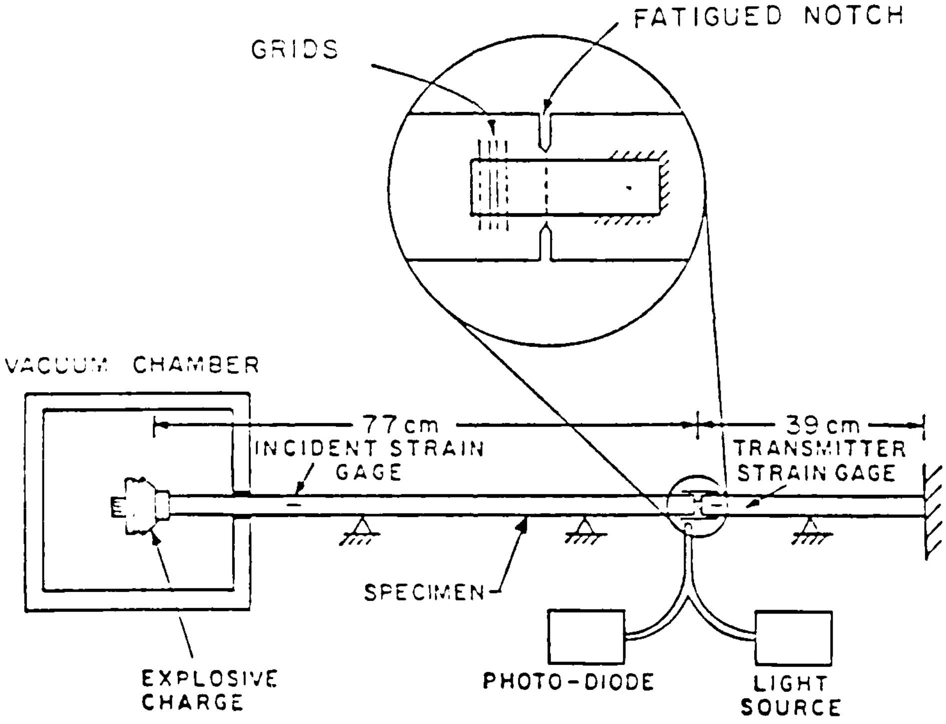


Figure 12: Schematic diagram of apparatus for dynamic fracture initiation experiment.

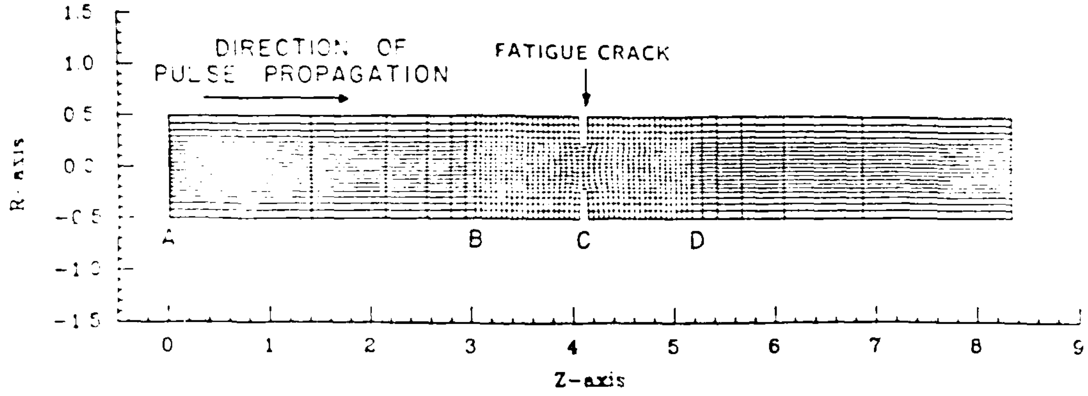


Figure 13 Axisymmetric finite element model of an externally notched round bar with a R = 0.6.

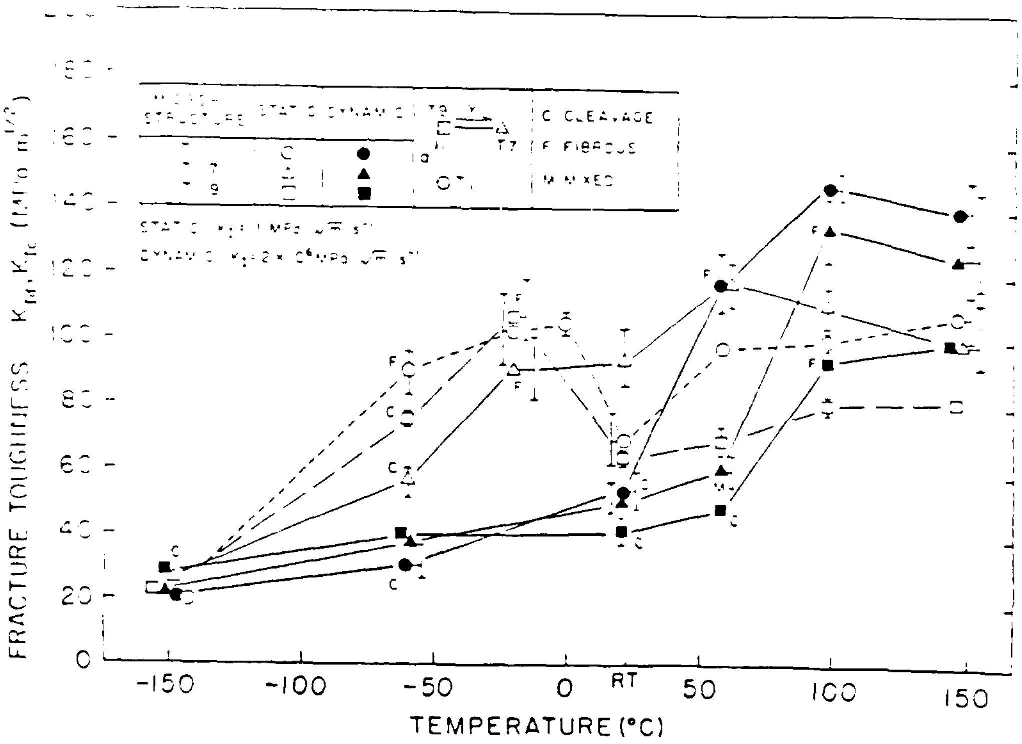


Figure 14: Quasi-static and dynamic values of fracture toughness for the different microstructures as a function of temperature. The fracture initiation mode is indicated qualitatively by the letters 'C', 'F', or 'M' depending upon whether initiation is by cleavage, fibrous, or mixed cleavage-fibrous mechanisms.

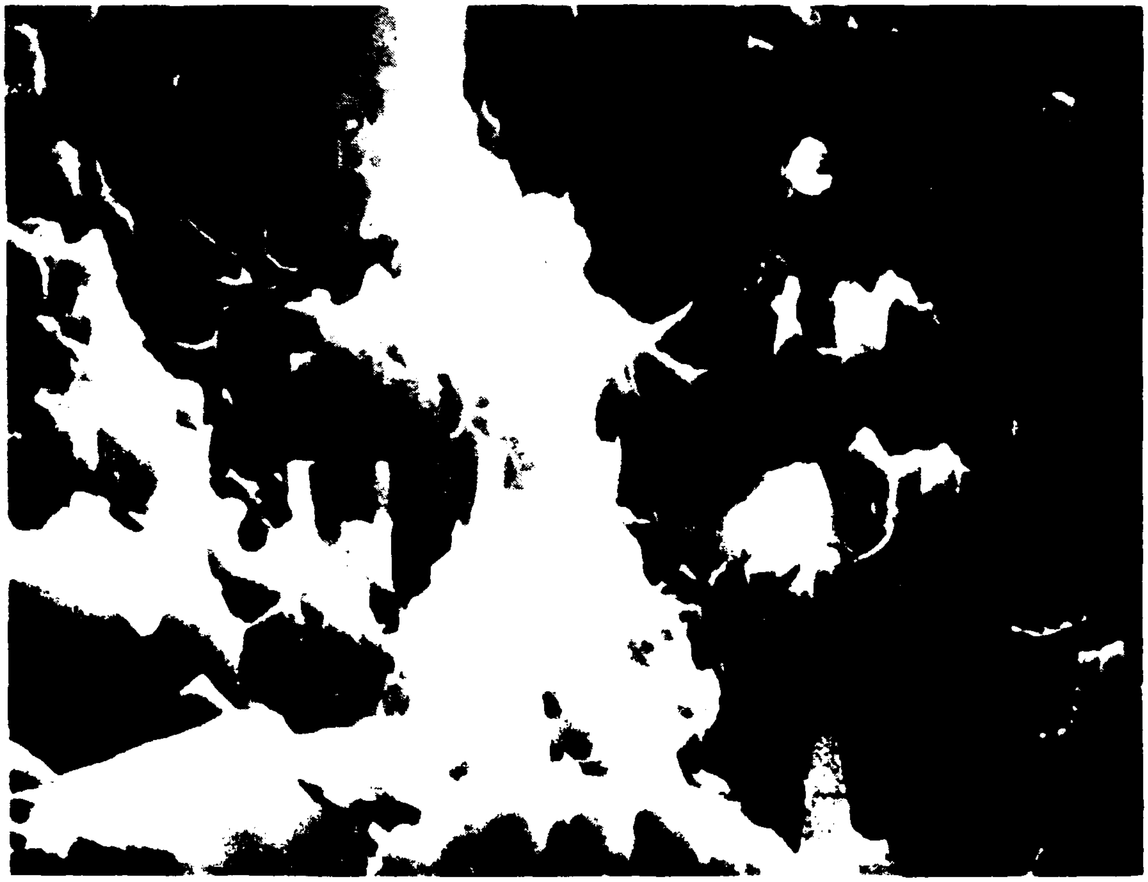


Figure 15 SEM photograph of fractured surface of Al-SiC$_w$ composite taken at 45° tilt.

Publications

J. Duffy, C.F. Shih, L.B. Freund and R.H. Hawley, "Fracture Initiation by Stress Wave Loading," *Journal de Physique*, 46, Colloquium C5, Supplement to No. 8, August 1985. Proceedings of the International Conference on Mechanical and Physical Behavior of Materials under Dynamic Loading, pp. C5, 163-169.

H. Couque, R.J. Asaro, J. Duffy and S. Lee, "Correlations of Microstructure with Dynamic and Quasi-Static Fracture in Plain Carbon Steel," Brown University Report, submitted for publication, March, 1987.

A. Marchand, J. Duffy, T.A. Cristman and S. Suresh, "An Experimental Study of the Dynamic Mechanical Properties of an Al-SiC$_w$ Composite," Brown University Report, submitted for publication, December, 1986.

H. Couque, "Correlations of Microstructure with Dynamic and Quasi-Static Fracture in Plain Carbon Steel," Ph.D. Thesis, May, 1986.

Plastic Flow in Single Crystals and Polycrystals at High Strain Rates

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

Personnel: R. W. Klopp, Graduate Student, Division of Engineering
W. Tong, Graudate Student, Division of Engineering
S. Huang, Research Associate, Division of Engineering

Sources of Support: ARO and MRL

Objectives and Approaches:

To obtain fundamental understanding of plastic flow at high strain rates, pressure-shear experiments are being conducted on single crystals and polycrystals of high-purity fcc metals. Results of experiments on aluminum single crystals, oriented in various directions relative to the applied loading, are being used to obtain the response of individual slip systems. Slip theory is being used to obtain the response of polycrystalline aluminum from the inferred response of individual slip systems. This predicted macroscopic plastic response is compared with the results of experiments on polycrystals. Further understanding of the generality of the observed macroscopic response is being obtained through similar experiments on polycrystalline copper.

Research Achievements:

A technique has been developed for lapping specimens to thicknesses as small as 30μm while maintaining the flatness and parallelity required for plate impact experiments. With this technique the maximum strain rate attainable in pressure-shear experiments on bulk materials has been raised from approximately $10^5 s^{-1}$ to $10^6 s^{-1}$. A series of experiments has been conducted on aluminum single crystals to determine the shear stress required for simple shearing on (112) planes, in three different directions. Attempts to correlate the measured stresses with predictions based on viscoplastic constitutive models for the response of individual slip systems have, so far, been unsuccessful. The most likely explanations for the observed discrepancies appear to be the lack of a satisfactory model for the plastic response of a single slip system over a wide range of values of the resolved shear stress and the lack of consideration of so-called non-Schmid effects in which the plastic slipping on one slip system depends also on the resolved shear stress on other slip systems. Agreement between predicted and measured responses for polycrystalline aluminum is also not fully satisfactory. In research on high-purity, polycrystalline copper, the dynamic plastic response has been established up to strain rates of $10^6 s^{-1}$. Preliminary experiments have been conducted to determine the effects of strain-rate history and temperature on the plastic response of copper at strain rates of $10^5 s^{-1}$ to $10^6 s^{-1}$.

Publications:

R. W. Klopp, "Plasticity of Aluminum and Iron at High Shear Strain Rate and High Pressure," Ph.D. Thesis, Brown University, October, 1986.

Ultrasonic Studies of Materials During Deformation

Principal Investigator: C. Elbaum, Professor, Department of Physics and Division of Applied Mathematics

Personnel: A. Hikata, Professor (Research), Applied Mathematics
M. Han, Graduate Student, Department of Physics

Sources of Support: DOE, MRL

Objectives and Approaches:

This research aims at achieving an understanding of microscopic deformation mechanisms in materials at various strain rates. Special emphasis is placed on the dynamics of dislocations in solids subjected to short duration (approximately 100 microseconds) stress pulses. The studies focus on measuring high freq2uency ultrasonic wave attenuation and velocity changes concurrently (i.e., in real time) with the application of a stress pulse, and for any time following the passage of this pulse. This is accomplished by means of instrumentation that permits one to sample the ultrasonic attenuation and velocity changes at approximately 10 microsecond intervals. Thus, the behavior of dislocations can be determined before, during and after the deformation due to the stress pulse.

Research Achievements:

Experimental studies of dislocation dynamics in LiF single crystals, using the approach outlined above, were performed at room temperature, and in the temperature range 25-300°K. From the former, the time dependence of the ultrasonic attenuation was found to result from dislocation multiplication followed by the evolution of mobile dislocations to immobile ones under large stress. From the latter, the temperature dependence of the ultrasonic attenuation was interpreted as due to the motion of dislocation loops overcoming the periodic Peierls potential barrier in a manner analogous to the motion of a thermalized sine-Gordon chain under a small stress. The Peierls stress obtained from the experimental results by application of a relaxation model with exponential dislocation length distribution was 4.26 MPa, which is consistent with the lowest stress for the linear relation between the dislocation velocity and stress observed by other workers.

A comparison of the results obtained here with those of many related sutdies on other materials leads us to the following conclusions.

The behavior of dislocations under large external stress (in excess of the macroscopic yield stress), such as delayed yield and rapid strain hardening, is usually due to material-specific properties; however the behavior of dislocations under small stress (ultrasonic probe) can be described by a very general model.

The ultrasonic attenuation in a LiF crystal, due to dislocations, can be understood with the generalized string model, including Peierls stress effects. In terms of the damping coefficient, the viscous damping is the result of a combination of phonon drag and the thermal generation of kink pairs. If either of these two components is neglected, the description of the dislocaiton damping is incomplete. However, due to the different temperature dependences of the relaxation times at low and at high temepratures, the incomplete description, obtained by neglecting phonon drag or thermal kink pair generation processes constitute a good approximation within limited temperature ranges. More specifically, the string model is a good approximation at high temperatures, where the relaxation time due to phonon drag dominates, while the relaxation model (or thermal activation process) characterized by an Arrhenius relation governing kink pair generation is a good approximation at low temperatures, where exponential temperature dependence dominates. The inclusion of both the phonon drag and the thermal activation yields a satisfactory descriptin of dislocation damping over the whole temperature range (at least up to room temperature).

Crystal Defects and Deformation Studies in Quantum Solids

Principal Investigator: C. Elbaum, Professor, Department of Physics and Division of Applied Mathematics

Personnel:
M. B. Manning, Graduate Student, Department of Physics
M. J. Moelter, Graduate Student. Department of Physics

Sources of Support: NSF

Objectives and Approaches:

The study of defects in solid helium is motivated largely by the possibility that any defect in a quantum solid may become a delocalized excitation which can move with little hindrance through the crystal. In this context, there have been many theoretical investigations of such effects as they apply to impurity atoms, vacancies, and dislocations in solid helium. Much of the earlier experimental work, however, has been carried out for the case of impurity atoms, typically small concentrations of ^{3}He in ^{4}He. In this case the motion of the ^{3}He impurity can be studied by NMR techniques and its delocalized nature has been fairly well-established. Experimental studies of the behavior of other defects in quantum solids have followed more recently and in some of these plastic deformation has played a major role.

Plastic flow in classical crystalline solids may be understood in terms of the motion of dislocations within the solid under an applied stress. Impurity atoms, intersections with immobile (network) dislocations, and the Peierls potential are examples of obstacles of dislocation motion. The mechanisms by which the dislocations of a crystal overcome such barriers determine the rate of crystal deformation under stress. An investigation of plastic flow, the temperature dependence of the crystal strain rate under constant stress in particular, provides a means for the study of crystal defects which mediate these processes. Examples of such defect involvement in plastic deformation are the formation of dislocation double kinks by thermal activation or tunneling of the Peierls barrier (dislocation glide) and the dislocation climb controlled by vacancy diffusion.

In the case of quantum solids, plastic flow studies may explicitly verify the quantum-mechanical tunneling behavior of point defects (e.g., vacancies and dislocation kinks), where unambiguous evidence of such delocalization effects form other kinds of experiments is not available.

We have carried out several investigations of plastic flow in solid He, previous to the present study. In the case of hcp ^{4}He, plastic flow appears to proceed by thermally activated dislocation motion. Plastic flow in the bcc phases of ^{3}He and ^{4}He, however, has been both less thoroughly investigated and less readily attributable to dislocation slip than in the case of the hcp ^{4}He. In fact, we proposed, on the basis of the small ultrasonic attenuation increases and evidence for localized deformation in bcc ^{4}He during its deformation, that the role of dislocation slip in this process is secondary, at least in the usual (classical) sense. This is in contrast to the behavior of dislocations in hcp ^{4}He deformation, as determined by large ultrasonic attenuation increases while deformation proceeds. In the bcc phases of the He solids the diffusion of mobile vacancies is considered to be a possible mechanism for mass flow. It is precisely in such diffusion processes that the quantum nature of the He solids is expected to be most evident.

Research Achievements:

We have studied plastic deformation of bcc ^{3}He as a function of temperature and strain rate, for various stress levels. Ultrasonic attenuation changes were measured concurrently as a function of strain. A model based on vacancy diffusion (by quantum mechanical tunneling) and dislocation slip was developed to account for the experimental results. It was possible to deduce, on the basis of this model, the energy bandwidth for delocalized vacancies of ~0.25 K.

Publications:

M.B. Manning, M.J. Moelter and C. Elbaum, "Plastic Deformation, Vacancy Diffusion and Vacancy Delocalization in Solid ^{3}He," *Physical Review*, B33, p. 1634 (1986).

Fundamental Studies of Interface Fracture

Principal Investigators: R. J. Asaro, Professor, Division of Engineering
C. F. Shih, Professor, Division of Engineering

Personnel: M. Symington, Graduate Student, Division of Engineering
A. Varias, Graduate Student, Division of Engineering

Sources of Support: ONR and MRL (Central Facilities)

Objectives and Approaches:

Nearly all fractures, whether they occur by ductile or brittle-like mechanisms, initiate at interfaces. Intergranular fractures in ductile alloys and more brittle fractures in ceramics are common examples. For alloys that rupture by completely fibrous mechanisms involving void initiation, growth, and coalescence the initiation of damage typically occurs at interfaces such as those between second phase particles and the matrix. At present, however, very little exists in the way of complete solutions for the mechanics of interface cracks that may be used to model interface separation mechanisms. The present work is concerned with the development of a rigorous framework for analyzing separation of interfaces in materials modelled with phenomenological elastic-plastic constitutive laws as well as physically based models for crystalline slip. The theoretical and computational work is to be coupled to experimental studies of the mechanics of separation at interfaces in model systems comprised of metal/metal interfaces.

Research Achievements:

Asymptotic Elastic Analyses

An incomplete series solution for a crack on the interface between two dissimilar media was obtained by Williams (1957) [1]. Using the eigenfunction expansion method employed by Williams, the complete power series in r, the radial distance from the crack tip, has been obtained. The power series in r contains both complex fractional powers and real integer powers [2]. By including integer order terms, the domain of validity of the series solution can be extended and this is helpful for computational studies for the evaluation of stress intensity factors and small scale yielding studies.

Computational Studies of Interface Cracks

Full field numerical solutions for a crack which lies along the interface between two dissimilar media have been obtained. In particular we have investigated an elastic-plastic medium bonded onto a) rigid substrate; b) elastic substrate and c) elastic-plastic substrate. The solutions are obtained using a small strain J_2 deformation theory with power law strain hardening. Guided by the full field solutions and with the help of dimensional considerations, we have obtained an explicit form for the dependence of the plastic zone size and shape on the bimaterial constant and strain hardening properties. Under small scale yielding conditions, the elastic singular fields are described by the magnitude of the complex stress intensity factor and its phase angle. The plastic zone (size and shape) and the elastic-plastic fields are members of a single family parameterized by a parameter which is linearly dependent on the phase angle of the elastic singular fields and mildly dependent on the product of the bimaterial constant and the magnitude of the elastic singular fields. The structure of the elastic-plastic fields has been verified by extensive and detailed deformation theory calculations. The zone of contact of the crack faces (if any) within the plastic zone has been determined in terms of the above-mentioned parameter. Large scale yielding solutions for a periodic array of cracks along a bimaterial interface have also been obtained.

Computational Studies of Cracks in Crystalline Media

Computational studies of crack mechanics in crystalline media have been initiated this past year. The constitutive laws that are used are based on a large strain, strain rate dependent constitutive theory for crystalline slip. These laws are based on fully nonlinear kinematical descriptions of both the deformation and rotation of the material and of the crystal lattice. Our aims are to carry out detailed computations of the stress and strain fields of cracks on grain boundaries for the purpose of modelling interface fracture mechanisms. We have now completed the first full solutions for crack tip fields for cracks in homogeneous crystals. The two orientations analyzed are indicated in Fig. 16. The slip system geometries correspond to what has been previously analyzed by us in connection with our shear band studies described in the section entitled "Development of Physically Based Constitutive Models for Crystalline Materials." Our calculations have shown that for the case where $\phi = 35.27^\circ$. The plastic zones are characterized by two discrete bands of deformation which are nearly aligned with the active slip systems. Each band of concentrated straining is dominated by slip on the particular slip system to which the bands are nearly parallel. For the case where $\phi = 54.73^\circ$ the plastic fields are again characterized by discrete bands of deformation. The bands in this case are nearly perpendicular to each of the active slip systems. In addition, the deformation in each band is dominated by slip on the slip system to which the band is nearly perpendicular. Although the overall patterns of plastic deformation are similar, the crystallography of these deformation modes is quite different. In the first case the banded deformation patterns are kinematically similar to shear bands whereas in the second they resemble the "kink modes" discussed by Asaro and Rice (*Journal of the Mechanics and Physics of Solids*, 1977), Asaro (*Applied Mechanics Reviews*, 1983) and more recently by Rice (Harvard University Report, Mech-106, 1987). The calculations also indicate that large, nonuniform, lattice rotations occur in the crack tip region which effectively form high angle *subgrain* boundaries.

These calculations are being extended to other orientations with the intention of providing the framework for more quantitative analysis of fracture processes in crystals and at crystal interfaces.

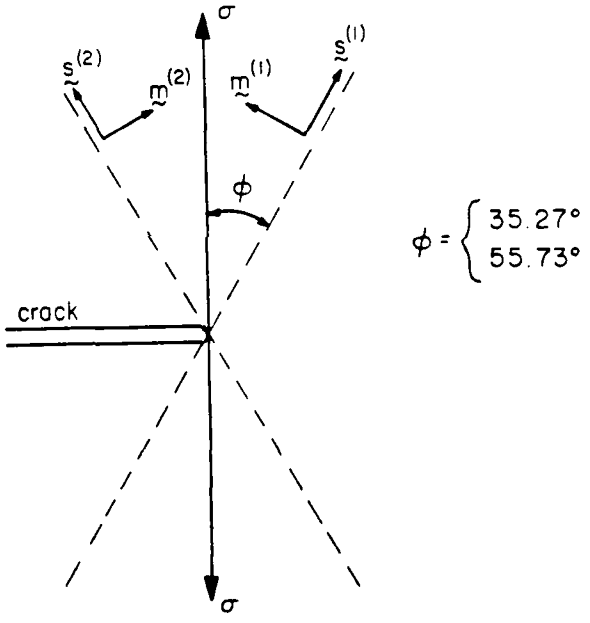


Figure 16: Crystal Crack Geometry

<u>Publication</u>:

R. J. Asaro and C. F. Shih, "Elastic-Plastic Analysis of Cracks on Bimaterial Interfaces Part I: Small Scale Yielding," *Journal of Applied Mechanics*, to appear.

Mechanics of Thin Film Structures

Principal Investigator. L. B. Freund, Professor, Division of Engineering

Personnel: J. C. Ramirez, Graduate Student, Division of Engineering

Sources of Support: MRL, IBM

Objectives and Approaches:

A thin solid film bonded to the surface of a relatively large sample of a second material, that is, to the solid substrate, is a common configuration in a variety of areas of technology, including microelectronics, photovoltaic solar cells, micro-optics, lubrication and wear. In virtually all of these areas of potential application, development of techniques for controlling composition and internal structure of films, and a basic understanding of properties and influences of interfaces between thin films and their substrates will have a beneficial impact on the relevant technologies. In order to pursue some of the outstanding problems in this general area, a research program has been initiated that focuses on the mechanical fields that can exist in thin film structures, and the implications of such fields for both mechanical and non-mechanical phenomena. Several specific problems are identified for study. These include: (i) development of an analytical model for description of the stress and deformation fields that exist near a metal-semiconductor interface as in a field-effect transistor and comparison with experiments on a simple structure involving a WSi micron gate on a GaAs substrate, (ii) study of the crystalline defect structure in a strained epitaxial layers and the influence of stress arising from mismatch strain in nucleating and moving defects, and (iii) edge stress concentration and plastic strain localization in thin films bonded to substrates.

Research Achievements:

The continuum theory of elastic dislocations has been applied to estimate the critical thickness of a strained layer bonded to a substrate for a given mismatch strain. The formation of strained epitaxial layers is of interest due to their special electronic or optical properties, and critical thickness is understood to be the smallest thickness at which interface dislocations can form spontaneously by some mechanism. The criterion invoked in this work was based on the work done by the layer stress in driving a threading dislocation to lay down a misfit dislocation along the layer-substrate interface, and it is applied in a way that leads to a result that is independent of the deflected shape of the threading dislocation. The general form of the dependence of critical layer thickness on mismatch strain was found to be similar to that based on equilibrium dislocation analysis. The configuration analyzed is shown in Fig. 17, where the threading dislocation is shown as the heavy dashed line, α is the angle between the glide plane of the dislocation and the normal to the interface, and h is the layer thickness. The variation of critical thickness normalized by the magnitude of the Burgers displacement with mismatch strain is shown in Fig. 18 for three values of the angle α. As in the case of earlier work, the predictions are quite good for metal layers, but the critical thickness is underestimated for layers of covalent materials.

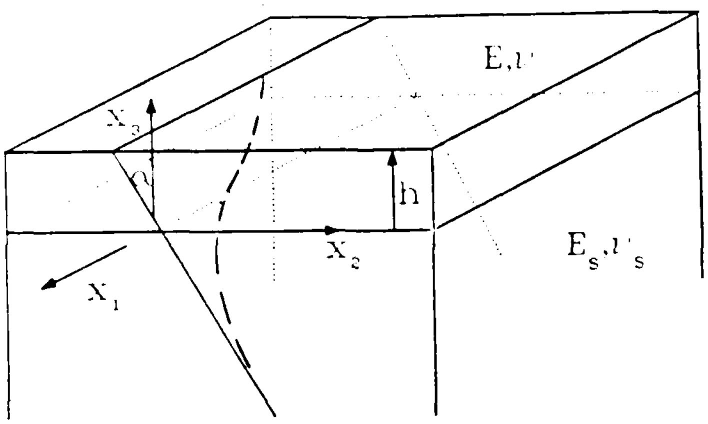


Figure 17: Strained layer of thickness h on a substrate with a threading dislocation shown as the dashed line on the glide plane, which is inclined at angle α to the interface normal.

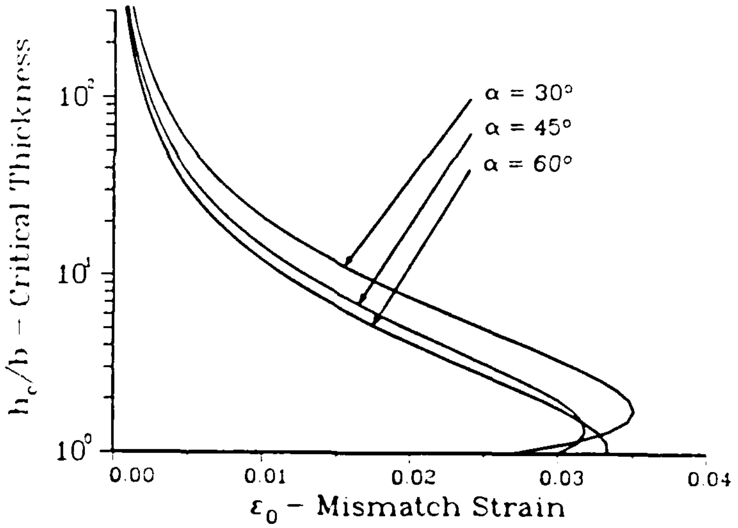


Figure 18: Critical thickness normalized by Burgers displacement of dislocation versus mismatch strain in the layer at which spontaneous formation of interface dislocations is possible.

<u>Publications</u>:

L. B. Freund, "The Stability of a Dislocation Threading a Strained Layer on a Substrate," *Journal of Applied Mechanics*, to appear.

Mechanics of Interfacial Debonding

Principal Investigators: A. Needleman, Professor, Division of Engineering
S. R. Nutt, Assistant Professor, Division of Engineering

Personnel: J. Koplik, Graduate Research Assistant, Division of Engineering
G. Povirk, Graduate Research Assistant, Division of Engineering

Sources of Support: NSF, ONR

Objectives and Approaches:

The nucleation of voids from inclusions and second phase particles plays a key role in limiting the ductility and toughness of plastically deforming solids, including common structural metals and advanced composites. The voids initiate either by inclusion cracking or by decohesion of the interface, but the focus here is directed toward void nucleation by interfacial decohesion. We have developed a framework for describing the evolution of voids from initial debonding through complete separation and subsequent void growth that is both quantitative and predictive. This forms the basis for analyzing the effects of matrix and inclusion material properties, inclusion size, shape and distribution, interface characteristics and imposed stress state and loading rate on the nucleation process.

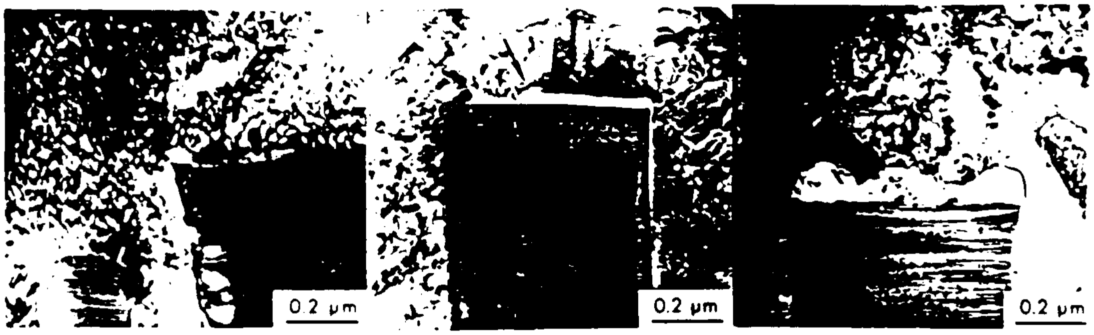
Research Achievements:

Our model is based on a purely continuum formulation using a cohesive zone type model for the interface but with full account taken of finite geometry changes. Constitutive relations are specified independently for the matrix, the inclusion and the interface. The constitutive equation for the interface is such that, with increasing interfacial separation, the traction across the interface reaches a maximum, decreases and eventually vanishes so that complete decohesion occurs. Since the mechanical response of the interface is specified in terms of both a critical interfacial strength and the work of separation per unit area, dimensional considerations introduce a characteristic length.

In one investigation, we analyzed a boundary value problem simulating a periodic array of rigid spherical inclusions in an isotropically hardening elastic-viscoplastic matrix. Matrix material and interface properties representative of iron carbide particles in spheroidized carbon steels were used. The aggregate is subject to both axial and radial stresses and a circular cylinder surrounding each inclusion is required to remain cylindrical throughout the deformation history in order to simulate the constraint of the surrounding material. By considering histories with different ratios of radial to axial stress the effect of stress triaxiality on nucleation is studied. The numerical results exhibit a ductile to brittle transition in the mode of separation. For sufficiently large inclusions (relative to the characteristic length) equilibrium solutions do not exist for increasing extension during debonding. The interface debonds in a 'brittle' manner, with an abrupt stress drop. One can speculate that if this were to occur at a particular weak inclusion, the stress drop could lead to load shedding to nearby inclusions. The increased stress could then precipitate further nucleation, leading to another stress redistribution and so on, so that a profusion of voids are nucleated over a rather narrow strain interval. By way of contrast, the smooth load drop associated with a more 'ductile' interface (smaller inclusions) suppresses this mechanism of void profusion. In this regard it is important to note that the range of strain over which voids nucleate can affect stability against flow localization; void profusion over a narrow range of strain is potentially destabilizing. The numerical results were related to the description of void nucleation within Gurson's phenomenological constitutive framework. The onset of nucleation at various levels of triaxiality of the imposed stress state was correlated in terms of a critical nucleation stress. This critical nucleation stress depends linearly on the hydrostatic tension, but with a coefficient that is less than unity.

Aluminum alloys reinforced with short fibers (whiskers) of SiC exhibit marked increases in yield strength, ultimate tensile strength, and elastic modulus, as well as improved resistance to creep and fatigue. However, these composites also exhibit poor ductility and consequently low fracture toughness. One of the mechanisms that appears to be responsible for the low tensile ductility observed in Al-SiC composites involves void nucleation via interfacial decohesion at the fiber ends. We used the model for void nucleation described above to analyze void initiation at SiC fiber ends and compared predicted and observed modes of failure initiation in reinforced aluminum composites. Experimental observations were made by transmission electron microscopy (TEM) of deformation microstructures immediately beneath tensile fracture surfaces.

Figure 19 shows interfacial decohesion modes at fiber ends. Figure 19a shows a void 20 to 30 nm in size that has nucleated at the sharp corner formed by the whisker end. Similar voids of different sizes were frequently observed at distances up to 50 micrometers below the fracture surface. In most cases, the voids appeared to have nucleated on the fiber end corner and to have grown toward the center of (as well as away from) the fiber end. A second damage process occurring at fiber ends was less frequently observed and is shown in Fig. 19b. Debonding was probably preceded by the nucleation of a void (or voids) at the site indicated by the arrow. Although the void appears near the center of the fiber end, nucleation at a corner site outside of the specimen plane cannot be ruled out. The image in Fig. 19c shows a pair of voids at a fiber end located about 10 micrometers from the fracture surface. The voids have grown to about 0.1 micrometers in size, or about one fourth the whisker diameter, and the surrounding matrix is highly dislocated. In addition, there is a local depression in the specimen surface at the center of the fiber end, the result of a third void between the two corner voids. It is not possible to determine the site at which this void initiated, although possibilities include the center of the fiber end and a corner site outside the specimen plane.



(a) (b) (c)

Figure 19a, b, c. Observed modes of void initiation in tensile specimens of 6061 Al-SiC composite.

Predicted modes of void development are shown in Fig. 20, where the only property that differs in the three calculations is the interfacial strength; other interface parameters, the material properties and the inclusion geometry are the same in each case. Fig. 20a corresponds to a very weak interface and Fig. 20c to a rather strong interface, with Fig. 20b representing an intermediate case. In all three calculations, debonding initiates near (but not right at) the fiber corner and the fibers debond from the top, but not from the side. The interfacial strength levels in Figs. 20a, 20b and 20c correspond to 996 MPa, 1660 MPa and 1992 MPa, respectively, based on a matrix flow strength of 332 MPa. With an inclusion diameter of 0.5 micrometers, the corresponding values of the work of separation are 2.8 J/m^2, 4.7 J/m^2 and 5.6 J/m^2. The similarities between observed and predicted modes of void evolution suggest that it is possible to quantify interface properties in composites by comparisons between experimental observations and predictions based on model calculations. In addition, the comparisons provide important insight into how voids nucleate and coalesce prior to failure and how the process of failure depends on controllable parameters of the microstructure. Detailed understanding of the process of void initiation and growth is critical to explaining the low ductility of composites, which is currently the major limitation preventing their use.

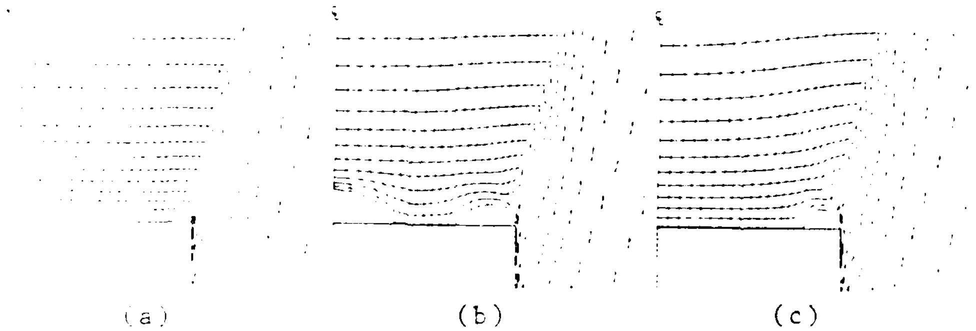


Figure 20: Deformed finite element meshes in the vicinity of the fiber end with the interface strength increasing from (a) to (c). The SiC inclusion is shaded and, for reference, the axis of symmetry is marked. The fiber axis is aligned with the tensile axis.

Publications

A. Needleman, "A Continuum Model for Void Nucleation by Inclusion Debonding," *Journal of Applied Mechanics*, Paper 87-WA/APM-9, in press.

S. R. Nutt and A. Needleman, "Void Nucleation at Fiber Ends in Al-SiC Composites," *Scripta Metallurgica* 21, pp. 705-710 (1987).

Analysis of Ductile Rupture

Principal Investigator: A. Needleman, Professor of Engineering

Personnel: V. Tvergaard, Visiting Professor of Engineering
R. Becker, Graduate Research Assistant, Division of Engineering
J. Koplik, Graduate Research Assistant, Division of Engineering

Sources of Support: NSF, ONR, ALCOA

Objectives and Approaches:

In the traditional approach to fracture analysis, the constitutive characterization of the material and the fracture behavior are specified separately. We have carried out analyses of ductile rupture phenomena using a constitutive relation that incorporates a physically based model of micro-void nucleation, growth and coalescence leading to the complete loss of stress carrying capacity. Hence, in these analyses ductile fracture occurs as a natural outcome of the deformation process, without any explicit failure criterion being employed. This type of analysis permits the prediction of macroscopic fracture toughness and ductility in terms of the fracture mechanism operating on the microscale.

Research Achievements:

In a recent study we have used this framework to carry out an analysis of crack growth under small scale yielding conditions. In structural metals, failure by ductile void growth often involves two populations of void nucleating particles; large particles that nucleate voids at relatively small strains and small particles that nucleate voids at much larger strains. In our calculations the distribution of the small particles is taken to be uniform, while the large particles are modelled as discrete "islands" of increased nucleation density. We account for both the coupling of progressive micro-rupture with the surrounding continuum fields and the interaction between a crack tip and a number of large voids, so that issues related to the material's resistance to crack growth can be addressed. Our model enables us to explore questions that could not be addressed in previous studies.

The specific boundary value problem analyzed is "small scale yielding" at an initial crack tip which is a boundary layer formulation where the elastic singular deformation fields are imposed at a distance remote from the crack tip. The fracture behavior depends on the distribution and nucleation characteristics of the particles as well as on material properties such as yield strength, strain hardening and strain rate sensitivity. Figure 21 shows two stages of crack growth for one particular set of parameters. Within the shaded region, the void volume fraction exceeds 0.10 and nearly all material has undergone a complete loss of stress carrying capacity so that this region indicates the current crack tip. As illustrated in this figure, the crack growth involves both failure of large particles and localized shearing in the form of a void sheet. Crack growth is characterized quantitatively in terms of the relation between Rice's J-integral, which measures the intensity of the crack driving force, and the amount of crack growth. From this curve, crack initiation conditions are determined via a back extrapolation method that mimics the procedure used experimentally. Figure 22 depicts predicted dependence of crack initiation on inclusion size and spacing, together with a summary of experimental results.

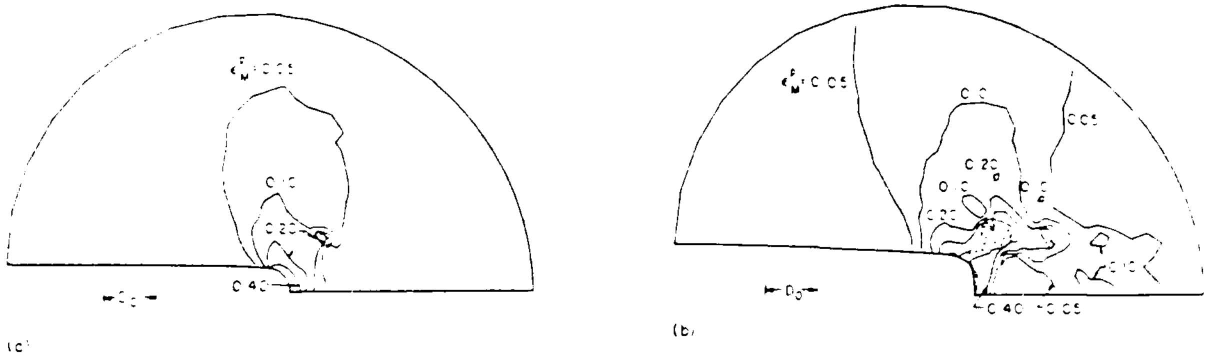


Figure 21: Computed contours of constant plastic strain at a crack tip. The dotted region is where the void volume fraction exceeds 0.10 and indicates the current crack location.

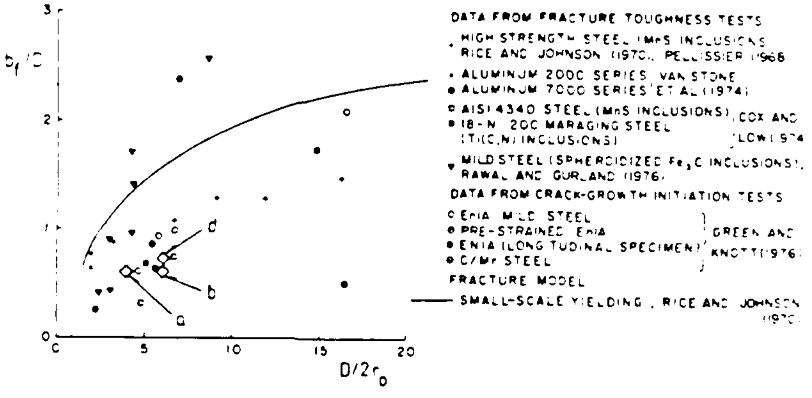


Figure 22: Crack-tip opening at fracture initiation related to particle size, $2r_0$, and spacing, D. Here, A, b and d indicate results of the present computations which are plotted along with a summary of experimental results and predictions of a previous analysis.

Analyses aimed at developing more accurate constitutive descriptions of progressive micro-rupture are also being carried out. In a recently completed investigation, the effect of a nonuniform distribution of porosity on flow localization and failure has been analyzed. The void density distributions and the matrix material properties used in the calculations were obtained from measurements on sintered powdered iron specimens with residual porosity. The failure modes that emerge in the calculations reproduce observed behavior in remarkable detail. For example, Fig. 23 shows an observed void distribution near a fracture surface (which is at the large dark area to the lower right). Figure 24 depicts computed porosity contours prior to failure and the calculated fracture path.

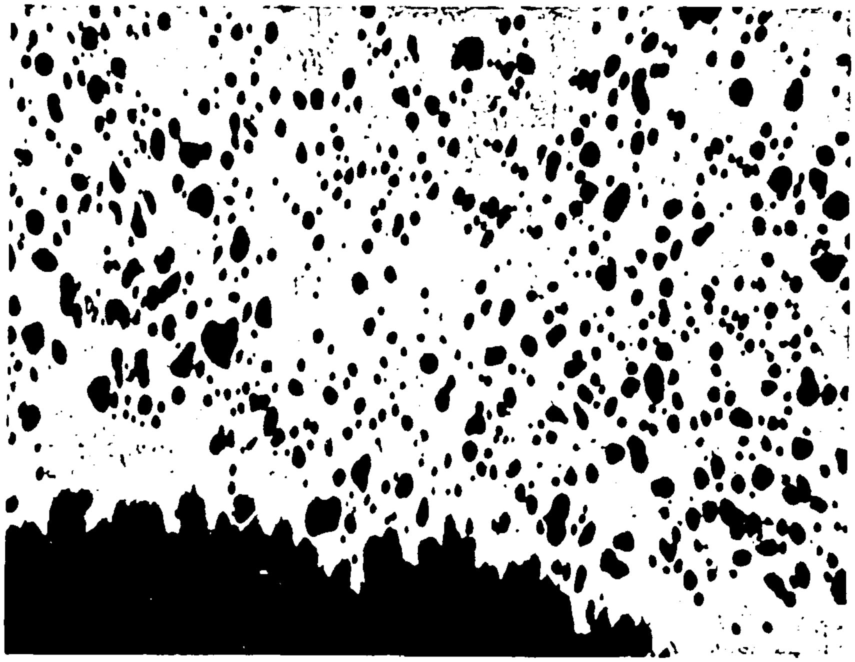


Figure 23: *Observed porosity distribution near the fracture surface in a sintered iron* specimen. The fracture surface is the large dark area to the lower left.

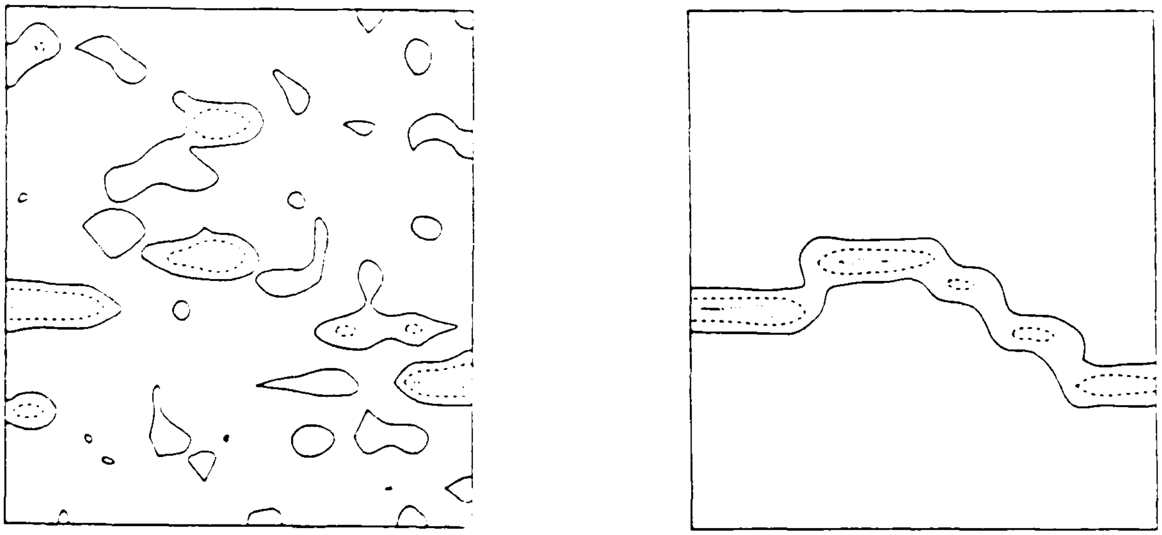


Figure 24: (a) Computed porosity contours prior to fracture. (b) The predicted fracture surface created by void coalescence.

The predicted initial overall response, including the stress-strain behavior as well as the void volume fraction evolution shown in Fig. 25, for the nonhomogeneous solid is nearly identical to that in a material containing the same average initial void volume fraction spread uniformly throughout the material. However, when the deformation localizes the response is found to depend significantly on details of the distribution. The numerical results indicate that the concept of a critical void volume fraction for coalescence, as has been used in the constitutive characterization of micro-void coalescence is a reasonably accurate description, and also suggest a quantitative modification to the constitutive description of coalescence for use in the analysis of full boundary value problems, such as the crack tip fracture analysis described above.

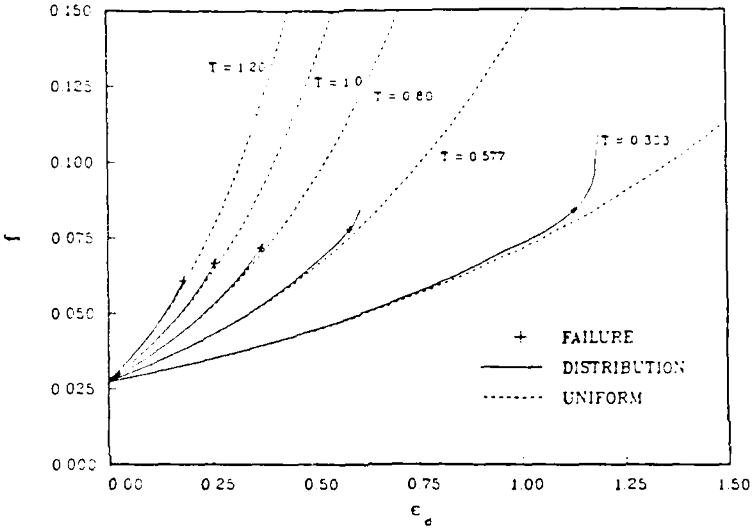


Figure 25: Evolution of void volume fractuion for various values of stress triaxiality, T. Failure occurs at nearly the same void volume fraction for the range of triaxialities shown.

Publications:

A. Needleman and V. Tvergaard, "An Analysis of Ductile Rupture Modes at a Crack Tip," *Journal of the Mechanics and Physics ofSolids*, 35, pp. 151-183 (1987).

R. Becker, "The Effect of Porosity Distribution on Failure," *Journal of the Mechanics and Physics of Solids*, in press.

Constitutive and Computational Aspects of Finite Deformation Plasticity

Principal Investigators: C. F. Shih, Professor, Division of Engineering
M. Ortiz, Associate Professor, Division of Engineering

Personnel: B. Moran, Graduate Student, Division of Engineering

Sources of Support: ONR and MRL

Objectives and Approaches:

With a view toward a common understanding of both the proper formulation of the field equations for finite deformation plasticity and their numerical implementation, some constitutive and computational aspects of finite deformation elastoplasticity are considered. Attention is focussed on formulations which are *covariant* in the sense that they remain invariant when formulated in a spatial or material setting, or in any other convenient reference configuration, reduce to classical *hyperelasticity* in the absence of plastic deformations and are amenable to both *explicit* and *implicit* methods of solution.

Research Achievements:

Two numerical schemes with the above properties have been formulated. A semi-implicit scheme with equilibrium iteration based on the notion of consistent tangents has been derived. The method is specially tailored to take advantage of the hyperelastic response and thus circumvents problems associated with finite rotations in an increment of deformation. An explicit scheme is also derived and the two methods are compared for the case of plane strain necking of a tensile specimen. Implications for a class of problems involving abrupt changes in the deformation pattern are discussed. For problems in which small time steps are required to accurately model the material response explicit schemes appear to offer a distinct advantage.

Publications:

B. Moran, M. Ortiz and C.F. Shih, "Constitutive and Computational Aspects of Finite Deformation Elastoplasticity," Brown University Report, 1987.

Fracture of Cermaics under Far-Field Cyclic Compression

Principal Investigator: S. Suresh, Associate Professor, Division of Engineering

Personnel: J. R. Brockenbrough, Graduate Student, Division of Engineering
L. Ewart, Graduate Student, Division of Engineering
X. Han, Graduate Student, Division of Engineering

Sources of Support: DOE, ALCOA, MRL (Use of Central Facility)

Objectives and Approaches:

The interaction of an applied compressive stress field with internal defects and stress concentrations in a brittle solid determines the mode of progressive microfracture and final failure. The fracture in monotonic, quasi-static compression of brittle solids has been the topic of numerous investigations in the past. A survey of published work on the fracture behavior of brittle solids containing pre-existing cracks reveals that unconstrained axial or radial compression results in "splitting," with the crack propagating parallel to the principal compression axis. Whereas a small confining pressure leads to the coalescence of microcracks to produce a shear failure, large confining pressures promote a more homogeneous, pseudo-ductile deformation by limiting the coalescence of micro-defects. Although there is now a considerable body of information on the failure of brittle solids subjected to quasi-static compression, very little is understood about the micromechanisms of failure under cyclic compressive loads. Indeed, the fracture behavior of brittle materials, such as ceramics and ceramic composites, under varying compressive loads is a topic of significant interest in a wide range of potential engineering applications. Some examples of these applications include cutting tools, ball bearings, internal combustion engines, and gas turbines. The present work was undertaken with the objective of developing the framework for a general theory of compression fatigue in notched brittle solids.

Research Achievements:

Our recent work has shown that the application of cyclic compressive stresses to notched plates of ceramics and ceramic composites can lead to significant amounts of stable fatigue crack growth even at room temperature. The fatigue cracks propagate along the plane of the notch and in a direction macroscopically normal to the far-field compression axis. Constitutive formulations have been developed whereby the "driving force" for such Mode I fatigue crack are determined. Firstly, for the particular case of microcracking ceramics, it is demonstrated through finite element analysis that residual tensile stresses are induced ahead of the notch during unloading from the maximum far-field compressive stress. We propose that it is this region of residual tensile stresses at the notch tip which promotes Mode I fatigue crack growth under far-field cyclic compression. Next, an experimentally-substantiated, generalized constitutive formulation, which incorporates both volumetric and shear strains produced by martensitic transformation, is developed. A finite element analysis is performed whereby the near-tip residual stress field is determined in notched plates of magnesia-partially stabilized zirconia subject to cyclic compression. Numerical results obtained for microcracking single phase cermaics and transformation-toughened ceramics clearly illustrate the inducement of notch-tip residual tensile stresss upon unloading from a far-field compressive stress. The residual tensile stresses, of magnitude considerably greater than the tensile strength of the solid, are created over a distance which is substantially larger than any characteristic microstructural dimension, but comparable to the experimentally-observed distance of crack growth after one compression cycle. The results obtained or ceramics are compared and contrasted with our previous studies of notch-tip residual tensile fields for metallic materials. A significant outcome of this exercise is the realization that notch-tip residual tensile stresses generated upon unloading from a far-field compressive stress promote stable Mode I fracture in both brittle and ductile solids, irrespective of whether the deformation mechanism that produces permanent strains is dislocation plasticity (slip), microcracking or phase transformation. Despite vast differences in their microscopic modes of deformation, a macroscopically similar, stable fracture behavior is exhibited under far-field cyclic compression by brittle and ductile solids because the local zone of residual tension at the notch-tip is embedded in material elastically strained in compression. Strategies have been developed for the applications of crack growth in cyclic compresison as a pre-cracking method for the fracture toughness measurement of brittle solids.

Publications:

L. Ewart and S. Suresh, "Crack Propagation in Cermaics under Cyclic Loads," *Journal of Materials Science*, 22, p. 1173 (1987).

J. R. Brockenbrough and S. Suresh, "Constitutive Behavior of a Microcracking Brittle Solid in Cyclic Compression," *Journal of the Mechanics and Physics of Solids*, 35, (1987) in press.

S. Suresh and J. R. Brockenbrough, "Theory and Experiments of Fracture in Cyclic Compression: Single Phase Ceramics, Transforming Ceramics and Ceramic Composites," Brown University Report DE-FG02-84ER-45167/1/87.

Microstructural Development in Metal-Matrix Composites

Principal Investigator: **S. Suresh, Associate Professor, Division of Engineering**

Personnel: **T. A. Christman, Graduate Student, Division of Engineering**

Sources of Support: **NSF, MRL (Use of Central Facility)**

Objectives and Approaches:

With the advent of new processing techniques, the technological interest and research activity in the development of metal-matrix composites has increased rapidly in recent years. Fiber-reinforced metal-matrix composites (MMC) offer many advantages in applications where low density, high strength and high stiffness are of prime concern. Discontinuous fiber or whisker-reinforced MMCs offer the additional advantage of being machinable and workable. The disadvantage of all MMCs, however, is that they frequently suffer from low strain to failure (mostly less than 5%) and low values of fracture toughness. These problems are tipics of extensive research work and recent gains show promise for potential structural applications of MMCs in many engineering situations.

A topic of fundamental scientific interest and practical importance is the development of matrix and interfacial microstructure in MMCs (particularly those reinforced by whiskers or particulates) in response to aging treatments and thermo-mechanical processing. There is sufficient evidence in the literature indicating that the presence of particulates or whiskers of a brittle material in a ductile matrix can lead to accelerated aging of the matrix in the composite as compared to the unreinforced matrix alloy subjected to identical heat treatment procedures. Such early nucleation and/or growth of the strengthening precipitates in the matrix and/or at the interface of the composite may drastically alter the mechanical properties of the material. The design of composite microstructures and aging treatments, based directly upon the precipitation characteristics of the unreinforced matrix material may lead to erroneous indications of properties without fully utilizing the potential of the composite material. This is particularly significant because the macroscopic yield and ultimate strength values of some composites show little variation in response to the aging treatment, although such aging treatments induce marked changes in matrix strength, ductility and fracture resistance of the composite. An understanding of the accelerated aging phenomenon is also essential to a rigorous develpoment of composite strengthening theories. For example, the widely used rule of mixtures for composite strength assumes perfect bonding between the reinforcement and the matrix. The matrix microstructure, upon which the composite properties are strongly dependent, is generally assumed to be unaffected by the presence of the reinforcement. These strong assumptions may become highly questionable when the concentration of the reinforcement is large enough to affect the microstructural development of the composite matrix. Although to date, there are no systematic and quantitative studies of aging kinetics and microstructural development currently available in the literature. In an ongoing project, the issues essential to a thorough understanding of microstructural evolution in metal-matrix composites are examined in an attempt to lay the foundation for subsequent studies on the relationship between microstructure and mechanical properties.

Research Achievements:

Microstructural development in a 2124 aluminum alloy-SiC whisker composite subject to controlled and systematic aging treatments has been investigated using analytical transmission electron microscopy, quantitative analysis of precipitate growth, matrix microhardness measurements and studies of changes in electrical conductivity. In order to build a basis for comparison, the precipitation characteristics of the unreinforced matrix material with an identical processing history were also examined. The results indicate that the matrix of the composite material has a much greater density of dislocaitons than the control alloy. The increased dislocation density facilitates the nucleation of strengthening precipitates whereby the incubation time for precipitate nucleation and the aging time to achieve peak hardness in the matrix are significantly reduced for the composite as compared to the unreinforced matrix material. Prior theoretical analysis of dislocation generation due to differential thermal expansion anisotropy and of the punching of dislocations at whisker ends are examined in the context of microstructural development in the metal-matrix composite. In an extension of this work, we are currently investigating the effects of the *matrix microstructure* on the quasi-static and cyclic crack growth characteristics of the metal-matrix composite.

Publications:

T. Christman and S. Suresh, "Microstructural Development in an Aluminum Alloy-SiC Whisker Composite," Brown University Report MSM-8451092/1/87, July 1987.

Fracture Behavior of Hardmetals

Principal Investigators: J. Gurland, Professor, Division of Engineering

Personnel: R. Godse, Graduate Student, Division of Engineering

Sources of Support: MRL

Objectives and Approaches:

The present experimental study is aimed at investigating the relationship between fracture properties of hardmetals and their microstructure. A generally accepted view that the fracture of hardmetals needs to be modelled as a ductile event (their macroscopic brittle behavior not withstanding) to account for the microplasticity of the binder phase, lead to various attempts in the past to apply the Rice-Johnson model for ductile failure to the fracture of hardmetals. These attempts were only partially successful and involved empirical considerations. The present work seeks to take the previous analyses a step further by relating the Rice-Johnson model to the improved understanding of fracture phenomena attained in recent years.

In the present approach, the hardmetal microstructure is viewed as being composed of three components - the contiguous carbide, the non-contiguous carbide and the binder. The contiguous carbide forms a skeleton that bears most of the load and therefore is most severaly stressed when compared to the other microstructural components. Subsequent analysis is based on the concept of a crack tip process zone in which the contiguous carbide is broken by microcracking due to elevated stresses and therefore does not contribute to the load carrying capacity of the process zone.

Research Achievements:

The above analysis along with the application of the Rice-Johnson model leads to a relationship between fracture toughness and the microstructural parameters of hardmetals that closely predicts the observed variations in fracture toughness. It is shown that the same relationship can also be derived from considerations of energy terms involved in the fracture process modified by a law of mixtures applied to the two-phase microstructure of hardmetals. The relationship contains one floating parameter for which a reasonable value is obtained when the present model is fitted to experimental data. Although there is good agreement between the model and the experimental data, some of the underlying assumptions may need further elaboration, and are being investigated as a part of ongoing research.

Publications:

R.V. Godse and J. Gurland, "Aspects of Modeling Fracture Behavior of Hardmetals," Accepted for presentation at the Third Conference on The Science of Hard Materials, November 13-17, 1987, Nassau, Bahamas, and publication in "Science of Hard Materials III," V. Savin, ed., Elsevier Press, 1988.

Plastic Deformation in Two-Phase Alloys with Coarse Microstructure

Principal Investigator: J. Gurland, Professor, Division of Engineering

Personnel: K. Cho, Graduate Student, Division of Engineering
H. Stanton, Technical Assistant, Division of Engineering

Sources of Support: DOE, MRL Central Facilities

Objectives and Approaches:

The plastic deformation behavior of two-phase alloys is characterized by the mutual interactions between constituents, which result from plastic incompatability between the phases. The major objective of our work is to estimate the partition of stress and strain between the constituents in two-phase alloys during plastic deformation. A model has been developed which uses modified laws of mixtures as a framework to relate composite alloy deformation to that of the constituent phases.

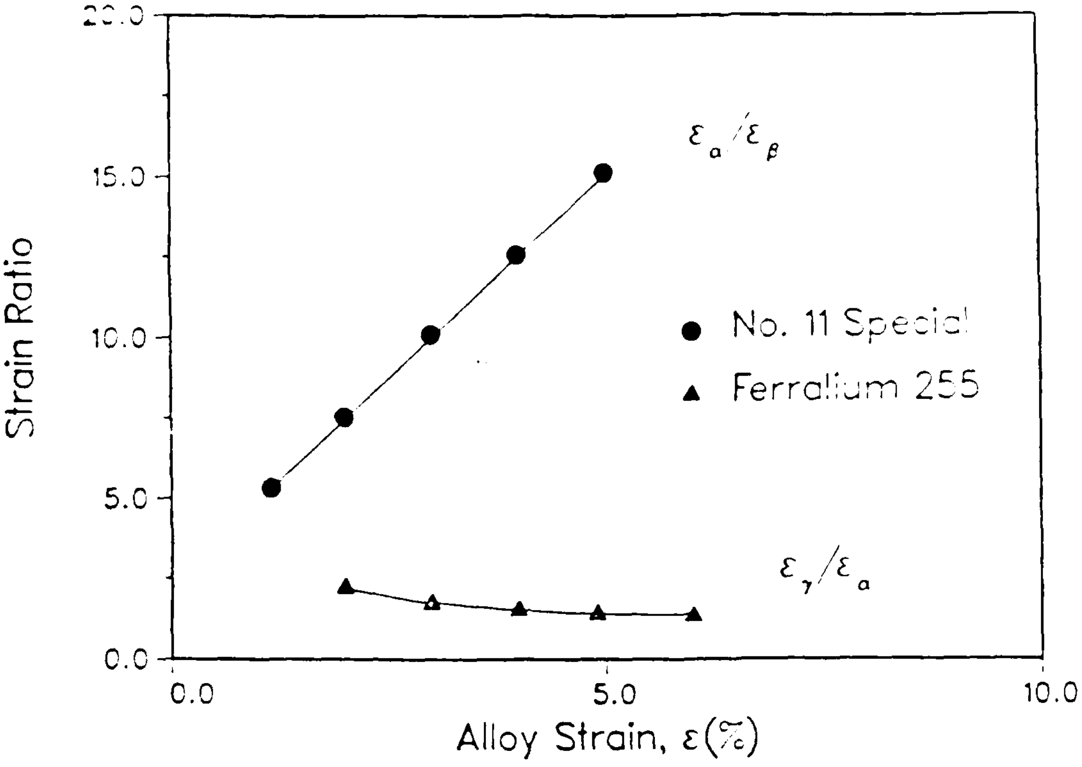
Research Achievements:

Plastic deformation behavior in two representative two-phase alloys, i.e., a spheroidized high-carbon steel and a α-γ duplex stainless steel, was studied by taking into account the mutual interactions between constituent phases. It was attempted to evaluate the partition of the in-situ stress and the in-situ strain in each constituent separately. Microstrain measurements in ferrite and austenite were performed by means of microgrids in the case of the α-γ duplex stainless steel. The plastic strain of ferrite calculated from the alloy strain by the modified law of mixtures was used for the spheroidized high-carbon steel. In both cases, the back stress was estimated in a Bauschinger test. The in-situ stresses in the constituent phases were calculated on the basis of the dislocation-continuum strain-hardening theory. The modified laws of mixtures were applied to obtain the flow stress and flow strain of the alloys. The modified laws of mixtures were derived on the basis of stereological analysis. The stress and strain partitions, so obtained, are shown in Fig. 26.

Publications:

Y.L. Su and J. Gurland, "Strain Partition, Uniform Elongation and Fracture Strain in Dual-Phase Steels," Materials Science and Engineering, to be published.

J. Gurland and K. Cho, "Stereological Basis of the Modified Laws of Mixtures Applied to the Plastic Deforamtion of Two-Phase Alloys," Proc. 7th Int. Congress for Stereology, J. L. Chemant, ed., 1987, Univ. of Caen, France.



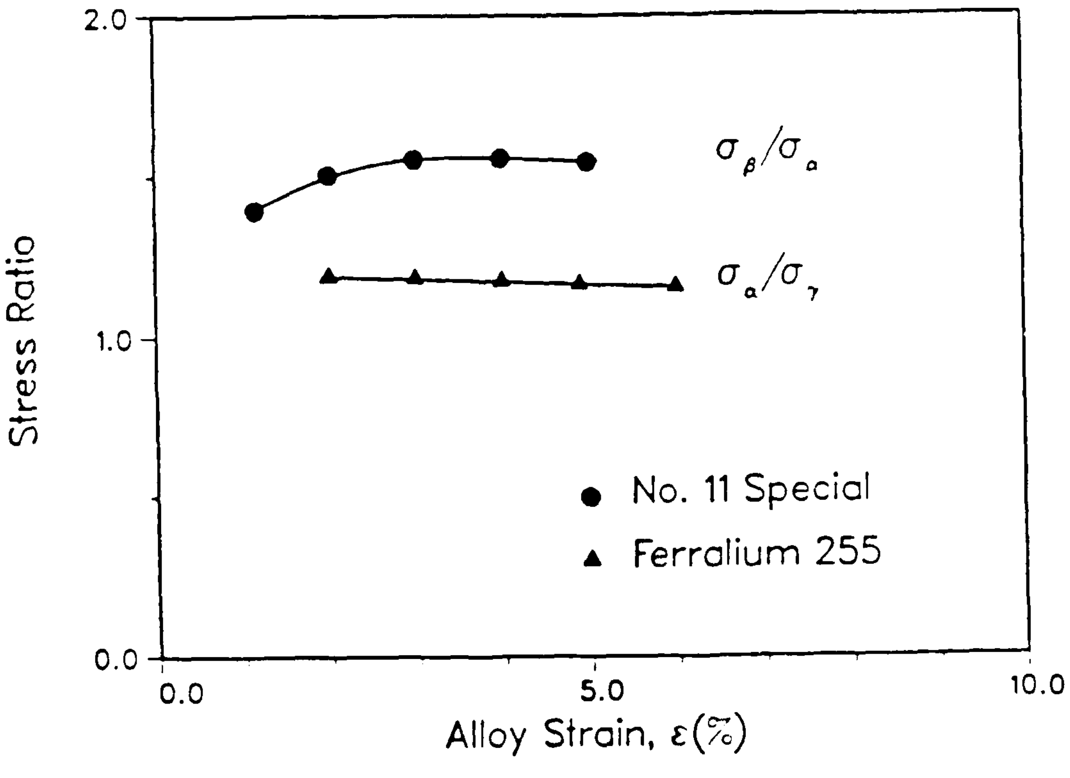


Figure 26: Stress and strain ratios versus alloy strain for No. 11 special steel (spheroidized high-carbon steel) and Ferralium alloy 255 (α-γ duplex stainless steel).

Crack Growth under Far-Field Cyclic Compression in Metal Matrix Composites

Principal Investigators: J. Gurland, Professor, Division of Engineering
S. Suresh, Professor, Division of Engineering

Personnel R. Godse, Graduate Student, Division of Engineering

Sources of Support: MRL

Objectives and Approaches:

The present experimental study is aimed at (a) investigating the micromechanisms underlying crack growth under far-field cyclic compression in metal-matrix composites and (b) exploring the possibility of employing such crack growth as a viable technique for precracking specimens used in crack-growth-related studies.

The experiments were conducted with cemented carbides chosen as a representative metal matrix composite. Crack growth was monitored as a function of number of compression cycles in a study of micromechanisms, and fracture toughness was measured by using the pre-cracked specimens

Research Achievements:

a) Results indicate that crack growth occurs in a composite of a hard and a soft phase through a combination of the mechanisms observed in ceramics and metals. Therefore, plasticity in the soft binder phase and generation and coalescence of microcracks in the neighborhood of the notch are contributing factors.

b) An important requirement in crack growth testing is that the obtained results are not influenced by the presence of residual stresses at the crack tip. The present work has shown that such residual stresses can arise from mechanical effects of the pre-cracking procedure when cyclic compression is used to obtain sharp pre-cracks. In particular, it has assessed the effects of the maximum stress and the R ratio of the compression cycle upon the measured fracture toughness. To obviate the influence of residual stresses, a method is advocated in which the pre-cracked specimen is subjected to tensile fatigue in order to ensure that the crack tip is approximately free of stresses arising from prior cyclic compression and thus yields a valid measure of fracture toughness. Experimental results obtained support the validity of this technique.

Publications:

R.V. Godse, J. Gurland and S. Suresh, "Crack Growth under Far-Field Cyclic Compression in Hardmetals," TMS-AIME Annual Meeting, February 23-26, 1987, Denver, Colorado. To be published in "Science of Hard Materials III," V. Savin, ed., Elsevier Press, 1988.

Modelling of Microfracturing Materials

Principal Investigators: M. Ortiz, Assistant Professor, Division of Engineering

Personnel: Y. Leroy, Graduate Student, Division of Engineering
A. Gianakopoulous, Graduate Student, Division of Engineering
A. Molinari, Research Associate, Division of Engineering

Sources of Support: MRL, ONR

Objectives and Approaches:

Processes of damage and failure of solids pose new challenges to researchers in solid mechanics. Interest in the subject has sharply increased during recent years due to the development of a new generation of advanced ceramic materials. In spite of this renewed interest, a thorough understanding of the mechanics of failure of these materials is yet to emerge. For instance, some aspects of damage by microcracking cannot be adequately characterized within the context of constitutive theory or fracture mechanics. There is a critical need for new analytical and numerical tools capable of dealing with these new classes of problems. Of primary interest is the analytical characterization of nucleation, growth, interaction and coalescence in dense populations of microcracks, phenomena which are only partially understood at present. A comprehensive picture of the microstructural mechanisms which lead to the development of a critical flaw in a ceramic component is critical for the effective use of these materials.

A principal objective of past research under the project has been to develop an understanding of damage by microcracking and its effect on the strength and toughness of brittle materials such as ceramics and composites. A more specific goal of this study has been to ascertain the role played by microcrack nucleation, growth and coalescence in crack growth initiation and toughness enhancement of monolithic ceramics. Results were also obtained in the area of numerical procedures for the analysis of failure in solids exhibiting material instabilities. Some selected results of this research are summarized below.

Research Achievements:

Microcracking is known to play a dual role in relation to the toughness of ceramics. On one hand, extensive microcracking about the tip of a macrocrack has the effect of shielding it from the remotely applied loads, thus reducing the intensity of the near-tip singular fields. On the other hand, the presence of dense populations of microcracks ahead of the crack reduces the fracture resistance of the material. A question of fundamental interest is to determine which effect dominates and whether microcracking has indeed a net beneficial influence on the fracture toughness of the material.

A precise answer to this question necessitates the quantification of two phenomena: a) The microcrack shielding mechanism, and b) Microcrack growth and coalescence with the main crack. Crack shielding was investigated using a constitutive model which accounts for elastic degradation due to microcracking. The model assumes an initial linear elastic stage followed by a transition range in which the elastic properties of the material steadily degrade as a consequence of microcrack nucleation. As the number of nucleation sites which are favorably oriented to the loading axes is exhausted, a saturation regime is reached beyond which no further elastic degradation takes place Microcracks are assumed to nucleate preferentially normal to the direction of maximum tension As a result, the material response becomes highly anisotropic. In spite of this anisotropy and of the strongly nonlinear character of the problem, a closed form solution of the near-tip asymptotic fields can be found (Ortiz, 1987). Using the J-integral formalism, the stress intensity factor at the crack tip can be related to the intensity of the remote K-field The results exhibit a significant reduction of the stress intensity factor as a function of the extent of damage.

This work has been continued by a J-dominance study of the asymptotic solution under small scale damage conditions. Here, one aim is to ascertain whether the J integral provides a valid characterizing parameter for predicting the onset of crack growth. Another outcome of the analysis is an estimate of the minimum flaw size beyond which conventional fracture mechanics applies. Thus, these results establish a clear divisory line between microcrack coalescence, i.e., the coalescence of microcracks of roughly the same size, and crack growth, i.e., the process of coalescence of a main crack with microcracks ahead of the tip. To decide the question of J-dominance, the asymptotic fields were compared against a full field solution obtained by means of a finite element analysis. The calculations were conducted on the Cray X-MP/12 computer of the Navy Research Laboratory's Central Computer Facility. The asymptotic fields are seen to dominate over a distance $R = K_{tip}^2/2\pi\sigma_s^2$, where K_{tip} is the near-tip stress intensity factor and σ_s is the stress at which the saturation ensity of microcracks is attained.

Past work has also been concerned with the issue of microcrack growth and coalescence with a macrocrack. As discussed earlier, this study is a necessary counterpart to the theoretical work on crack shielding, in that it focusses on the weakening effect of microcracks ahead of a main crack. A micromechanical model has been devised (Ortiz, in press) on the basis of which a relation between microcrack density and effective toughness can be established analytically. When combined with the crack shielding predictions, this result makes it possible to determine the net toughness enhancement due to microcracking and to correlate it with micromechanical parameters such as grain size. A noteworthy outcome of the analysis is that the loss of toughness due to the weakening effect of microcracks almost exactly offsets the gains due to shielding. Additional toughening mechanisms such as crack deflection need to be taken into consideration in order to bring the analytical results into correspondence with experimental evidence.

One final problem addressed (in collaboration with Dr. A. Molinari of the University of Metz, France) concerns the analytical characterization of the state of residual stress in a polycrystalline ceramic material following cooling from the fabrication temperature. These thermal stresses exert a strong influence on the mechanical behavior of the material. It was shown (Ortiz and Molinari, to appear) that, under mild assumptions on the behavior and microstructure of the material, the covariance matrix of the microstructural residual stresses can be obtained in closed form from the equations of elasticity. The analysis does not take thermally induced microcracking into consideration and the solid is idealized as remaining essentially intact during the cooling process. However, the results so obtained were used to derive first-order estimates of microcrack densities.

Publications:

M. Ortiz, "A Continuum Theory of Crack Shielding in Ceramics," *Journal of Applied Mechanics*, Vol. 54, pp. 54-58 (1987).

M. Ortiz, "A Model of Microcrack Coalescence and Crack Growth Initiation in Brittle Solids," *Journal of Applied Mechanics*, (in press).

M. Ortiz and A. Molinari, "Microstructural Thermal Stresses in Ceramic Materials," *Journal of the Mechanics and Physics of Solids*. (to appear).

Constitutive and Computational Modelling of Inelastic Deformation and Fracture

Principal Investigators: C. F. Shih, Professor, Division of Engineering
R. J. Asaro, Professor, Division of Engineering

Personnel: B. Moran, Graduate Student, Division of Engineering

Sources of Support: ONR and MRL

Objectives and Approaches:

A finite strain numerical analysis of a circumferentially cracked round bar is carried out. The material is characterized by a rate dependent version of Gurson's [1] constitutive model which allows for progressive microrupture through void nucleation and growth. The analysis is motivated by an experimental technique to evaluate the stress intensity factor K_{Ic} under dynamic loading conditions [2,3]. The accuracy of the technique was initially assessed in [4] on the basis of a small strain finite element analysis under both static and dynamic loading conditions. In the present analysis we investigate the development of the stress and strain fields in the crack tip region during crack blunting and examine the extent to which the HRR fields dominate in the axisymmetric specimen. Inertial effects are neglected in the present analysis but we examine the effects of material rate sensitivity on the mode of fracture initiation for a material model characterized by strain controlled nucleation of voids. A similar analysis was carried out in [5] for the Charpy V-Notch specimen.

Research Achievements:

The mode of fracture initiation depends on the critical stress for cleavage. The nucleation and growth of voids is confined to the region of intense strain at the blunting crack tip and the development of a high triaxial stress state ahead of the crack may be sufficient to promote cleavage fracture. Although strain rate sensitivity has a stabilizing effect on material behavior, resisting localization and promoting higher toughness, it can also produce more brittle behavior as higher stress levels are achieved through strain rate dependent hardening.

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[1] A.L. Gurson, "Continuum Theory of Ductile Rupture by Void Nucleation and Growth: Part I - Yield Criteria and Flow Rules for Porous Ductile Materials," *Journal of Engineering Materials Technology*, **99** pp. 2-15 (1977).

[2] L.S. Costin, J. Duffy and L.B. Freund, "Fracture Initiation in Metals under Stress Wave Loading Conditions," Fast Fracture and Crack Arrest, ASTM STP 627, pp. 302-318 (1977).

[3] H. Couque, R.J.Asaro, J. Duffy and S.H. Lee, "Correlations of Microstructure with Dynamic and Quasi-Static Fracture Toughness in a Plain Carbon Steel," to appear in *Metallurgical Transactions*.

[4] T. Nakamura, C.F. Shih and L.B. Freund, "Elastic Plastic Analysis of a Dynamically Loaded Circumferentially Notched Round Bar," *Engineering Fracture Mechanics*, p. 22 (1985).

[5] V. Tvergaard and A. Needleman, "Effects of Material Rate Sensitivity on Failure Modes in the Charpy V-Notch Test," *Journal of the Mechanics and Physics of Solids*, 34 p. 213-241 (1986).

Fracture at Ultra-High Loading Rates

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

Personnel: G. Ravichandran, Graduate Student, Division of Engineering

Sources of Support: ARO and MRL (Central Facilities only)

Objectives and Approaches:

In order to study the dynamic fracture of materials at the ultra-high loading rates that occur under impact loading, a plate impact experiment has been developed for simulating the loading of a semi-infinite crack by a plane tensile wave at normal incidence. This approach has the advantage of providing well-characterized, plane strain loading conditions which cause fracture initiation in times as short as 0.1μs and crack propagation at velocities greater than 50% of the Rayleigh surface wave speed. Because the crack advance occurs in the interior of the plate specimen, the crack advance cannot be monitored directly. Consequently, the examination of the validity of various crack propagation models must be done indirectly by comparing model predictions with interferometric records of the motion of the rear surface of the plate and with post-experiment measurements of the total advance of the crack.

Research Achievements:

During the reporting period the emphasis of this research has been on the computer simulation of the experiment as a means of investigating the validity of various crack propagation models. A second order accurate finite difference method has been developed for solving the problem of the interaction of the incident pulse with the crack and with the front and rear surfaces of the specimen. The material (4340 VAR steel) is modeled as elastic for low temperature (-110 °C) experiments in which fracture occurred primarily by cleavage and as elastic-viscoplastic for room temperature experiments in which fracture occurred primarily by ductile void growth and coalescence. Results of the low temperature experiments have been compared with predictions for three crack propagation models: constant energy release rate, constant stress intensity factor, and constant crack velocity. Comparisons such as those shown in Figure 27 suggest that, during the loading of the incident pulse, best agreement is obtained for the constant crack velocity model. For the room temperature experiments, comparisons have been made only for a constant crack velocity model. Measured rear surface motions agree reasonable well with this model which, for these simulations, corresponds roughly to crack propagation at a critical crack opening displacement.

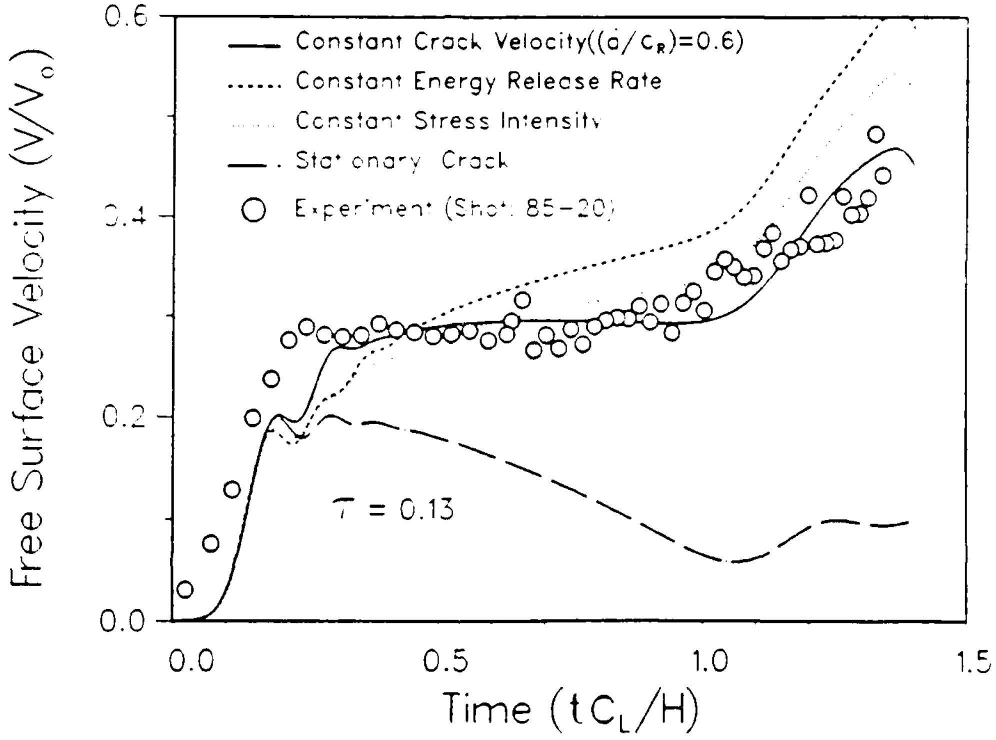

Figure 27: Comparison of measured, free-surface, velocity-time profile for a low temperature (-100°C) plate impact experiment with profiles predicted for three crack propagation models: (i) constant energy release rate; (ii) constant stress intensity factor; (iii) constant crack velocity. The predicted velocity-time profile for a stationary crack is included to show the sensitivity of the free surface motion to the motion of the crack.

Publications:

G. Ravichandran, "Dynamic Fracture under Plane Wave Loading," Ph.D. Thesis, Brown University, October, 1986.

G. Ravichandran and R. J. Clifton, "Dynamic Fracture under Plane Wave Loading," Brown University Technical Report No. DAAG29-85-K-0003/3, December, 1986.

Three Dimensional Effects in Dynamic Fracture

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

Personnel: J. C. Ramirez, Graduate Student, Division of Engineering
C. Champion, Research Associate, Division of Engineering

Sources of Support: MRL, ONR, NSF

Objectives and Approaches:

The continuing need for accurate descriptions of dynamic fracture phenomena in the power industry, as well as in other areas of structural engineering, provides motivation for further study of such phenomena at a fundamental level. Various phenomenological features of dynamic fracture that arise in experimental research and in engineering practice have thus far eluded analysis and fundamental understanding. Because most models that have been developed for the study of these phenomena are two dimensional, it is possible that three dimensional effects could account for observations. Consequently, a study of the influence of three dimensional effects during dynamic fracture of materials has been initiated. The project involves analytical work based on a novel mathematical technique for determination of transient stress intensity factors for a class of three dimensional elastodynamic crack problems. It also involves computational work in which numerical solutions are to be sought for certain three dimensional dynamic fracture problems which have the potnetial for leading to results of general significance in dynamic fracture mechanics.

It appears that now is an opportune point in the development of the subject for a re-examination of dynamic fracture, with a view toward studying three dimensional effects, beginning with elastodynamic phenomena. There are two reasons for this assessment. First, we have found an exact stress intensity factor solution for a particular transient three dimensional crack problem, and the method appears to have potential for extension to a class of three dimensional elastodynamic crack problems. Second, accessibility to large computers in the National Science Foundation supercomputer program provides the opportunity to formulate and solve certain key three dimensional problems in continuum mechanics.

Research Achievements:

A procedure has been developed for determining dynamic stress intensity factor histories for a half plane crack in an otherwise unbounded elastic body, with the crack faces subjected to tractions that result in variation of the stress intensity factor along the crack edge. The procedure is based on the integral transform methods and the properties of analytic functions of a complex variable. The procedure has been illustrated for the case of a pair of opposed line loads suddenly applied on the crack faces along a line perpendicular to the crack edge. An exact expression has been obtained for the resulting mode I stress intensity factor as a function of time for any point along the crack edge. A graph of this history is shown in Figure 28, where the time dependent stress intensity factor has been normalized by its long-time value. It is noteworthy that the stress intensity factor is negative for very early times in the process and that the approach to the long-time value is relatively slow. The same technique has been applied for the case of a pair of opposed point loads moving on the crack faces in a direction perpendicular to the crack edge, and for the case of crack growth under the action of a pair of opposed point forces on the crack faces.

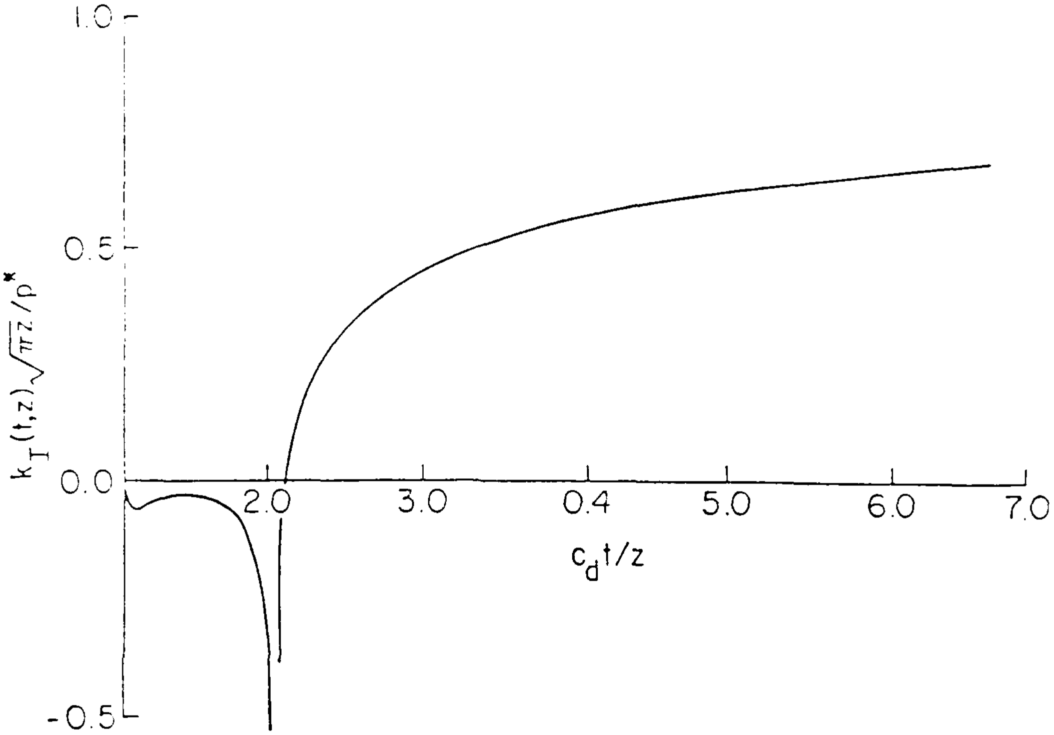

Figure 28: Transient three dimensional stress intensity factor at point z along the crack edge due to suddenly applied line load at z = 0, normalized by the equilibrium value for line load of strength p*.

Publications:

L. B. Freund, "The Stress Intensity Factor History due to Three Dimensional Transient Loading on the Faces of a Crack," *Journal of the Mechanics and Physics of Solids*, 35, p. 61-72 (1987).

J. C. Ramirez, "The Three Dimensional Stress Intensity Factor due to the Motion of a Load on the Faces of a Crack," *Quarterly of Applied Mathematics*, to appear.

C. R. Champion, "The Stress Intensity Factor History for an Advancing Crack under Three Dimensional Conditions," *International Journal of Solids and Structures*, to appear.

Mechanics of High Strain Rate Crack Growth in Rate-Dependent Elastic-Plastic Solids

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

Personnel: J. Leighton, Graduate Student, Division of Engineering
H. Stanton, Technical Assistant, Division of Engineering

Sources of Support: ONR, MRL, ARO

Objectives and Approaches:

The phenomenon under study is high strain rate crack growth as it occurs, for example, in structural steels and other strain rate sensitive materials. It is well-known that such materials may or may not experience rapid crack growth in a predominantly cleavage mode, depending on the state of stress, the temperature, and the rate of deformation. Evidence on the influence of stress state and temperature is abundant in the literature, and data on the influence of loading rate on the variation of fracture toughness with testing temperature has been provided by Duffy and coworkers in recent years. The physical processes that underlie the growth of cleavage cracks in steels have been of interest for many years. The purpose of the present work is to focus on the mechanics of rapid growth of a sharp macroscopic crack in an elastic-plastic material which exhibits a fairly strong variation of flow stress with strain rate, particularly at very high strain rates. Data on the flow stress levels of iron at very high strain rates is currently being obtained by Clifton and coworkers in their pressure-shear impact apparatus. The general features of the crack growth process as experienced by a material particle on or near the crack path are straightforward. As the edge of a growing crack approaches a material particle, the stress magnitude tends to increase there due to the stress concentrating effect of the crack edge. The material responds by flowing at a rate related to the stress level in order to mitigate the influence of the crack edge. It seems that the essence of cleavage is the ability to elevate the local stress to a critical level before plastic flow can accumulate to dilute the influence of the crack tip. The phenomenon is being studied from this point of view.

Research Achievements:

A model of the high strain rate crack growth process was developed in collaboration with Professor J. W. Hutchinson of Harvard University, based on several observations. First, estimates of material strain rates near the edge of a crack growing in an elastic-plastic material under common conditions suggest that values in the range 10^4 - 10^6 per second may be anticipated. Experiments on iron conducted at such rates, under more or less homogeneous states of deformation, indicate that the high strain rate response may be divided into two major regimes. For strain rates below a certain level, the flow stress is relatively insensitive to changes in strain rate, where above this level, the dependence is quite strong. The problem is then studied from the small scale yielding point of view of nonlinear fracture mechanics. Crack growth is assumed to occur in a body that remains elastic at points remote from the crack tip. The applied loading is reflected in a remote stress intensity factor or, equivalently, a rate of energy flux into the crack tip region per unit crack advance. In the crack tip region, the potentially large stresses are relieved to some extent through viscoplastic flow. Thus, crack growth is accompanied by a zone of active plastic deformation and a wake region of permanently deformed but unloaded material along the crack flanks. Within the inner portion of the active plastic zone, where the strain rates are such that the response is in the high rate regime, the stress field is also strongly singular or, equivalently, the rate of energy flux into the crack tip is nonzero. The criterion adopted for sustained cleavage crack growth is that the value of this energy flux must have a certain material specific value. The problem, then, is to determine the influence of the intervening plastic flow in screening the crack tip region from the remotely applied loading. The analysis led to conditions that must be satisfied for sustained steady cleavage crack growth in the materials of interest. The conditions depend on the flow characteristics of the material, the crack tip speed, and the level of applied loading. Of particular interest is the result that, for given material and temperature, there is a minimum crack driving force below which the propagation of a sharp crack cannot be sustained under any conditions. The details have been described in previous reports.

This work has continued with emphasis on incorporating refinements in the analytical model that have been suggested by detailed numerical simulations of the dynamic viscoplastic crack growth process. For example, in the original study, it was assumed that crack tip plastic dissipation was controlled by the near tip stress intensity factor alone in the high strain rate plastic zone. However, it has been shown through numerical simulations that this assumption results in the dissipation being underestimated. Therefore, the model has been modified in such a way that the dissipation estimated is based on an average of the remote and near tip stress intensities, and the dissipation estimates obtained in this way agree much better with the former estimates. A plot of the mechanical conditions necessary to sustain steady growth of a sharp cleavage crack in a viscoplastic material is shown in Figure 29. For states above

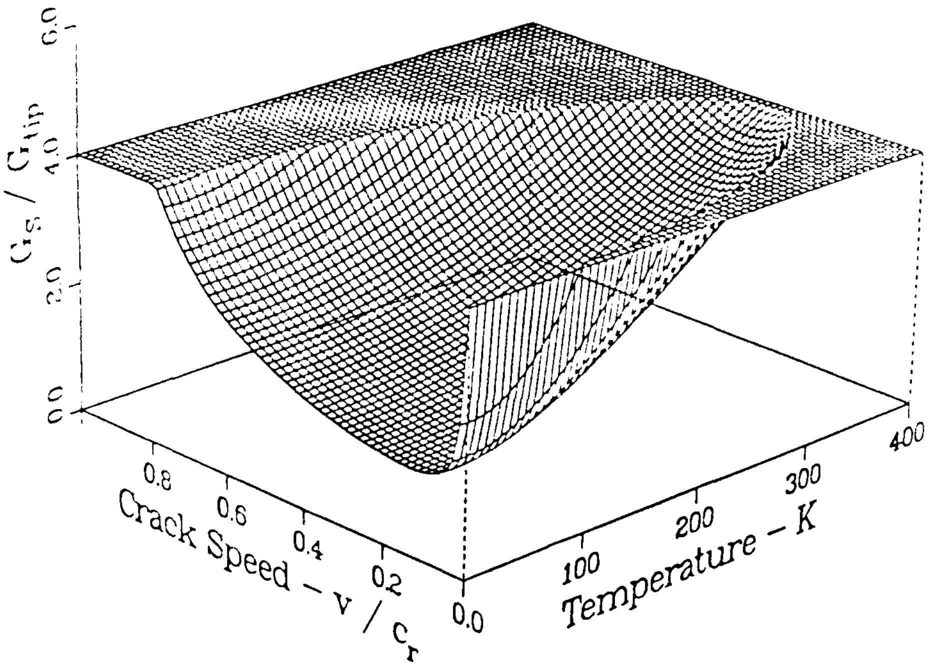

Figure 29: **The surface specifies the mechanical conditions on crack driving force normalized by the crack tip value, the crack speed normalized by the Rayleigh wave speed of the material, and the temperature for steady cleavage crack growth according to the viscoplastic analysis.**

the surface, the crack will presumably accelerate toward the surface, whereas growth as a sharp crack is not possible for states below the surface. The spine of the surface represents the variation of the minimum driving force, or arrest toughness, as a function of temperature. More recently, the same problem has been approached from the dislocation dynamics point of view. The energy dissipated during the interaction of a growing crack and a mobile dislocation is calculated. A uniform distribution of such dislocations is then assumed to calculate the difference between the rate of energy supply to the crack tip region and the rate of energy consumption at the crack tip due to the dislocation field. The implications for crack propagation and arrest are qualitatively identical to those based on the continuum plasticity analysis.

Publications:

P. A. Mataga, L. B. Freund and J. W. Hutchinson, "Crack Tip Plasticity in Dynamic Fracture," *Journal of the Physics and Chemistry of Solids*, (1987) to appear.

L. B. Freund, "Dynamic Crack Propagation in Solids," in Computational Methods in the Mechanics of Fracture, edited by S. Atluri, Elsevier (1986) p. 86-120.

Molecular Theory of Rubber Elasticity

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

Personnel: J. Gao, Graduate Student, Department of Physics

Sources of Support: MRL, NSF and Gas Research Institute

Objectives and Approaches:

The molecular theory of rubber elasticity deals with the mechanical behavior of amorphous, cross-linked networks of long-chain molecules. As such the subject has much broader application than its name might indicate, including synthetic elastomers, some biological systems, and amorphous regions in semi-crystalline polymeric solids. Indeed, as Flory has stated, the theory of rubber elasticity is central to polymer science.

From the viewpoint of the thermal motion of its atoms, a rubber-like material occupies a position intermediate between a glassy solid and a fluid. The long-time average positions of its atoms are approximately uniformly distributed in space as is the case for a glassy solid, but the amplitudes of their thermal motion about these mean positions are much larger due to the flexible nature of the long-chain molecules. Furthermore, the cross-linking of these molecules permits the system to support an anisotropic state of stress as in an elastic solid.

In view of the highly complex atomic systems involved, the development over fifty years ago of the basic concepts of the subject and particularly the recognition of the molecular character of entropic elasticity were remarkable steps forward. Inevitably, the theory which was developed by the ealry workers in the field rested on several assumptions made to render calculations tractable. We have been re-examining some of these assumptions on the basis of classical statistical mechanics and computer simulation studies.

Research Achievements:

Our work on rubber elasticity has been directed at the following questions:

(a) Natural state. In the usual theory, the specific volume of the natural, stress-free state is postulated phenomenologically and the molecular theory applied only to deformations from this natural state. We have attempted to gain insight into this question by generalizing the pressure equation for fluids to macromolecular systems. This generalization reveals the important role played by the mean tensile force in the covalent bonds of the system. In the stress-free state, the internal pressure due to the thermal motion and non-covalent interactions is balanced by the covalent tension in the network.

(b) Excluded volume. An important noncovalent interaction in a rubber-like system is the strongly repulsive excluded volume interaction which prevents two atoms from occupying the same place in space. We have used computer simulation tecyhniques to determine excluded volume effects on long-chain molecules with up to 200 bonds. They are found to introduce a compressive region into the force-length relation; in fact, the latter shows all of the generally observed characteristics of experiments on rubber-like materials in uniaxial tension.

(c) Virial stress formulation. The virial formula has long found application in the theory of fluids and has more recently been extended to the study of general states of stress in crystals. We have employed it to treat rubber-like systems and find that it provides a new and valuable physical picture for the stress, one which is more local in character than the usual chain view.

(d) Ideal chain assumption. A model of a linear macormolecule which neglects any interactions, such as that of excluded volume, between atoms which are widely separated along the chain but happen to be in close proximity because of the chain's long-range flexibility, is said to be ideal. A basic assumption in most molecular theories of rubber elasticity is to regard the network as a collection of *non-interactging ideal chains*. We have performed molecular dynamics simulation of a model network corresponding to the familiar three-chain model of rubber elasticity. The virial stress formula was employed to determine the state of stress in the model corresponding to a given extension ratio when intra- and inter-chain excluded volume effects were present and this was compared with the state of stress as computed on the basis of the ideal chain assumption. Substantial, density-dependent, discrepancies were found between the two calculations.

Publications:

J.H. Weiner, "A Generalization of the Pressure Equation for Fluids to Macromolecular Systems," *Journal of Chemical Phyiscs*, **85**, pp. 2910-2912 (1986).

J. Gao and J.H. Weiner, "Excluded Volume Effects on Force-Length Relations of Long-Chain Molecules," *Macromolecules*, **20**, pp. 142-148 (1987).

J.H. Weiner, "Entropic vs. Kinetic Viewpoints in Rubber Elasticity," *American Journal of Physics* (in press).

J. Gao and J.H. Weiner, "Excluded-Volume Effects in Rubber Elasticity I. Virial Stress Formulation," *Macromolecules* (in press).

J. Gao and J.H. Weiner, "Excluded-Volume Effects in Rubber Elasticity II. Ideal Chain Assumption," *Macromolecules* (in press).

SECTION 2

MICROSCOPIC BASIS OF GLASS PROPERTIES

Introduction

The Inoganic Glasses group has obtained significant new results on a wide range of glass systems which are reported in this section. The studies have in common a focus on the microscopic basis of glass properties, whether through structural, synthetic, relaxational or theoretical research. There are many projects reported, so it is useful to highlight several themes.

Through development of picosecond and femtosecond optical methods, Tauc, Maris and coworkers have probed the phonons of amorphous superlattices and amorphous solids, and they have studied carrier transport in amorphous multilayer structures and photocarrier dynamics in hydrogenated amorphous silicon. Both these studies and the associated methods development, including picosecond interferometry, are reported.

Key issues in the central field of oxide glasses studied by Bray, Cole and Risen include the development of synthetic methods to obtain novel glasses in composition regions which have been inaccessible but permit study of phenomena in optically and magnetically active high field strength cations, the exploration of the structures of ionic oxide glasses by novel NMR techniques and Raman spectroscopy, and the study of ion motion by NMR and dielectric techniques.

Glass formation in metals and ceramics is an important area because of the role of the amorphous phase in determining the macroscopic properties and because it is possible to observe in them phenomena which may be characteristic of the glassy state. Elbaum has employed ultrasonic methods in studying glassy - or disordered - phases in sintered crystals and in studying amorphous metals. He has explored their two level tunneling systems, whose observation is characteristic of disordered materials, and has shed new light on sintering of ceramics.

Theoretical studies reported by Houghton, Pelcovits and Stratt represent new approaches to understanding glasses, quasicrystals and disordered solids. Further studies, related to the glassy state are reported here, in the case of Clifton's observation of the glassy response of lubricants at high pressures and high shearing rates, and in the New Initiatives section in the case of Morse's work on optical fibers and establishment of the Laboratory for Lightwave Technology.

W. M. Risen, Jr., Coordinator

Structure of Cesium Gallate Glass Elucidated by High-Resolution NMR

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

Personnel: J. Zhong, Graduate Student, Physics Department

Sources of Support: MRL

Objectives and Approaches:

Gallium and aluminum appear in the same column of the periodic table. Due to the importance of aluminum in some major fields of industrial chemistry and its favorable NMR characteristics -- high sensitivity and large chemical shift range, -- ^{27}Al has continued to be the most extensively studied. But the limited glassforming range for the alkali aluminate glasses restricts extensive study of the binary system. It was found recently that in some glass-forming systems the glassforming range is larger in the gallate than in the aluminate case. The close similarities of aluminum and gallium provide another opportunity to explore the glass system by using gallium in the place of aluminum. The structural models used to explain the property variations will be quite similar for the glasses formed in both binary systems. Study of the structure of alkali gallate glasses will therefore yield additional insight regarding the structure of alkali aluminate glasses and alkali aluminosilicate glasses.

High-resolution solid-state NMR spectroscopy was used to study the cesium gallate glass system with the gallium oxide content ranging up to 70 mol%, at two different magnetic fields. Computer simulation was used to obtain parameters related to microscopic structures of the glass system, and a structural model is proposed based on ^{71}Ga and ^{69}Ga static and MASS spectra at room temperature, and relaxation time measurements (spin-lattice relaxation time T_1 and spin-spin relaxation time T_2).

Research Achievements:

The NMR signals provide direct evidence for the existence of both 4-coordinated and 6-coordinated gallium atoms and changes of their ratio as a function of composition of the glass system. The results of this study suggest that NMR is an effective tool in studying gallium-containing glass systems. Separated features can be identified without magic angle spinning in the case of ^{71}Ga, and with the help of MASS in the case of ^{69}Ga. Larger separations between the features from 4-coordinated and 6-coordinated gallium in the ^{71}Ga spectra make ^{71}Ga superior to ^{27}Al for NMR studies. The study of frequency-dependent features of ^{71}Ga spectra shows that the isotropic chemical shift contributes most to the separation of peaks from different gallium sites, and quadrupole interaction causes broadening of lines in the static spectra and a small shift of the resonance peaks in MASS and static spectra. Relaxation time studies further distinguish signals from galliums in different coordination environments and will be useful in the study of ion hopping and other motional process in the glasses.

Publications:

J. Zhong and P.J. Bray, "Determination of Gallium Coordination in Cesium Gallate Glasses by High-Resolution Pulsed NMR," accepted for publicaiton in the *Journal of Non-Crystalline Solids*.

NMR Study of Sol-Gel Fabricated Lanthanum Silicate Glasses

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

Personnel: S.-P. Szu, Graduate Student, Physics Department

Sources of Support: NSF

Objectives and Approaches:

The characteristics of binary silica based rare earth glasses are particularly interesting for optical applications, such as isolators, circulators, and magnetic field sensors. Due to the extremely high melting points of rare earth oxides and SiO_2, the preparation of binary rare earth silicates from melts requires temperatures of 1800 °C or higher. Moreover, the melt method is limited to compositions for which quench techniques are sufficiently fast to avoid phase separation problems. This has caused experimental difficulties and often leads to low quality glasses. The sol-gel method for preparing silica based glasses has been used successfully in the past few years. In this project lanthanum silicate glasses prepared in the research group of Professor William Risen in the Department of Chemistry have been studied by ^{1}H, ^{29}Si, ^{13}C and ^{139}La NMR in specimens subjected to different heat treatment. The ^{139}La NMR has also been studied during the conversion from solution to solid gel.

Samples with batch composition $4La_2O_3$-$96SiO_2$ have been investigated. Specimens were heat treated at 50 °C, 500 °C, 500 °C and 800 °C after the gel was formed. All the ^{1}H, ^{13}C, ^{29}Si and ^{139}La NMR spectra were obtained after each heat treatment. To understand the role of the lanthanum ions in the solutions, another sample with less hydrochloric acid was prepared. Since the hydrochloric acid is used as a catalyst for hydrolysis, the time for the gel to develop from the solution was increased from ten hours to sixty hours. The ^{139}La NMR spectrum was obtained repeatedly during the solution-to-gel process. Since the time interval for each measurement was relatively short, each measurement can be regarded as a point in plotting properties versus time.

All the NMR spectra were recorded on a Bruker MSL-300 NMR spectrometer. The powdered samples were packed in alumina rotors and spun at 5 KHz in a magic angle sample spinning probe.

Research Achievements:

The proton spectra indicate that even this 800 °C heat treatment did not take away the OH group completely. The samples will absorb water molecules from the atmosphere because of the porous character of the material. The ^{29}Si spectra show that all the ethyl radical does not disappear until 800 °C and the lanthanum ions will not affect the silicon network until 800 °C. The static spectrum of ^{29}Si shows that the ratio between the $[SiO_4]$ units with one NBO and $[SiO_4]$ units without NBO is 1:3 which is very close to the theoretical value. This indicates that the lanthanum ions are modifiers in the silicate glass.

Because the OH ions are replaced by water molecules during the solution-to-solid gel process, the chemical shift of ^{139}La changes from 172 ppm to 23 ppm. The decreasing of the line width of the ^{139}La response indicates that the environment of the lanthanum ions becomes more symmetric during the solution-to-gel process. The ^{139}La signal is not observable for the solid sample with the 50°C heat treatment because of the very distorted environment around the lanthanum ion, but a very broad signal reappears again for the sample heated at 800°C.

^{19}F and ^{11}B NMR Investigations of Fluorine Doped Silica

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

Personnel: P. E. Stallworth, Graduate Student, Physics Department

Sources of Support: Mitsubishi Cable Industries Ltd.

Objectives and Approaches:

It is widely known that the optical transmission properties of silica glass can be altered through the incorporation of certain dopants into the silica matrix. For instance, when small quantities of fluorine are added, the net effect is a reduced index of refraction of the material. It is believed that the reduced index of refraction is a result of the chemical bonding and spatial distribution of the fluorine atoms. This implies a strong dependence of the optical properties upon the structure of the glass. The structure, in turn, depends upon the type and amount of dopant as well as on the thermal processing of the glass. Of particular interest in this work is the use of BF_3 and/or SiF_4 as dopants in the incorporation of fluorine into silica glass. ^{19}F and ^{11}B nuclear magnetic resonance (NMR) has been employed to understand the glass structure since NMR serves as a sensitive probe for the local environment of the nucleus in question. The symmetry of the boron environment (indicative of bonding) is reflected in the ^{11}B NMR spectrum. In considering the second moment calculation for fluorine, a model is proposed for the fluorine distribution. The objective is to find differences of glass structure for those BF_3-doped as compared with the SiF_4-doped glasses, and to determine in the BF_3-doped materials whether the fluorine atoms are bound to boron atoms and/or silicon atoms (the possibility of oxyfluoride units is quite remote).

Research Achievements:

The ^{11}B NMR responses indicate that boron exists in the three-fold coordination state. That is, boron is bound to only three neighbors. The ratio of oxygen neighbors to fluorine neighbors has not been determined. However, the compositions of the glasses show that the fluorine content is generally less than 1.5 wt. percent and the boron to fluorine mole ratio is about .2 (for the BF_3 doped glasses). It is expected, due to the heteronuclear interaction between the magnetically sensitive boron and fluorine neighbors, that the boron NMR spectrum would reveal some degree of broadening. However, the ^{11}B response indicates for these doped glasses a smaller distribution of quadrupolar coupling constants and asymmetry parameters (sharper features in the spectra) compared to that of pure B_2O_3 glass.

The ^{11}B results are not very sensitive to the local presence of fluorine, yet the ^{19}F NMR response is sensitive to both the local presence of boron and fluorine. It is found that the fluorine spectra yield difference in linewidth for the two glass types; i.e., either BF_3 or SiF_4 dopant. The BF_3-doped glasses exhibit larger NMR linewidths than those of the SiF_4-doped samples. This broadening reflects the heteronuclear boron-fluorine interaction and is found to be greater than the homonuclear fluorine-fluorine linewidth by 30% or more. Actually, a larger width was expected for the BF_3-doped glasses than that found. This exception was based upon a second moment calculation which allows determination of internuclear distances. The boron-fluorine distance was initially postulated to be 1.31 angstroms (which is the B-F bond length of the BF_3 molecule) and yields through a second moment calculation a ^{19}F NMR linewidth of 38 KHz. In contrast, the experimental results give linewidths around 5 KHz and thus indicate larger boron-fluorine distances. The evidence of the larger linewidth remains in the wings of the fluorine spectra. There appears to be a broadened response in some of the samples studied. However, greater resolution is required to identify this feature.

Using the ^{19}F NMR halfwidths, the second moment calculation was also performed in order to arrive at a satisfactory model for the fluorine distribution in the SiF_4-doped glasses. The model proposes that the fluorine atoms occur in units of monofluorides and to a much lesser degree difluorides. The spatial distribution of these units is not homogeneous; there is favoring of 2 monofluoride units where the fluorine-fluorine distance is about 3 to 4 angstroms apart. The next nearest neighboring fluorine atoms occur 12 or more angstroms away. In light of the similar bond energies of the B-F bond and the Si-F bond (6.36 eV and 5.86 eV respectively), it is expected that a similar model will describe the fluorine distribution in the BF_3 glasses as well. Further studies are being performed at higher magnetic field strengths (7.2 Tesla) in order to observe chemical shift effects of the ^{19}F line.

NMR Studies of Binary Alkali Germanate Glasses

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

Personnel: S.-P. Szu, Graduate Student, Physics Department

Sources of Support: NSF

Objectives and Approaches:

The coordination number of germanium atoms in inorganic glasses has attracted much attention since it is a network-forming cation which can be present in 4-coordinated and 6-coordinated states, whereas silicon appears only in the 4-coordinated state except at extremely high pressure.

Several spectroscopic techniques have been used to study the structure of binary alkali germanate glasses, such as EXAFS, Raman, IR, ESR. All these techniques show the number of 6-coordinated Ge atoms increases with an increase of the alkali content, reaches a maximum value and decreases again with a further increase of the alkali content. But these different techniques do not agree with each other quantitatively.

NMR has been used as a very powerful technique to study the micro-structure in all kinds of glass systems. In the past, the study of germanium coordination by ^{73}Ge NMR has been hampered by its low resonance frequency. With the Bruker MSL-300 superconducting high-field magnet installed in this laboratory, we can bring the ^{73}Ge resonance frequency up to 10.4 MHz, at which it is feasible to carry out ^{73}Ge NMR studies.

Differences in the quadrupole interaction (^{73}Ge has $I = 9/2$) and chemical shift interaction for the different coordination configurations can bring about resolution of the NMR responses from the 4-coordinated and 6-coordinated configurations.

Research Achievements:

An acoustic ring-down time of 350 microseconds has been measured. It is not surprising to have such a long acoustic ring-down time at this frequency. But, although it is very easy to observe the Ge signal in a liquid sample, the long acoustic dead time hampers efforts to observe any signal in the solid samples. Various pulse sequences have been tried to cut down the effect of the acoustic ringing. The pulse sequence proposed by Paul Ellis[1] can cut the acoustic ringing time from 350 microseconds to 80 microseconds. However, this is still not short enough for observing the signal from a GeO_2 sample.

A new RF coil which uses brass wire as the coil instead of copper is under construction. It is hoped that this will reduce the acoustic dead time down to 40 microseconds or less.

References:

[1] J. B. Lambert and F. G. Riddell, The Multinuclear Approach to NMR Spectroscopy (D. Reidel Publishing Company, Dordrecht, Holland, 1983).

NMR Study of Glasses in the System K_2O-B_2O_3-SiO_2

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

Personnel: S.-P. Szu, Graduate Student, Physics Department

Sources of Support: NSF

Objectives and Approaches:

Nuclear magnetic resonance (NMR) studies have been successful in determining the structure of glasses in the system Na_2O-B_2O_3-SiO_2. In particular, NMR has been used to determine the fraction of BO_4 units, BO_3 units with all bridging oxygens and BO_3 units with one or two non-bridging oxygens (NBO). ^{11}B NMR has now been used to study glasses in the K_2O-B_2O_3-SiO_2 system, and N_4 values (the fraction of the BO_4 units), N_{3S} values (the fraction of the BO_3 units with all bridging oxygens), and N_{3A} values (the fraction of BO_3 units with one or two NBO) have been determined. A model is proposed to describe the structure of glasses in this oxide system. The points in this model are very similar to those in the model for Na_2O-B_2O_3-SiO_2 glasses proposed by W. Dell and P. J. Bray, but new suggestions are introduced to bring the model into agreement with all of the data.

Various potassium borosilicate glass samples have been made. They were grouped into six K families, each K family having the same K value but different R values, where K = mole%SiO_2/mole%B_2O_3, and R = mole%K_2O/mole%B_2O_3. The slow passage modulation technique was applied to obtain the derivative of the NMR absorption spectrum. ^{11}B NMR spectra at 14.1 MHz were obtained by using a Varian Associates model V2100B current-regulated electromagnet. The standard area method, obtained by double integration of the derivative spectra, was used to obtain N_4. The technique of nonadiabatic rapid passage was also used to reduce the standard deviations inherent in measurements of N_4. Finally, computer simulation techniques have been employed to fit the derivative spectra to get N_{3S} and N_{3A} values.

Research Achievements:

The model displays the resemblance between glasses of the K_2O-B_2O_3-SiO_2 and Na_8O-B_2O_3-SiO_2 systems, which can be seen by comparing the fractions of BO_4 units, BO_3 units with all bridging oxygens, and BO_3 units with one or two non-bridging oxygens for both systems. There are, however, some differences in micro-structure between these two systems. The major difference is the forming of non-bridging oxygens at $R = 0.2$ in the K_2O-B_2O_3-SiO_2 system, due to the presence of the triborate unit with one NBO. In the Na_2O-B_2O_3-SiO_2 system, the non-bridging oxygens do not appear until $R = 1/2 + (1/4)K$. The early forming of non-bridging oxygens complicates quantitative development for the K_2O-B_2O_3-SiO_2 system.

An NMR Study of Glasses in the System Li_2O-CdO-P_2O_5

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

Personnel: S.-P. Szu, Graduate Student, Physics Department

Sources of Support: NSF

Objectives and Approaches:

Recently the role of cadmium atoms in glass systems has been studied by several authors. It has been proposed that CdO may become a glass former in some glass systems. In this project, we have studied the role of cadmium and lithium atoms in the glassforming region of the Li_2O-CdO-P_2O_5 system and developed a micro-structural model for the glasses.

Thirty RLi_2O-KCdO-P_2O_5 glass samples were prepared in the glassforming region. They were grouped into five K families, each K family having the same K value but different R values where K = mole%CdO/mole%P_2O_5, and R = mole%Li_2O/mole%P_2O_5.

^{31}P, ^{113}Cd and ^{7}Li NMR measurements were performed at 121.487 MHz, 66.56 MHz and 116.640 MHz, respectively, on a Bruker MSL-300 spectrometer. Some ^{31}P magic angle spinning experiments were performed.

Research Achievements:

All the ^{7}Li absorption spectra display a single Lorenzian line shape. The line width at half intensity varies between 5.2 KHz and 6.4 KHz, except for the R = 1.0, K = 1.0 glass for which the line shape is closer to Gaussian and the line width is 3 KHz.

All the ^{113}Cd spectra are structureless symmetric lines. The isotropic chemical shifts relative to polycrystalline CdO are around -330 ppm except for the R = 1.0, K = 1.0 glass for which it is -290 ppm. The chemical shift of ^{113}Cd indicates that the Cd atoms in the glasses have more ionic character than in CdO.

The ^{7}Li and ^{113}Cd spectra indicate that all of the Li and Cd atoms in the glasses are modifiers. From this point of view, at the beginning, when the Li and Cd atoms are added into the pure phosphate glass, they will transform the branching $(PO_4)^{-3}$ units into middle units. For K+R < 1, only branching and middle phosphate units exist. When K+R = 1, all the phosphate units are middle units. For K+R > 1, only middle and end phosphate units exist. Finally, when K+R = 2, all the phosphate units are end units. The static spectra of ^{31}P also support this simple model since the line shapes of the static spectra are almost identical for those samples with the same R+K values. The magic angle spinning method will be used to obtain the ^{31}P isotropic chemical shift of the various phosphate units.

NMR Study of Lead-iron Phosphate Nuclear Waste Glasses

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

Personnel: J. Zhong, Graduate Student, Physics Department

Sources of Support: MRL

Objectives and Approaches:

Lead-iron phosphate glasses as a promising new host for the safe immobilization of both high-level defense and high-level commercial radioactive waste have been studied by Sales et al.[1,2] Even though the usability of the glass as nuclear waste is still controversial it has been proven to be very chemically durable and thermally stable. The glass system was studied with NMR and the structure of the glass system has been postulated on the basis of the NMR experimental results.

Lead-iron phosphate glasses of the composition $PbO \cdot P_2O_5 \cdot xFe_2O_3$ with $x = 0.002$, 0.023, 0.069, 0.114, 0.160 and 0.206 (0.15, 1.0, 3.0, 5.0, 7.0 and 9.0 wt%) Fe_2O_3 added respectively were studied by low and high field ^{31}P NMR at different frequencies and different temperatures. The same samples were also studied with DSC and DTA thermal analysis techniques.

Research Achievements:

It is found that due to the interaction of part of the phosphous ions with the paramagnetic irons, the ^{31}P NMR absorption spectrum is split into two peaks separated by up to 0.3 percent of the resonance frequency. The separation as a function of resonance frequency and temperature follows the calculation based on the effect of paramagnetic interactions. Changes in the NMR signals as the iron content increases suggest the more stable structure, and thermal analysis confirms the postulation.

In normal paramagnetic crystals it is possible to observe a shift in the nuclear resonance line, due to the average electronic magnetic field superimposed upon the applied field. The additional average field exerted on the resonant nuclei is that produced by a classical dipole

$$\delta H = \mu \left(\frac{\mu H_0}{kT} \right) \frac{1}{a^3} = \beta^2 g^2_{eff} \frac{H_0}{kT\, a^3} ,$$

where a is the interatomic spacing, β is the Bohr magneton, g_{eff} is the effective g factor of the paramagnetic atom and H_0 is the external magnetic field. Distances between the Fe and P ions can therefore be deduced from either the $\delta\nu$ vs. ν_0 relation or the $\delta\nu$ vs. 1/T relation. The values of a for samples with different iron content was thus obtained from the slope of $\delta\nu$ vs. ν_0 plot and from $\delta\nu$ vs. 1/T relation at fixed resonance for samples with the same iron content. From the good fit of the calculated line with the experimental results we suggest that iron atoms in the glass are in the paramagnetic state, and that there exist two nonequivalent phosphate structures, one having iron in its vicinity at less than 3Å and one having no iron atoms in the immediate environment. Dipole interaction between the paramagnetic irons and phosphous nuclei in the two different sites causes splitting of the ^{31}P resonance lines. Magnetic susceptibility broadening is found to be the major contribution to the linebroadening at high iron oxide content. The contribution from the anisotropic chemical shift cannot be ignored at low iron oxide content, since the lineshape for sample with 0.15 wt% Fe_2O_3 is typical for the anisotropic chemical shift interaction.

References:

[1]B. C. Sales and L. A. Boatner, *Science*. 226, 45 (1984).

[2]B. C. Sales, R. S. Ramsey, J. B. Bates and L. A. Boatner, *Journal of Non-crystalline Solids*. 71, 103 (1985).

Incorporation of Alkali Ions in Alkali Borate and Mixed Alkali Borate Glasses

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

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

Sources of Support: NSF

Objectives and Approaches:

^{11}B NMR of alkali borate glasses and compounds has shown that the number of non-bridging oxygens in these glasses depends on the amount of alkali that exists in the glass. NMR studies of the alkali nuclei have not yielded such useful information because of the large second-order quadrupolar and dipolar broadening found for these nuclei. By using our new high field (7.2 Tesla) superconducting magnet, the second-order quadrupolar broadening is reduced by a factor of four as compared to the highest field previously available to us. In addition, the dipolar broadening can be eliminated by the use of Magic Angle Sample Spinning (MASS). By combining these two techniques (MASS in a high magnetic field) the small variations in the isotropic chemical shifts for alkalis in different environments can be resolved. These experiments are interesting in that they provide an independent test of the theories of glass structure that have been formulated in this laboratory based on the ^{11}B NMR studies.

Research Achievements:

Two series of glasses in the system $RNa_2O \cdot B_2O$, $R^6Li_2O \cdot B_2O_3$ ($R = 0.1 \rightarrow 2.0$) and a mixed alkali glass of composition $R(0.5^7Li_2O\ 0.5Na_2O) \cdot B_2O_3$ $R = 0.5$ have been measured. MASS NMR has been done on both ^{23}Na and ^{6}Li nuclei. With both nuclei a significant variation of chemical shift and line width with composition is observed. The variation is supportive of a model in which the alkali are in close proximity to bridging oxygens at low R values which are gradually replaced by non-bridging oxygens at high R values.

An interesting effect is that the mixed alkali glass exhibits significantly different chemical shifts and line widths than those for either of the pure alkali glasses. The effect will be studied in greater detail to see if it can yield any understanding of the well known mixed alkali effect. In the mixed alkali effect, the mobility of both alkali ions is reduced several orders of magnitude below what one would expect from a model based on simple mixing. Many previous studies have failed to find any structural phenomena associated with the mixed alkali effect. (Except for recent study in this laboratory that has shown that the ratio of four-coordinated borons in alkali borate glasses is affected by mixing alkali ions.)

This study will be extended to the complete range of R values in both the sodium and lithium systems. MASS NMR will also be extended to other alkali nuclei.

Local Ion Environments in Mixed Lithium-Potassium Silicate Glasses

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

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

Sources of Support: NSF

Objectives and Approaches:

In the mixed-alkali effect the mobility of alkali ions is reduced several orders of magnitude when different alkalis are mixed in the glasses. This reduction in mobility is greatest near a 1:1 ratio of differing alkali ions, and is much greater than can be explained by the simple mixing of the alkali ions. Many explanations have suggested structural reasons for this effect. The two main ideas are that the ions form pairs or that the ions avoid each other. No evidence for pairing has yet been reported but some evidence has supported ions clustering with similar ions. The aim of this study is to see what the dipolar interaction between the ions can tell us about the distribution of the ions in the glass.

Research Achievements:

A series of glasses of composition $(1\text{-}x)K_2O \cdot x^7Li_2O \cdot ySiO_2$, $y = 0.2$, $x = 0.1 \rightarrow 1.0$ has been made. The dipolar broadening of the ^7Li nuclei was measured at 200°K in order to assure that the ions were not mobile due to thermal effects. Lithium and potassium were chosen because of their large difference in magnetic moment giving rise to a large difference in dipolar broadening. It has been shown that the mixed alkali effect does not occur in mixed ^6Li - ^7Li alkali silicate glass. For this reason a similar series of glasses of composition $(1\text{-}x)^6Li_2O\ x^7Li_2O\ ySiO_2$, was studied.

For all glasses the dipolar broadening was found to be larger than the broadening expected if the ions were placed in the glasses randomly. In both series the compositions near a 1:1 mixture of ions showed a slightly larger dipolar broadening indicating that the lithium ions are affecting each other even more effectively then when the glass is made predominantly of only one type of ion.

The effect is small so more samples will be measured to assure repeatability.

References:

1. H.L. Downing, N.L. Peterson and H. Jain, *Journal of Non-crystalline Solids*, **64** [7] 335-49 (1984).

High Field Frequency Swept NMR at Low Frequencies

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

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

Sources of Support: NSF

Objectives and Approaches:

A significant experimental problem of pulsed NMR at low frequencies is the long ring down times encountered due to acoustical ringing of the NMR probe. This dead time puts a drastic limit on the observable width of an NMR resonance. Mainly in an effort to study ^{32}Ge NMR (Lamour frequency = 10.4 MHz in a field of 7.2 Tesla) this laboratory has been exploring several means of reducing this dead time. One approach will be to use a swept frequency Robinson type continuous wave (CW) spectrometer. This has the advantage that it can sweep very large frequency widths without sacrificing sensitivity and is insensitive to acoustical ringing. In pulsed NMR if the acoustical ringing problem is solved one still has to lower the Q of the probe in order to cover a sufficiently large frequency range. This is not ideal because the sensitivity of the probe is proportional to the Q.

For NMR lines less than a few hundred gauss wide this spectrometer can be used in Nonadiabatic Rapid Passage (NARP) mode with its improved sensitivity especially for easily saturated samples.

Research Achievements:

This spectrometer has been built in this laboratory and has been used to search for pure quadrupole resonances at frequencies from less than 1 MHz to over 30 MHz. It can sweep over a factor of two in frequency easily. The data acquisition has been automated using an IBM PC with a Techmar Lab-Tender installed. The use of computerized acquisition has allowed several improvements in sensitivity. Because the frequency is measured and stored along with the spectrum, the experiment can be repeated and added to previous runs without error. This allows for all the advantages of signal averaging which would otherwise not be available for this type of single sweep experiment. A real time averaging filter has been digitally realized with this system. This filter allows a 50% decrease in the time need to obtain a given signal to noise ratio over a conventional low-pass RC filter.

What remains to be done is for a probe to be built that will fit inside the 7.2 Tesla superconducting magnet that is part of the Bruker MSL-300 instrument in this laboratory. For Nonadiabatic Rapid Passage operation a set of sweep coils will have to be constructed also.

Incorporation of Lithium and Sodium in Alkali Borate Glasses

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

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

Sources of Support: NSF

Objectives and Approaches:

Models of the incorporation of alkali ions in alkali borate glasses are based on the crystal structures of compounds of similar composition.* Additional evidence in support of these models is being obtained by studying the environment of the four-coordinated borons in these glasses and crystals. The local environment of the four-coordinated borons is being studied by looking at the first-order quadrupole interaction for the ^{11}B nuclei in four-coordinated borons in the crystals and glasses. This study is being done to supplement previous work which measured the distribution of lithium ions about four-coordinated borons.

Research Achievements:

Crystals in the series $RNa_2O \cdot B_2O_3$ and $RLi_2O \cdot B_2O_3$, (R = 0.25, 0.33 and 0.5) have been fabricated. The Q_{cc} (quadrupole coupling constant) and η (asymmetry parameter) have been measured by using a high field magnet to reduce the seconed-order quadrupole broadening due to the three-coordinated borons. Q_{cc} and η have also been measured for glasses in the same composition range. The crystals were characterized by distinct values of Q_{cc} and η. The glasses showed large distributions of Q_{cc} and η with the distributions increasing with R. These results are consistent with the Krogh-Moe model in which the glasses consist of randomly connected structural groupings found in the crystalline compounds similar *composition.*

References: *J. Krogh-Moe, *Phys. Chem.. Glasses.* 6, 46 (1965).

NMR of Silicon in Mixed Sodium-Cesium Silicate Glasses

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

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

Sources of Support: NSF

Objectives and Approaches:

Another approach to exploring the structure of mixed alkali glasses is to observe the isotropic chemical shifts of the ^{29}Si nuclei in mixed alkali glasses. MASS ^{29}Si NMR has been very fruitful in determining structural variations in glasses and crystal.

Research Achievements:

Glasses in the system $(1\text{-}x)Na_2O \cdot xCs_2O \cdot ySiO_2$, (y = 1/3 and y = 1/2, x = 0.0 → 1.0) have been fabricated. The static NMR spectra have been recorded and have shown the presence of two sites with different anisotropic chemical shifts in the pure glasses but only one site in the mixed glasses. MASS ^{29}Si NMR will be done to see if the isotropic chemical shift contains additional information.

Raman Investigation of Cadmium Borate and Borogermanate Glasses

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

Personnel: G. D. Chryssikos, Graduate Student, Chemistry Department

Sources of Support: MRL and National Hellenic Research Foundation

Objectives and Approaches:

Among the cadmium borogermanate glasses there are compositions which are reported to exhibit ohmic photoconductivity. Because of the technological potential of this property in such a readily accessible composition and theoretical interest in the mechanism of the phenomenon in these materials, collaborative studies of the structure of the ternary $CdO/B_2O_3/GeO_2$ system were initiated involving vibrational and NMR spectroscopic studies. The NMR and infrared studies by Bray, Risen and coworkers have been reported and published.

In this work, the laser Raman spectra were investigated. Such an investigation is complicated by the presence of two network-forming oxides and the fact that both boron and germanium are known to have more than one stable coordination geometry. Moreover, CdO can act through either ionic or covalent bonding, that is as a modifier or as a glass former. To sort these effects, it is necessary to investigate a range of compositions.

Research Achievements:

In order to investigate the structures of these complex ternary glasses, and, in particular, to understand how they are related composition, it was necessary to synthesize a number of cadmium borate and cadmium borogermanate glasses in a systematic fashion. By doing so in such a way that series of glasses were made to constitute families in which a key stoichiometric parameter was held constant, it was possible to study the roles of the components in determining the structure. Increasing the amount of cadmium oxide in glasses of constant germanium to boron ratio, for example, was found to modify both boron and germanium network forming centers. The formation of non-bridging oxygen-containing groups was favored especially by this introduction. When the mole fraction (content) of cadmium oxide was held constant and the boron to germanium ratio was varied, a competitive modification of boron over germanium was observed. These trends in addition to the observation of spectral features associated with the structural units postulated for these glasses and the NMR and infrared spectral studies were coordinated to develop a structural model for these glasses.

Publications:

G.D. Chryssikos, E.I. Kamitsos and W.M. Risen, Jr., "A Raman Investigation of Cadmium Borate and Borogermanate Glasses," *Journal of Non-crystalline Solids*, in press (1987).

Rare Earth Phosphate Glasses: Preparation and Properties

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

Personnel: K. Sun, Graduate Student, Chemistry Department

Sources of Support: AFOSR, MRL

Objectives and Approaches:

The characteristics of glasses containing high concentrations of rare earth ions are of considerable interest for applications in optical data transmission, detection, and sensing, and laser technologies as well as nuclear waste disposal and other technologies. Such glasses can have high nagnetic susceptibilities and strong, sharp electronic absorptions in the ultraviolet to near infrared region, and thus may be useful as Faraday rotator modulators, optical isolators, fiber lasers, and optical signal couplers.

While there are many complex multicomponent rare earth glasses, phosphates hold special interest as binary rare earth glasses of variable composition whose properties can be changed systematically. To gain control over such mateirals it is important to determine how their spectral, magnetic and thermal characteristics vary with composition in materials with well-known composition.

Research Achievements:

Praseodymium phosphate and dysprosium phosphate glasses with compositions $xLn_2O_3(1-x)P_2O_5$ were synthesized in the x=0.18-0.30 range and analyzed by electron microprobe to within 0.01 weight percent. They were shown to be x-ray amorphous and homogeneous on a scale of ca. 0.1μ by microprobe. Their structures have been studied by infrared, far infrared and laser Raman spectroscopy as a function of stoichiometry. This study produced clear correlations of Raman features, especially in the 1100-1300 cm^{-1} region, and composition, showing that changes in x of as little as ±0.01 cause clear changes in relative band intensities which can serve as an analytical probe

The magnetic and optical data obtained showed that the rare earth ions behave independently and that neither the liquid field of the network nor any interionic coupling is great enough to lift the (2J+1)-fold degeneracy of the ion states and that both are small. The glass transition temperatures of the glasses varied linearly with x, increasing from ca. 580°C to 650°C over the x=0.18 to x=0.28 range for the Pr glasses, and was significantly higher (660-720°C) for the smaller cation-containing Dy glasses

Publications:

K. Sun and W. M. Risen, Jr., "Rare Earth Phosphate Glasses," *Solid State Communications* 60, (1986) 697.

Sol-Gel Preparation and Properties of Binary Rare Earth Silicates

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

Personnel: K. Sun, Graduate Student, Chemistry Department
W-H. Lee, Graduate Student, Chemistry Department

Sources of Support: AFOSR, MRL

Objectives and Approaches:

The objective is to prepare binary silicate glasses with compositions which are not accessible using traditional glass forming techniques but are important to study and apply. The characteristics of binary silica-based rare earth glasses are of particular interest for optical applications in which silica-based materials with large Verdet constants and lasing ability are required. This is especially important in optical fiber technology, where binary rare-earth silicates are needed to create nonreciprocal devices, such as isolators and circulators, and magnetic field sensors. Of course, glasses with these compositions, containing high field strength optically and magnetically active cations, also are of interest in geological, chemical, nuclear waste storage, and other optical fields.

Due to the extremely high melting points of rare earth oxides and SiO_2, however, the preparation of binary rare earth silicates from melts requires temperatures of 1800°C or higher. In fact, partial success has been achieved only in the 2400-3000°C and with very high cooling rates. This has caused experimental difficulties and often leads to low quality glasses.

The sol-gel method provides an approach to obtaining binary rare earth silicates as pure, homogeneous glasses at much lower temperatures than required by conventional melt-quench techniques.

Research Achievements:

Rare earth silicate glasses were prepared by a new sol-gel method starting with the rare earth carbonates of Pr, Dy and Er and TEOS (tetraethylorthosilicate). Based on this method, which does not require the extensive chemistry involved in the synthesis of metal alkoxides demanded by certain other sol-gel approaches, the binary rare earth silicates of Nd and most of the rare earths were obtained. Expressed in the form $xLn_2O_3(1-x)SiO_2$, glasses have been prepared with compositions in the range $x=0.009$ to $x>0.06$, or 0.9 to 6 mole percent, which corresponds to about up to 25 weight percent. The compositions were determined by electron microprobe. The glasses were shown to be x-ray amorphous as well. The infrared and visible spectra and the magnetic susceptibilities were obtained and analyzed.

Publications:

K. Sun, Y.H. Lee and W.M. Risen, Jr., "Sol-Gel Preparation of Rare-Earth Silicate Glasses," *Journal of Non-crystalline Solids*, 92 (1987) 145.

Dielectric Behavior of Ionic Conducting Glasses

Principal Investigators: R. H. Cole, Professor, Chemistry Department
W. M. Risen, Jr., Professor, Chemistry Department

Personnel: D. E. Turcotte, Graduate Student, Chemistry Department
G. D. Chryssikos, Graduate Student, Chemistry Department

Sources of Support: MRL, NSF

Objectives and Approaches:

The principal objectives have been characterization of the dielectric properties of a variety of inorganic glasses with special emphasis on fast ionic conducting glasses. These have remarkably high electrical conductivities at elevated temperatures, with considerable promise for use in energy storage devices under such conditions. Appreciable concentrations of highly mobile ionic charge carriers are clearly required, but little is known about the necessary fast response to applied electric fields or about how fast transport is possible in a glassy environment. This part of the broad program directed toward a better understanding of such systems concerns results of electrical response measurements in the hitherto virtually unexplored megahertz to gigahertz region.

The systems so far studied are ternary borate glasses XM_2O, yMX, B_2O_3 with alkali metal oxide M_2O and halide MX at the mole fractions x and y, for $M = Li, Na, K$ and $X = F$ or Cl. These systems exhibit high conductivity over considerable range of glass forming compositions and were studied at temperatures from 20° to 375°C, using wide band time domain reflection methods for a corresponding frequency range from 30 MHz to 3 GHz.

Research Achievements:

At the start of this research, we anticipated finding either the high frequency end of so-called conducting relaxation seen at much lower frequencies ($<10^6$ Hz) near room temperature or the onset of damped quasi-resonant lattice modes in the gigahertz range (10^9 Hz). The former was found, although the data in all cases show little change in permittivity ('Dielectric constant') or excess conductance (absorption) over the frequency range.

With significantly improved instrumentation in the 10^6-$10^{9.5}$ Hz region, increased sensitivity made it possible to ascertain that apparent plateau values of permittivity, which were found to increase markedly at high temperatures, contained evidence for the high frequency end of the so-called conducting relaxation. Thus, the striking result that ($\partial\epsilon/\partial T>0$), does not originate at these frequencies entirely from partial disordering of ions with applied field. In order to obtain these results, substantial improvements were made in the instrumentation, including the construction of cells for reduction of fringe field effects, and of a new system for measuring dielectric data in the 5×10^5-5×10^7 Hz regime, but further improvements in the range and precision of the instrumentation are required to explore fully the phenomena associated with responses due to coupled conduction and quasi-resonant lattice vibrations.

Publications:

D. E. Turcotte, G. D. Chryssikos, J. P. Perl, P. W. Winsor, IV, R. H. Cole and W. M. Risen, Jr., "Time Domain Dielectric Measurements of Conducting Glasses," *Journal of Chemical Physics*, 84, p. 6518 (1986).

Observation of Molecular Vibrations in Real Time

Principal Investigator: H. J. Maris, Professor, Physics Department
W. M. Risen, Jr., Professor, Chemistry Department
J. Tauc, Professor, Division of Engineering and Physics Department

Personnel: J.M.Y. Ha, Graduate Student, Chemistry Department
Z. Vardeny, Visiting Professor, Division of Engineering

Sources of Support: DOE and MRL Optical Facility

Objectives and Approaches:

In a recent experiment ultrafast optical measurements on the large dye molecules, malachite green and nile blue have been reported.[1] A high-frequency oscillatory response was obtained, which was tentatively interpreted in terms of quantum beats. Our aim was to make further optical measurements on these molecules in order to understand the origin of the oscillations.

Research Achievements:

Raman and infrared measurements were made on malachite green and nile blue. We found several modes whose frequencies matched the frequencies found in the measurements of Rosker et al. Based upon this result we could conclude that the observed quantum beats were between states which had different quantum numbers. Thus, femtosecond optical measurements of photo-induced transmission can probe the vibrations of molecules in real time.

References:

1. Rosker et al., *Phys. Rev. Lett.* 57, 32 (1986).

Publications:

J.M.Y. Ha, H. J. Maris, W. M. Risen, Jr., J. Tauc, C. Thomsen and Z. Vardeny, "Observation of Molecular Vibrations in Real Time," *Physics Review Letters*, 57, p. 3302 (1986).

Phonons of Amorphous Superlattices

Principal Investigators: H. J. Maris, Professor, Physics Department
J. Tauc, Professor, Division of Engineering and Physics Department

Personnel: H. Grahn, Graduate Student, Physics Department

Sources of Support: DOE and MRL Optical Facility

Objectives and Approaches:

The aims of our studies of phonons in amorphous superlattices are 1) to develop a probe of superlattice structure, material properties, and interface quality and 2) to investigate the basic physics of phonons in layered materials. We use the picosecond pump and probe technique to generate and detect the phonons. A light pulse is absorbed in the structure and sets up a stress distribution. This stress pattern excites the different phonon modes of the superlattice, and the resulting oscillations of the superlattice are monitored by measurement of the change in optical reflectivity of the structure.

Research Achievements:

We have studied a series of Si-Ge amorphous superlattices prepared by B. Abeles at Exxon. The repeat distance varied from 190Å to 1134Å, and the superlattices were grown on SiO_2 substrates. We observed an oscillatory response with a frequency ν_L approximately equal to the frequency ν_A of the acoustic branch at the zone boundary for an infinitely thick superlattice. A detailed study showed that the major part of the response comes from a phonon made which is localized at the free surface of the superlattice, and whose frequency lies in the gap at the zone boundary. We have calculated the characteristic decay length and frequency of this mode and have compared it with the experimental results.

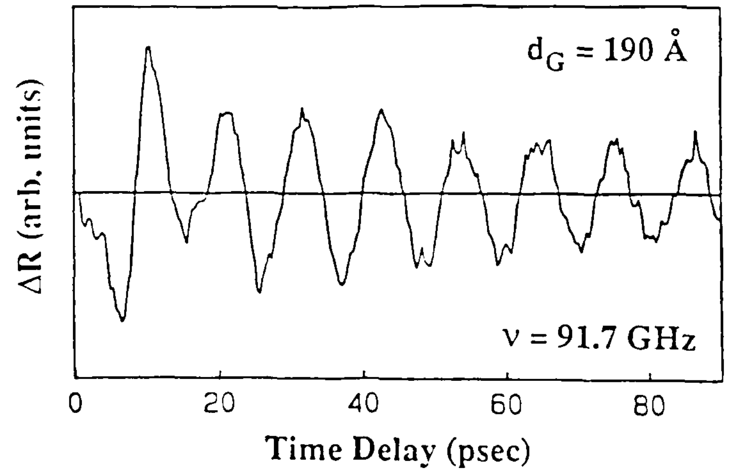

Figure 30: Oscillatory component of photoinduced reflectivity measured in real time with the pump and probe technique in a a-Ge:H/a-Si:H multilayer structure.

Publications:

H. J. Grahn, "Picosecond Carrier Transport and Acoustics in a-Si:H based Multilayer Structures," Ph.D. Thesis 1987.

H. J. Grahn, Z. Vardeny, H. J. Maris, J. Tauc and B. Abeles, "Picosecond Dynamics of Photo-excitations in Amorphous Multilayer Structures," MRS Proceedings, vol. 77 (to be published).

Heat Flow in Glasses on Short Length Scales

Principal Investigators: H. J. Maris, Professor, Physics Department
J. Tauc, Professor, Division of Engineering and Physics Department

Personnel: D. A. Young, Graduate Student, Physics Department
C. Thomsen, Graduate Student, Physics Department

Sources of Support: MRL and DOE

Objectives and Approaches:

The thermal conductivity of glasses is not understood at the microscopic level. One approach, due to R. Orbach et al., is to assume that the majority of phonons in glasses are localized excitations. Heat flow in glasses is then due to the hopping of phonons from one localized state to a neighboring state. The aim of our research is to test this theory by making a measurement of heat transport over a distance comparable to the size of a localized state. Over such a distance the apparent thermal conductivity should be much larger than the conductivity measured in a macroscopic experiment.

Research Achievements:

We have used the picosecond pump and probe technique to study the heat flow. A thin gold film is evaporated onto the surface of a-SiO_2. This film is heated by a 0.2 psec light pulse. The optical reflectivity R of the film depends on temperature, and so a measurement of R (by means of a time-delayed probe pulse) can determine the rate at which the gold film cools. The time resolution is of the order of 1 psec. We have measured the rate of cooling of the gold due to heat flow into the glass substrate, and can use these results to put an upper bound on the phonon localization length.

Publications:

D. A. Young, C. Thomsen, H. T. Grahn, H. J. Maris and J. Tauc, "Heat Flow in Glasses on a Picosecond Time Scale," in Phonon Scattering in Condensed Matter V, (ed. A. C. Anderson and J. P. Wolfe), Springer 1986, p. 49.

Optical Studies of Phonons in Amorphous Solids by Picosecond Spectroscopy

Principal Investigators: H. J. Maris, Professor, Physics Department
J. Tauc, Professor, Division of Engineering and Physics Department

Personnel: C. Thomsen, Research Associate, Physics Department
H. T. Grahn, Graduate Student, Physics Department

Sources of Support: MRL and DOE

Objectives and Approaches:

The technique for studying longitudinal phonons using picosecond pump and probe technique has been further developed and applied to studying phonons in glasses. The aim of these studies is to obtain information about phonon propagation in a frequency and temperature range inaccessible to the current methods, and also to demonstrate the potential of this method as a non-destructive diagnostic technique for measuring thin films.

Research Achievements:

Theory of surface generation and detection of phonons by picosecond light pulses has been developed as a theoretical basis for our method. The agreement between the theory and our experimental results is very good. The recent experimental work is focused on developing and using very thin film transducers deposited on the studied films for reaching very high frequencies. Both semiconductor and metallic transducers have been developed and applied. The highest frequency achieved so far has been 400 GHz using an Al transducer on pyrex. The transducers have also enabled us to study transparent thin films. A comprehensive study of the velocity and attenuation of

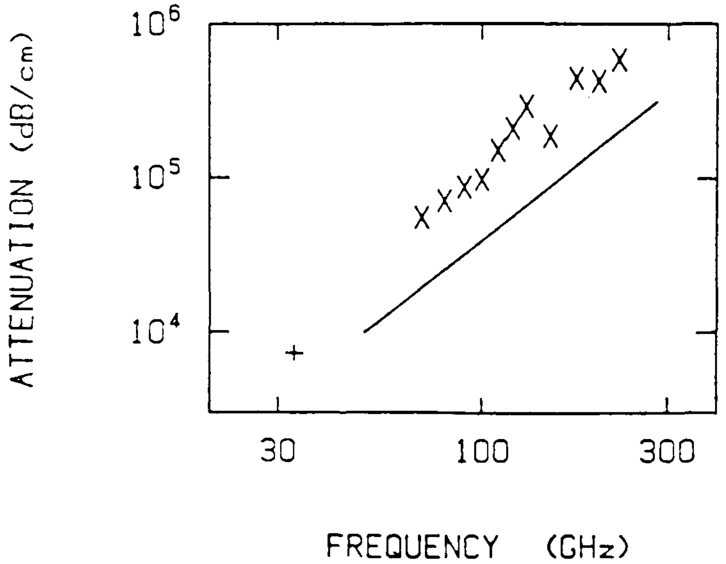

Figure 31: **Preliminary results for the attenuation of longitudinal phonons in SiO_2 at room temperature; the solid line shows an ω^2 frequency dependence.**

longitudinal phonons in fused silica films has been started. The aim is to obtain data in a broad frequency and temperature range that will be relevant for the resolution of a fundamental problem of phonon transport in glasses -- the origin of the universal appearance of a plateau of heat conductivity when plotted as a function of temperature. So far we have obtained data on longitudinal phonon attenuation in a-SiO_2 at room temperature in the range from 60 to 230 GHz; in this range it is proportional to the square of frequency (Fig. 31). Currently experiments are underway to increase the frequency and extend the temperature range. The potential interest for studying interfaces using this technique is the observation of the dependence of responses on the bonding between the film and the substrate. Figs. 32a and 32b show the responses of two very thin Al films deposited on a thick pyrex substrate which resonates at 290 and 400 GHz respectively. The difference in the damping can be explained by the difference in the bonding to the substrate. The response in Fig. 32a points to poor bonding which can be explained by postulating a layer of "dirt" only 3 to 4Å thick between the film and the substrate.

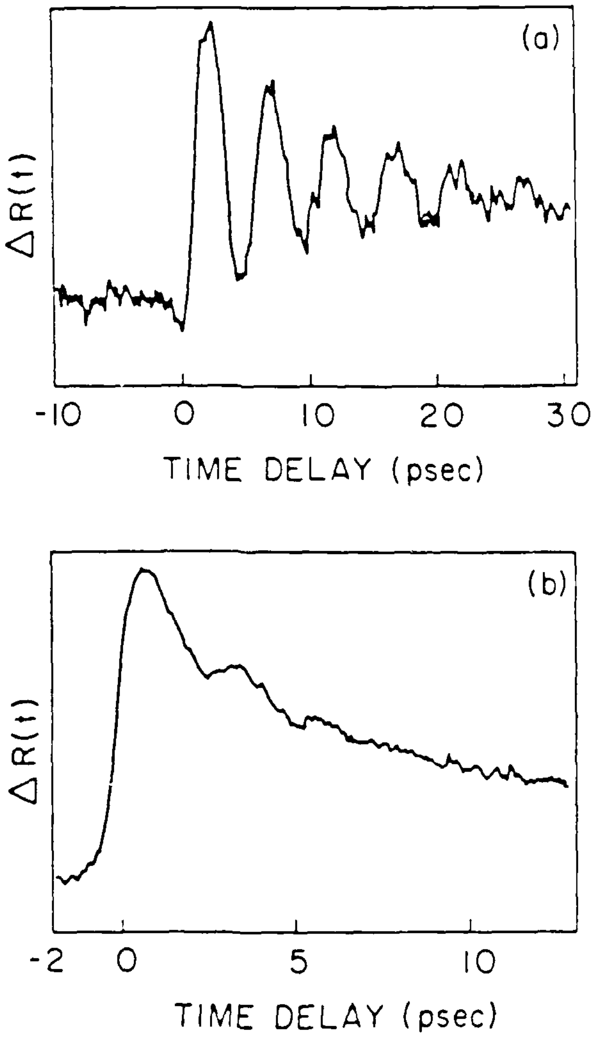

Figure 32: Responses of two Al film transducers.

Publications:

C. Thomsen, H. T. Grahn, H. J. Maris and J. Tauc, "Surface Generation of Detection of Phonons by Picosecond Light Pulses," *Physical Review* B 34, p. 4129 (1986).

H. J. Maris, C. Thomsen and J. Tauc, Studies of High Frequency Acoustic Phonons using Picosecond Optical Techniques," Phonon Scattering in Condensed Matter V (ed. A. C. Anderson and J. P. Wolfe), Springer 1986, p. 374.

C. Thomsen, H. J. Maris and J. Tauc, "Picosecond Acoustics as a Non-destructive Tool for the Characterization of Very Thin Films," *Thin Solid Films* (to be published).

Picosecond Interferometry for Studying Phonons in the Brillouin Frequency Range

Principal Investigators: H. J. Maris, Professor, Physics Department
J. Tauc, Professor, Division of Engineering and Physics Department

Personnel: C. Thomsen, Research Associate, Physics Department
H. T. Grahn, Graduate Student, Physics Department
D. A. Young, Graduate Student, Physics Department

Sources of Support: MRL

Objectives and Approaches:

Spontaneous, stimulated and impulsive Brillouin scattering are well established optical techniques for studying phonon velocity and attenuation in transparent solids and liquids. We discovered a new technique in which longitudinal phonons of Brillouin frequency can be measured in real time. This method is capable of providing a significantly higher accuracy in determining the phonon frequency and attenuation than the current methods.

Research Achievements:

The method is based on the picosecond pump and probe technique. The experimental arrangement is schematically shown in Fig. 33. The pump pulse is absorbed in the absorbing film deposited on the studied sample. It produces a strain pulse which propagates into the sample. The probe pulse is reflected on the absorbing film and also on the propagating strain pulse. Interference between these pulses produces an oscillatory signal in the detector shown also in the figure. The frequency of these oscillations is

$$\nu = 2\nu_{light}\,(v/c_m)\cos\theta$$

where v is phonon velocity, c_m is light velocity in the material and θ the angle of incidence. For normal incidence ($\theta = 0$)ν is the same as in Brillouin backscattering.

The attenuation of the observed signal depends on light absorption, pulse coherence and acoustic attenuation which can be determined after correcting for the two former contributions. From the measurement in pyrex shown in the figure we determined the longitudinal sound velocity (v = $(5.8 \pm 0.05)\times10^5$ cm/s at ν = 28GHz; the attenuation was too low to be measurable.

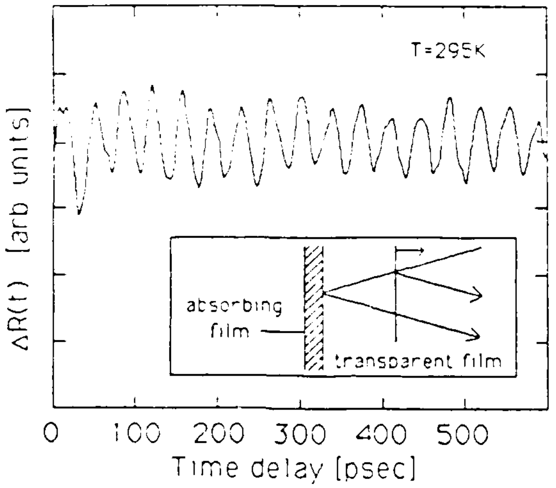

Figure 33: Picosecond interferometric signal is pyrex due to a propagating phonon pulse.

Publications:

C. Thomsen, H. T. Grahn, H. J. Maris and J. Tauc, "Picosecond Interferometric Technique for Study of Phonons in the Brillouin Frequency Range," *Optics Communications* 60, p. 55, (1986).

C. Thomsen, H. T. Grahn, D. A. Young, H. J. Maris and J. Tauc, "Picosecond Acoustic Interferometry," in Phonon Scattering in Condensed Matter V (ed by A. C. Anderson and J. P. Wolfe), Springer 1986, p. 392.

Picosecond Photocarrier Dynamics in Hydrogenated Amorphous Silicon

Principal Investigators: J. Tauc, Professor, Division of Engineering and Physics Department
Z. Vardeny, Visiting Professor from Technion, Israel

Personnel: C. Thomsen, Graduate Student and Research Associate, Physics Department
H. T. Grahn, Graduate Student, Physics Department

Sources of Support: NSF and MRL Optical Facility

Objectives and Approaches:

The picosecond pump and probe technique was applied to studying ultrafast carrier thermalization processes in undoped, phosphorus and boron doped, and compensated a-Si:H to obtain information about electronic states in the gap just below the mobility edge and about the relaxation processes associated with them. The goal is a contribution to an understanding of electronic processes in highly disordered materials, and in particular to elucidate what happens to photogenerated carriers shortly after excitation in a material with a great potential for optoelectronic applications.

Research Achievements:

Extensive data were taken at several temperatures on a selection of undoped, P-doped (10^{-4} and 2×10^{-2} doping level), B-doped (10^{-5}, 10^{-4} and 10^{-3}), compensated (10^{-3}P and 10^{-3}B) samples of a-Si; the samples were also subjected to different exposures of light. A typical response is shown in the figure. It is a very fast onset of photoinduced absorption followed by a fast decay into photoinduced bleaching which then slowly recovers. From the analysis of the data we determined that the fast decay is due to electron trapping (in an impurity state or a dangling bond, depending on the doping) while the slow recovery is due to hole trapping. We determined that the trapping mechanism is dispersive starting from the shortest time we can measure (about 1 psec). Multiple trapping prevails in lightly doped samples and at high temperatures, while hopping mechanism prevails in heavily doped samples. We determined the widths of the conduction and valence band tails (e.g. in the P-doped samples shown in the figure 280 and 635K), the dispersive parameter as a function of temperature (in the above example, $\alpha = 0.18 + T/280$ for electrons, $\alpha = 0.15 + T/635$ for holes) and doping, and the ratio of electron and hole mobilities (about 50). As a result, the work has identified the different trapping processes in the range of 1 to 200 psec and determined the fundamental parameters of the relaxation processes.

The work was done on thin films deposited on a substrate. For a meaningful analysis of the experimental data it was necessary to analyze the role of interference and develop methods for making appropriate corrections.

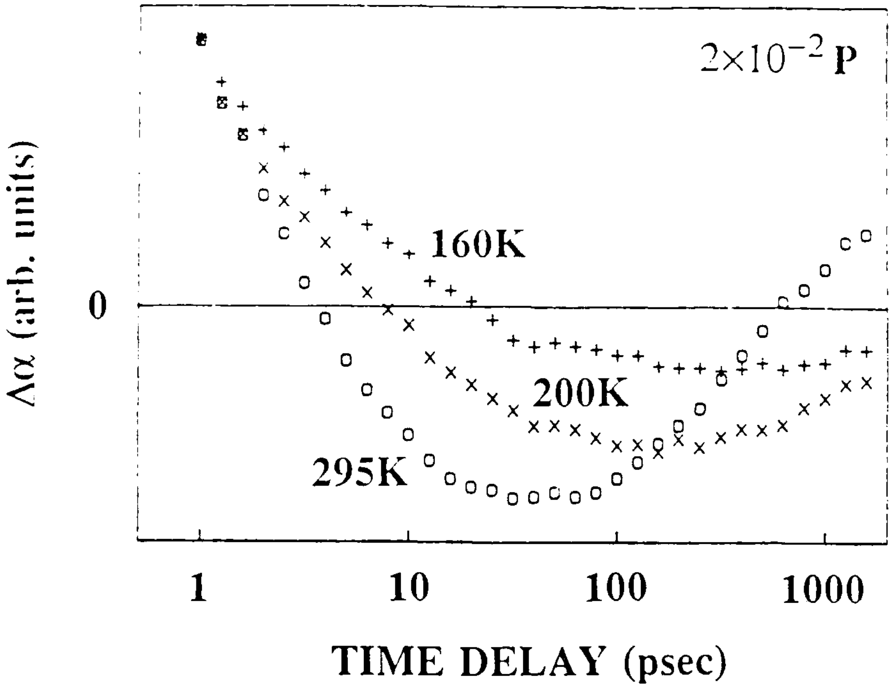

Figure 34: Photoinduced change in the absorption coefficient α in phosphorous doped a-Si:H at different temperatures.

Publications:

C. Thomsen, H. Stoddart, T. Zhou, J. Tauc and Z. Vardeny, "Photocarrier Dynamics in Compensated Amorphous Silicon," *Physical Review B*, 33, p. 4396 (1986).

C. Thomsen, Z. Vardeny and J. Tauc, "Identification of Electron and Hole Trapping Processes in Doped a-Si:H," (submitted for publication).

H. T. Grahn, C. Thomsen and J. Tauc, "Influence of Interference on Photoinduced Changes in Transmission and Reflection," *Optics Communications*, 58, p. 226 (1986).

Z. Vardeny and J. Tauc, Picosecond Photomodulation Studies of Carrier Trapping in a-Si:H, (*H. Fritzsche's Festschrift*, Plenum Press, 1987, to be published).

Z. Vardeny, C. Thomsen, H. T. Grahn and J. Tauc, "Picosecond Photomodulation Spectroscopy in Amorphous Semiconductors." *Proceedings of the SPIE Conference on Ultrafast Lasers Probe Phenomena in Bulk and Microstructure Semiconductors* (vol. 793, 1987, to be published).

Picosecond Time-of-flight Studies of Carrier Transport in Amorphous Multilayer Structures

Principal Investigators: J. Tauc, Professor, Division of Engineering and Physics Dept.
Z. Vardeny, Visiting Professor from Technion, Israel

Personnel: H. T. Grahn, Graduate Student, Physics Department

Sources of Support: NSF and MRL Optical Facility

Objectives and Approaches:

The time-of-flight technique is a powerful tool for studying carrier transport in thin amorphous semiconductor films. The standard technique is based on measuring the transient photocurrent generated by light pulse absorption; because the time resolution is limited by the RC response time of the sample and the circuit, only events occurring at times longer than 1 nsec can be studied. We have developed a purely optical method for time-of-flight measurements which has enabled us to study transport effects at times as short as 1 psec.

Research Achievements:

Our method is based on the picosecond pump and probe technique which we applied to a-Si:H/a-SiN_x:H and a-Si:H/a-SiO_x:H multilayer structures. In these structures, internal

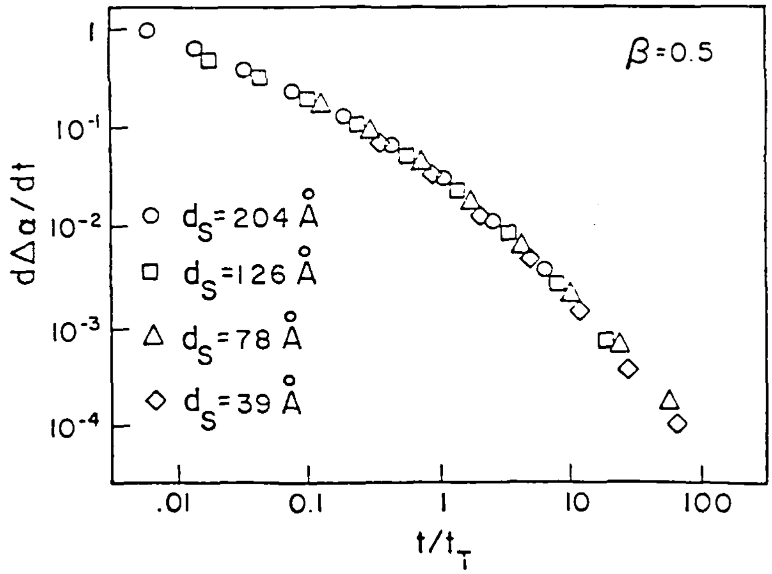

Figure 35: **An important feature of dispersive transport is "universality" shown in this figure. The derivative of the photoinduced absorption $d\Delta\alpha/dt$ is proportional to the electrical current flowing to the interfaces. This quantity, when plotted as a function of time measured in the units of average transit time t_T, has the same shape regardless of the thickness d_S of the a-Si:H layer and the intensity of the electric field in this layer.**

electric fields as high as 10^5V/cm can present due to the charge transfer from the interfaces. These electric fields produce carrier transport from the bulk of the a-Si:H film to the interfaces. The carriers trapped in the interface states have a lower optical absorption cross-section than in the bulk for transition at photon energy of 2 eV used in our experiments. Therefore as the carriers leave the bulk and get trapped at the interfaces the photoinduced absorption decreases. From the analysis of the decay curves we could determine the nature of the transport; it is dispersive starting at the shortest measured times (1 psec). We found the dispersive parameter of electrons in a-Si:H/a-SiN_x:H as a function of temperature and the average transit times from which approximate values of the average mobilities at very short times could be found using an estimate for the internal electric field.

Publications:

H. T. Grahn, "Picosecond Carrier Transport and Acoustics in a-Si:H based Multilayer Structures," Ph.D. thesis, 1987.

H. T. Grahn, Z. Vardeny and J. Tauc, "Picosecond Optical Time-of-Flight Studies of Carrier Transport in a-Si:H/a-SiN_x:H multilayers," (submitted for publication.)

Nature of Defects in Doped and Undoped a-Si:H, and Multilayer Structures Based on a-Si:H Studied by Photomodulation

Principal Investigators: J. Tauc, Professor, Division of Engineering and Physics Department
Z. Vardeny, Visiting Professor from Technion, Israel

Personnel: H. Stoddart, Graduate Student, Physics Department
T. X. Zhou, Graduate Student, Physics Department

Sources of Support: NSF and MRL Optical Facility

Objectives and Approaches:

We applied the technique of photomodulation spectroscopy, both cw and time resolved, to studying states in the gap of undoped, P and B-doped, and compensated a-Si:H, and a-Si:H/a-SiN_x:H superlattices. Our goal was to contribute to the determination of the energy levels, correlation energies and distributions of the states in the gap and at the interfaces in the multilayers. These states are of basic importance for the performance of a-Si:H in the applications.

Research Achievements:

We resolved the question of the origin of the photoinduced spectra in a-Si:H. In undoped samples, the spectra at low temperatures are due to optical transitions from the tail into the adjacent band while the high temperature spectra are due to transitions involving the dangling bonds. In doped samples, the transitions involve impurity states and charged dangling bonds. In undoped a-Si:H we found that the two dangling bond levels $D^{\pm}$ are symmetrically located about midgap with an effective correlation energy of 0.6 ± 0.2 eV. In P-doped a-Si:H D^{-} is pushed toward midgap by about 0.25 eV; the correlation energy is 0.4 ± 0.2 eV.

In a-Si:H/a-SiN$_x$:H multilayer structures with Si layer thicknesses smaller than 20Å the change of the photoinduced spectrum with respect to a-Si:H spectrum is apparently related to band tail broadening due to increased disorder. In multilayers with thicker Si layers, the changes are associated with the carriers trapped in defects at the interfaces. Because of the similarity with the photoinduced spectrum of a-Si:H:P, the interface defects are tentatively identified as charged dangling bonds.

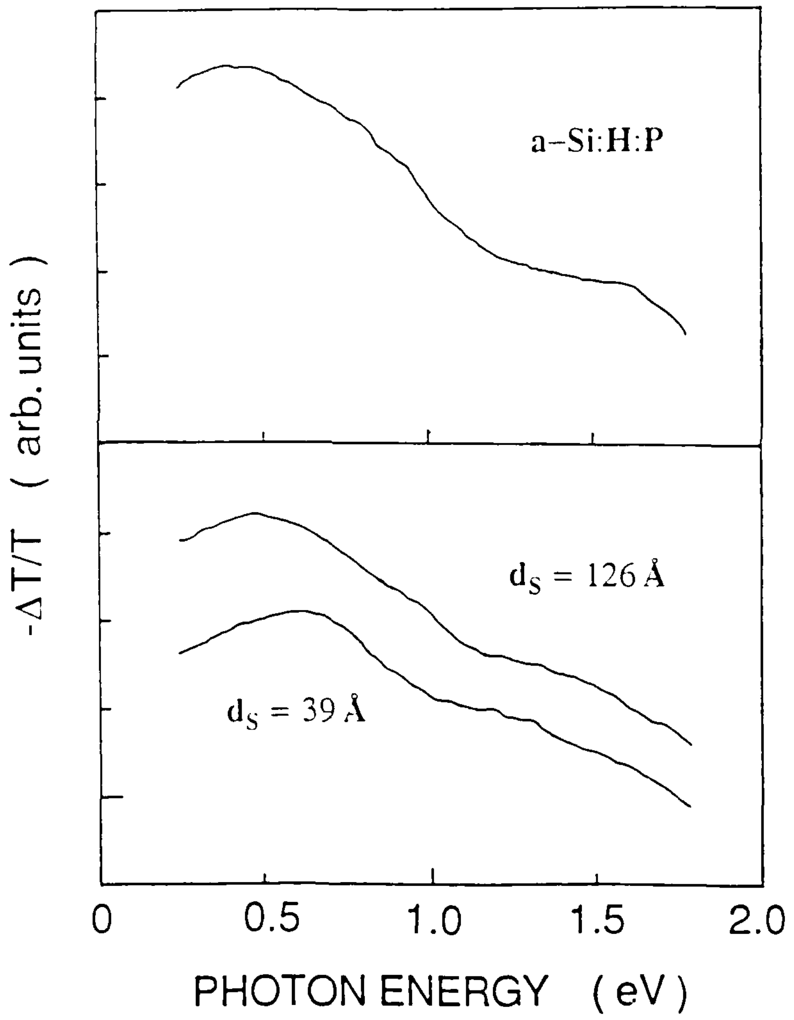

Figure 36: Photoinduced spectra (relative change in transmission) in phosphorous doped a-Si:H and two multilayer structures (d$_S$ is the thickness of Si layer).

Publications:

T. X. Zhou, Z. Vardeny and J. Tauc," States in the Gap of Doped and Undoped a-Si:H Studied by Photomodulation Spectroscopy," *Materials Research Society Proceedings* 77 (1986).

Z. Vardeny, T. X. Zhou, H. Stoddart and J. Tauc, "Photomodulation Spectroscopy of Dangling Bonds in Doped and Undoped a-Si:H," (submitted for publication).

H. T. Grahn, H. A. Stoddart, T. Zhou, Z. Vardeny, J. Tauc and B. Abeles, "Photoinduced Absorption in a-Si:H/a-SiN$_x$:H Multilayer Structures," *18th International Conference on the Physics of Semiconductors* in Stockholm 1986. *World Scientific*, p. 1037 (1987).

T. X. Zhou, H. Stoddart, Z. Vardeny, J. Tauc and B. Abeles, "Optical Modulation Spectroscopy of a-Si:H Based Superlattices," *MRS Proceedings*. 77. *(1986) Interfaces. Superlattices. Thin Films* (to be published).

T. X. Zhou, Z. Vardeny, J. Tauc and B. Abeles, "Steady State Photomodulation Spectroscopy of a-Si:H/a-SiN$_x$:H Multilayer Structures," *Physical Review B* 35, p. 7767 (1987).

Disordered Systems Theory

Principal Investigator: A. Houghton, Professor, Physics Department

Personnel: H. Won, Graduate Student, Physics Department
A. Sudbo, Graduate Student, Physics Department

Sources of Support: MRL

Objectives and Approaches:

Even the simplest disordered systems have proven very difficult to study via the conventional tools of the condensed matter experimentalist and theorist. In this research we have studied several simple systems which model different types of disorder occurring in nature.

1. The Ising model with quenched random fields:

The properties of this system realisable in the laboratory when a uniform magnetic field is applied to a site diluted by an antiferromagnet has provoked intense debate among both theorists and experimentalists. We have shown[1] how one can study critical phenomena in this system by high temperature series. The series provides evidence that the transition is fist order at high fields separated by a tricritical point from a second order transition at low fields. There is experimental evidence for this scenario.

2. The effect of local moments in both dilute and concentrated intermetallic compounds:

Functional integral methods allow a starting point for calculations in which the important hybridization effects between localized core electrons and bond electrons are taken into account: A Kondo resonance in the single impurity case[3] a renormalized band structure with heavy fermion quasi particles in the case of the lattice.[5] Correlation effects can then be taken into account perturbatively (1/N expansion). The nature of the superconducting ground state of the heavy fermion systems and the effect of spin fluctuations on this ground state can be discussed.[5]

3. High T_c superconductivity a 'gauge glass'?

Recently several experimental groups have interpreted some of their experimental results on the high T_c oxide superconductors as manifestations of granular superconductivity. We show that many of these properties can be explained if a pseudo spin model is used to describe the phase coherence between superconducting grains in particular the boundary in the B (field) T plane separating ergodic from non-ergodic behavior can be predicted in good agreement with experiment.[6]

4. Liquid crystal glasses

Molecular dynamics studies of liquids comprised of elliptical "molecules" of variable eccentricity are being undertaken. This is the first step in a program to extend the molecular dynamics of Lennard-Jones liquids to more realistic glass formers.

Publications:

[1] A. Houghton, A. Khurana and F.J. Seco, "High Temperature Series and the Random Field Ising Model," *Physical Review* B34, p. 1700 (1986).

[2] A. Houghton, S. Jain and A.P. Young, "Role of Initial Conditions in the Mean Field Theory of Spin Glass Dynamics," in "Spin Glasses: Theory and Beyond," eds. M. Mezard, G. Parisi and M.A. Virasoro, World Scientific, 1986.

[3] A. Houghton, N. Read and H. Won, "1/N Expansion for the Transport Coefficients of the Single Impurity Anderson Model," *Physical Review* B35, p. 5123 (1987).

[4] A. Houghton, A.J. McKane and H.A. Cerdeira, "The Effect of a Weak Magnetic Field," *Journal of Statistical Physics*, to be published September 1987.

[5] A. Houghton, H. Won and N. Read, "Spin Fluctuations and Superconductivity in Heavy Fermion Metals," submitted to *Physical Review Letters*, August 1987.

[6] A. Houghton and M.A. Moore, "The Superconducting Glass - Relevance to the High T_c Superconductors, submitted to *Physical Review Letters*, August 1987.

Theory of Quasicrystals, and the Formation of Liquid Crystalline Glass

Principal Investigator: R. A. Pelcovits, Associate Professor, Physics Department

Personnel: P. De, Graduate Student, Physics Department

Sources of Support: MRL, NSF, Alfred P. Sloan Foundation

Objectives and Approaches:

Our theoretical project has two objectives: to understand the elastic properties of quasicrystals, and to explore the nature and formation of the glassy phase composed of liquid crystalline molecules. Quasicrystals display quasiperiodic translational order, and long-range bond orientational order. They consist of local arrangements of atoms which can be energetically very favorable and are found to occur in computer simulations of quenched systems. We can view quasicrystals as a template for the glassy state, i.e. a phase to which the system is headed as it is quenched but is unable to reach due to kinetic constraints. Our studies involve the development of classical elasticity theory for the quasicrystalline phase.

Liquid crystalline glass is a novel glassy state in that it is optically anisotropic. It can arise by quenching a liquid crystal material. We are interested in understanding the formation and nature of this phase through two approaches: numerical simulations and a hydrodynamic theory. The simulations will involve the molecular dynamics technique and will be carried out on a supercomputer or array processor. The hydrodynamic theory will be an extension of the one developed by Das et al. for spherical molecules to molecules with uniaxial symmetry.

Research Achievements:

We have made considerable progress in our development of the elasticity theory for pentagonal quasicrystals. We have generated the general solutions to the elastic equations which minimize the free energy. These solutions have been used to calculate the strain fields due to dislocations and the interaction energy of an arbitrary distribution of dislocations. More recently, we have formulated the mathematical form of disclinations in these systems. These are topological defects which destroy the bond orientational order and could play a role in the melting of quasicrystals or quasicrystalline glass. We are currently examining the role of disclinations in the melting of pentagonal quasicrystals.

Publications:

P. De and R. A. Pelcovits, "Linear Elasticity Theory of Pentagonal Quasicrystals," *Physical Review B*, May 1987.

P. De and R. A. Pelcovits, "Disclinations in Pentagonal Quasicrystals," submitted to *Physical Review B*.

P. De and R. A. Pelcovits, "Melting of Pentagonal Quasicrystals," in preparation.

Theory of Glasses and Glassy Solids

Principal Investigator: R. M. Stratt, Associate Professor, Chemistry Department

Personnel: V. Dobrosavljevic, Graduate Student, Physics Department

Sources of Support: MR , NSF, Alfred P. Sloan Foundation

Objectives and Approaches

Two of the outstanding fundamental puzzles in the theory of glasses concern the origin of the so-called two-level-system behavior and the nature of the glass transition itself. Two level systems have been invoked to explain the observation of a pattern of low temperature heat capacity, thermal conductivity, and ultrasonic attenuation results that seems to recur in every glass (and glass-like-material) that has ever been studied. While the associated phenomenological model of tunneling centers in an amorphous setting invariably matches the data, there is, as of yet, no clue as to the origin or microscopic nature of these centers, much less an answer to specific questions such as what experimental control one has over the density of centers.

The glass transition is a far better characterized problem in a spectroscopic sense, but it, too, suffers from the lack of a microscopic underpinning. Moreover, there is no reason to expect the details of the formation of an inorganic oxide glass, say, to be analogous to the details of the vitrification of a metallic glass. Presumably there are deep similarities in the basic physics, at least at some level, but understanding the experimentally accessible mechanisms is likely to require a separate theoretical treatment for each broad category of glasses.

There have, nonetheless, been some recent experimental developments at Brown that hold a promise of allowing us to make progress on both of these fronts. Ultrasonic studies by Elbaum on the metallic glass PdSiCu indicate that the two level system density remains finite when the glass is annealed into a disordered crystal. Hence one should be able to begin an investigation of tunneling centers in the theoretically tractable setting of a crystal instead of having to start with the topological disorder present in true glasses. Simultaneously, far infrared measurements by Risen on the cation motion bands in inorganic oxide glasses strongly suggest that the glass transition in these materials bears a striking resemblance to a percolation transition. Thus, if one can formulate percolation theory in the appropriately disordered setting there is a chance of getting some insight into at least one kind of glass transition.

Research Achievements:

A possible way to pin down the identity of a tunneling system in a crystal would be to look for the signatures of different kinds of phonon coupling -- if there are any. Accordingly, we have been studying the role of phonon coupling in a number of different tunneling-mediated order-disorder phase transitions. Intriguingly, some of these phase transitions, such as those involving molecular orientation in solid D_2 and CH_4, seem to have their ordered phase at high pressure, whereas others, such as that in the hydrogen-bonded ferroelectric KH_2PO_4, are disordered by applied pressure. What we have discovered is that the distinction between those sets of transitions is understandable as simply a difference in the form of the direct phonon coupling to the tunneling entities. In particular by using newly discovered discretized path integral methods, we were able to get either kind of temperature versus pressure phase diagram just by

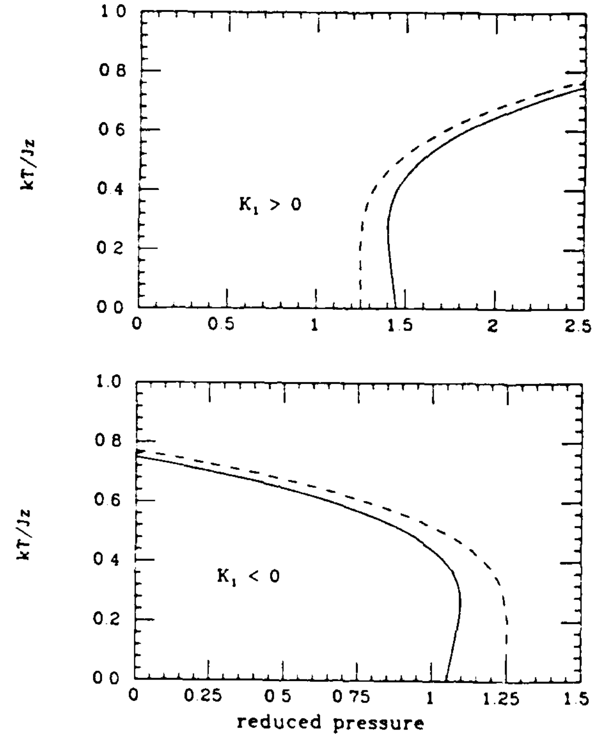

Figure 37

varying the sign of a particular phonon coupling constant. This kind of sensitivity to microscopic detail suggests that it may indeed by possible to use existing experimental techniques that probe the interaction of two level systems with phonons -- such as ultrasonic attenuation -- to get at the nature of two level systems.

By way of contrast with these lattice based calculations, the percolation studies we have been pursuing have not relied on crystalline order. We specifically decided to consider *continuum* percolation, that is, to find the critical density necessary to establish a connection throughout topologically disordered systems. Given the complexity of the problem, it was necessary to adopt a very simple model

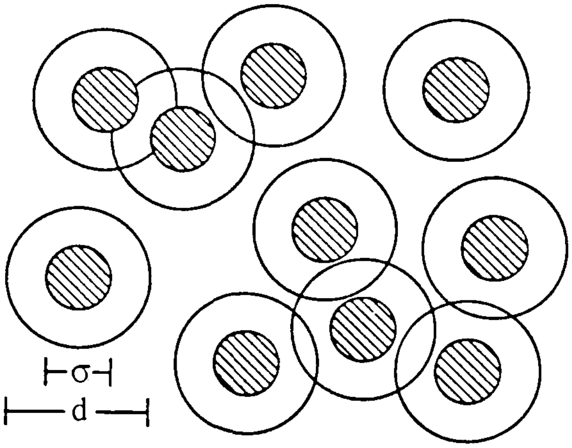

Figure 38

that of hard spheres which were considered to be connected if spheres were within a critical distance, d. However, this model not only proved to be solvable analytically within the (relatively sophisticated) Percus-Yevick approximation, but also yielded rather surprising results.

When the critical density was analyzed, the value turned out not to be a simple monotonic function of σ, the hard sphere diameter. In fact, there ended up being an optimum value of σ/d for percolation. Since what σ controls is the correlation between particle positions -- the *microscopic structure* -- this result meant that one could begin to make a correspondence between microscopic structure and percolation thresholds. We anticipate that there should be significant ramifications for any percolation based theory of the glass transition.

Publications:

R. M. Stratt, "Does Coupling to a Condensed Phase Increase or Decrease Tunneling?" *Physics Review Letters*, 55, p. 1443 (1985).
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R. M. Stratt, "Tunneling-induced Disorder in Solids," *Journal of Chemical Physics*, 84, p. 2315 (1986).

T. DeSimone, R. M. Stratt and S. Demoulini, "Continuum Percolation in an Interacting System: Exact Solution of the Percus-Yevick Equation for Connectivity in Liquids," *Physics Review Letters*, 56, p. 1140 (1986).

T. DeSimone, S. Demoulini and R. M. Stratt, "A Theory of Percolation in Liquids," *Journal of Chemical Physics*, 85, p. 391 (1986).

V. Dobrosavljevic and R. M. Stratt, "The Role of Conformational Disorder in Conjugated Polymers: Substituted Polydiacetylenes," *Physics Review B*, 35, p. 2781 (1987).

Metallic Glasses Formed by Solid State Amorphization

Principal Investigator: C. Elbaum, Professor, Physics Department and Division of Applied Mathematics

Personnel: A. Hikata, Professor (Research), Division of Applied Mathematics
M. J. McKenna, Graduate Student, Physics Department

Sources of Support: MRL

Objectives and Approaches:

The full understanding of glass formation processes in general, and of recently discovered solid state amorphization of crystalline materials in particular, continues to pose a major challenge. In the case of glass formation by supercooling a liquid, the disorder is linked to the occurrence of various random atomic arrangements, or in fact, various forms of short range order, usually thought of as being inherited, or quenched-in configurations of the liquid. Their occurrence as a result of a solid state reaction starting from crystalline solids, on the other hand, is less obvious, and thus bears further study. Moreover, it remains to be shown whether the structural characteristics of the two types of glasses (i.e., quenched from the liquid and formed from solids) are the same, even though their x-ray or electron scattering patterns are indistinguishable. One approach that offers the possibility of detecting such distinctions is the use of ultrasonic propagation methods. We have undertaken, therefore, such a study on metallic glasses formed by mechanical alloying, using ultrasonic velocity measurements at low temperatures as a probe of the two level tunneling systems (TLS) density. We note that the TLS model accounts well for the observed "anomalous" temperature dependence, at low temperatures ($T \leq 1$ K), of the ultrasonic velocity change, $\Delta v/v$, in amorphous and disordered materials. This dependence consists of a linear increase of $\Delta v/v$ *with* ℓnT *at low temperatures, followed by a maximum and a rapid* decrease as the temperature rises further. The slope of the logarithmic temperature dependence of $\Delta v/v$ yields the density of TLS.

(Mechanical alloying is a process in which constituent powder particles are repeatedly fragmented aned cold welded by the continuous impacting action of a milling medium. Eventually, composite powder particles, whose composition corresponds approximately to the percentages of the respective constituents in the original charges, are formed. For certain compositions it is possible, using this technique, to form amorphous alloys, starting from crystalline particles).

Research Achievements:

For our preliminary mechanical alloying experiments, we chose the $Co_{40}Sn_{60}$ system. We carried out two experiments; in one case, the constituent powders were simply mixed and compacted. This sample did not show any detectable ℓnT dependence of sound velocity at low temperatures, thus indicating the absence of TLS that are characteristic of amorphous or highly disordered solids. In the other case, the powders were mixed, mechanically alloyed for 12 hours and compacted. This latter sample showed distinctive ℓnT dependence of $\Delta v/v$ below ≈ 1 K, as can be seen in Figure 39. This is the behavior associated with TLS found in amorphous solids. X-ray diffraction patterns obtained on the powders after simple mixing and following 12 hours of mechanical alloying, are shown in Figure 40. This pattern indicates amorphization of the mechanically alloyed sample, thus corroborating the results of the sound velocity measurements.

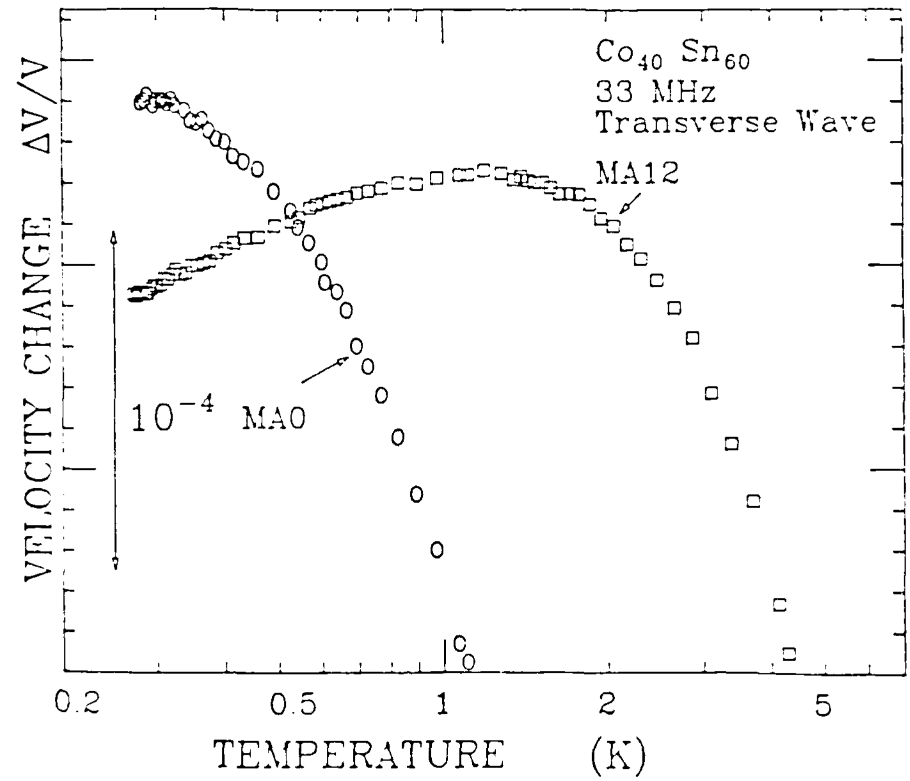

Figure 39. Ultrasonic velocity change as a function of temperature for $Co_{40}Sn_{60}$ samples. The vertical positioning of the curves is arbitrary. Sample MAO was prepared by compacting the constituent powders after simple mixing; thus, no mechanical alloying is involved. Sample MA12 was prepared by compacting the powders after 12 hours of mechanical alloying.

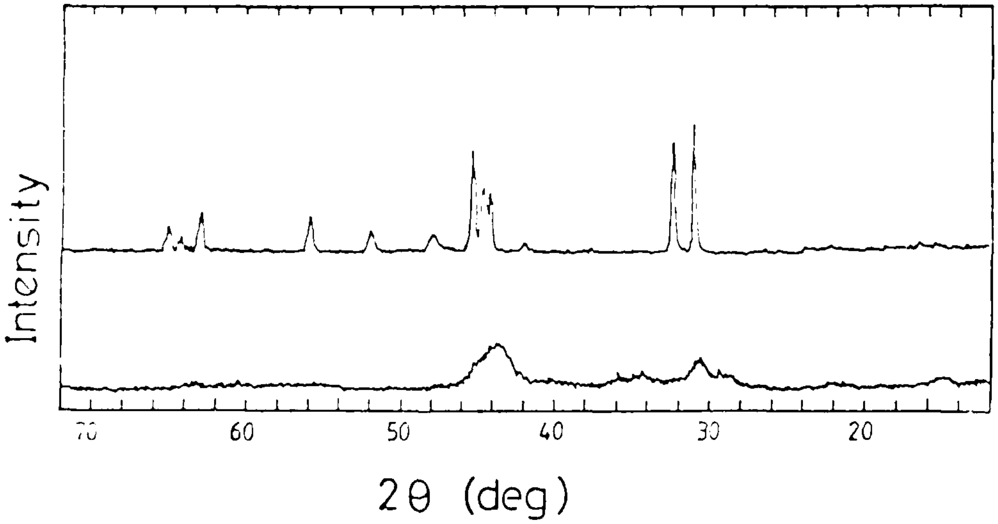

Figure 40: Comparison of x-ray diffraction patterns (before compaction) of mixed powders of $Co_{40}Sn_{60}$ (top) and of the same powder after 12 hours of mechanical alloying (bottom).

AD-A188 006 ANNUAL TECHNICAL REPORT OF THE MATERIALS RESEARCH LABORATORY AT BROWN UNI (U) BROWN UNIV PROVIDENCE RI MATERIALS RESEARCH LAB 30 APR 87 NSF-DMR83-16893 2/2

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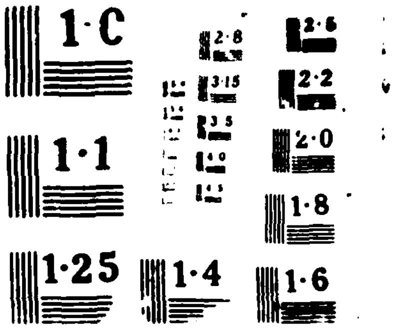

1·0
2·8
2·5
3·15
2·2
3·5
2·0
4·0
1·1
1·8
1·25
1·4
1·6

Publications:

A. Hikata, M.J. McKenna and C. Elbaum, "Ultrasonic Study of Mechanically Alloyed $Co_{40}Sn_{60}$," *Applied Physics Letters*, 50, p. 478 (1987).

Glassy Disorder in Sintered Ceramics

Principal Investigator: C. Elbaum, Professor, Physics Department

Personnel: A. Hikata, Professor (Research) Division of Applied Mathematics
M. J. McKenna, Graduate Student, Physics Department

Sources of Support:

Objectives and Approaches:

Sintered ceramics, such as silicon carbide (SiC), are regarded as promising candidates for the heat resistant materials of the next generation because of their excellent chemical and mechanical stability at elevated temperatures. This stability, on the other hand, makes it difficult to sinter these materials in the pure state, and various additives are used to promote the sintering processes. Sintered ceramics, therefore, have a composite structure consisting of ceramic matrices and possibly distinct grain boundary phases, where the additives are likely to segregate. While it has been suggested that these grain boundary phases are usually amorphous, and transmission electron microscopy studies have occasionally found results supporting this view, the evidence is not systematic. Structural disorder generated during the preparation of sintered ceramics is being studied and correlated with the resulting properties of these materials, such as mechanical relaxation at high temperatures and thermal conductivity as a function of temperature. Our earlier results, obtained by ultrasonic propagation studies at low temperatures, indicate the presence in many sintered ceramics of features commonly observed in amorphous and highly disordered materials, i.e. two level tunneling systems (TLS). The occurrence of TLS is found to be related to the type of binding substance used in the sintering process. Furthermore, a correlation appears to exist in these materials between the density of TLS and mechanical relaxation processes at high temperatures as well as with thermal resistivity at room temperature.

Research Achievements:

As a continuation of our work in this area we further investigated the effect of the amount of additives on TLS. For this we chose AℓN as additives. Three SiC samples prepared by nominally identical methods, except for the concentration of AℓN additives, were examined. It was found that the density of states of TLS increased almost linearly with the AℓN concentration in the range from 1 wt%. In order to check the possibility that AℓN itself contains TLS, a sintered AℓN sample was also investigated. It was found that in this case there was no $\ell n T$ dependence of $\Delta v/v$ and therefore no detectable TLS exist in this sample. We also studied sample of Si_3N_4 with different additives and different sintering processes (hot press sintering, pressureless sintering, and reaction sintering). Portions of these samples were also tested independently by Japanese investigators at elevated temperatures, using 5 MHz ultrasonic waves. The results suggest the existence of a correlation between the onset of the relaxation peak in ultrasonic attenuation observed in the high tempeature experiments and the nM^2 observed in the low temperature velocity measurement experiments carried out in our laboratory; the larger the nM^2 is, the lower the peak onset temperature.

Publications:

A. Hikata, M.J. McKenna, C. Elbaum, Y. Takeda and K. Maeda, "Ultrasonic Study of Silicon Carbide at Low temperatures," *Journal de Physique*. C1-629 (1986).

A. Hikata, M.J. McKenna, C. Elbaum, Y. Takeda and K. Maeda, "Ultrasonic Velocity Changes in SiC and AlN at Low Temperatures," *Materials Research Bulletin*. 22, p. 557 (1987).

Glassy Response of Lubricants at High Pressures and High Shearing Rates

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

Personnel: K. T. Ramesh, Graduate Student, Division of Engineering

Sources of Support: NSF and MRL

Objectives and Approaches:

In elastohydrodynamic (EHD) lubrication a thin layer of lubricant is compressed and sheared in the contact region between two heavily loaded moving parts. The pressures (several GPa) and shear rates ($10^5 s^{-1}$) are so severe that it has proved difficult to obtain definitive data on the rheology of the lubricant under the conditions that occur in the contact region. This difficulty has been overcome by introducing a new plate impact configuration for subjecting lubricants to simple shearing motion under uniform hydrostatic pressure. Thin layers (50μm thick) of the lubricant are confined between two hard metallic plates which are subjected to impact by a parallel plate that is inclined relative to the direction of approach in order to induce pressure-shear loading. Except for the special provisions necessary for confining the lubricant, the experiments are conducted in the same way as the pressure-shear experiments used to study the plastic response of metals at high strain rates.

Research Achievements:

The dependence of the shearing resistance on pressure has been measured for two lubricants (5P4E and Santotrac 50) at shear rates of approximately $10^6 s^{-1}$. The range of pressures in these experiments is from approximately 1 to 5 GPa. For these pressures the lubricants are in their glassy response regimes. The shearing resistance is characterized by a rate-insensitive limiting shear stress that increases proportionally with increasing pressure at pressures up to 2-3 GPa and less than proportionally at higher pressures. Mechanism-based constitutive models for describing the observed response are being investigated.

Publications:

K. T. Ramesh and R. J. Clifton, "A Pressure-Shear Impact Experiment for Studying the Rheology of Lubricants at High Pressures and High Shearing Rates," *Journal of Tribology*. 109, pp. 215-222 (1987).

SECTION 3

SURFACES AND INTERFACES

Introduction

The research program at Brown in the area of solid surfaces and interfaces has as its primary objective the development of a microscopic understanding of the dynamics of interface processes. To this end, studies are made of static properties such as the composition, atomic geometry, electronic structure and molecular bonding at the surface, which serve as basis for investigations of dynamic phenomena such as surface excitations by photons, electrons or atoms, surface diffusion, adsorption and desorption.

Progress made towards these objectives is described in the following section. The principal investigators who have participated in the MRL program during the period covered by this report are G. J. Diebold, C. Elbaum, P. J. Estrup, E. F. Greene, J. M. Kosterlitz, P. J. Stiles and S. C. Ying. Specific projects are listed under individual investigators but they are frequently part of an effort involving two or more members of the thrust. Collaborations fostered by MRL have made it possible to combine different experimental approaches and to obtain a close relationship between theory and experiment in many cases. As an example, Estrup, Kosterlitz and Ying have carried out a joint study of surface phase transitions on the H/Mo(110) and H/W(110) surfaces. The nature of the two-dimensional phases and the possibility of surface reconstruction were investigated experimentally by LEED, photoemission, EELS, and adsorption isobars. A mean field analysis, followed by extensive Monte Carlo simulations, showed for the first time that the observations can be explained by a lattice gas model on a deformable substrate, thus modifying the standard treatment of the chemisorbed layer in a fundamental way.

The importance of the development and refinement of surface techniques is reflected in several projects. Greene has significantly improved a method for the study of charge and energy transfer in collisions of atoms and ions with a surface. Diebold has completed preliminary studies of laser detection of the velocity distribution of atoms scattered from a surface. Stiles has further developed the "floating gate" technique by means of which changes in the electrochemical potential of an interface can be investigated. Finally, Elbaum has used the reflection of ultrasonic waves to study the dynamics of crystal growth at a helium solid-liquid interface.

P. J. Estrup, Coordinator

The Scattering and Ionization of Atoms at Surfaces

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

Personnel:
D. K. Stewart, Graduate Student, Chemistry Department
T. Tao, Graduate Student, Chemistry Department
J. S. Ha, Graduate Student, Chemistry Department
Y. Bu, Graduate Student, Chemistry Department
N. Thantu, Graduate Student, Physics Department
P. Williams, Undergraduate Student, Physics Department

Sources of Support: DOE and MRL

Objectives and Approaches:

Much can be learned about the interaction of atoms and molecules with surfaces from measurements of the yields of ions produced and the energy transferred when molecular beams strike surfaces. The interpretation of the results becomes more straightforward and revealing when the energy of the beam can be varied from a few meV to several eV. Atoms having energies at the lower end of this range are produced by being seeded into jet beams of carrier gas followed by selection from the jet of just those molecules having the small range of speeds desired. Faster atoms are made by accelerating ions and then neutralizing them by charge exchange with a stationary gas. The objectives of the work are: to find the rate of electron transfer between an atom and a surface as this varies with their distance of separation; to learn the extent to which atoms are trapped near the surface and the rate at which these trapped atoms diffuse across the surface; and to study energy transfer between the atoms and surfaces.

Research Achievements:

The results from two recent experiments illustrate some of the possibilities. Measurements of the energy dependence of the yields of Na^+ ions formed when beams of Na atoms hit a Si(111) surface at a temperature T are those expected for equilibrium for kinetic energies E of the incident atoms lower than about 1.5 eV. Above this threshold energy E_{th} the yields are nearly independent of T. They rise abruptly to a maximum of about 0.6 at $E=3$ eV and then decrease slowly to ca. 0.3 at $E=30$ eV. Interpretation of the results suggests that for $E<E_{th}$ the atoms ionize by transferring an electron to the surface at a distance of about 4Å. The ions are then trapped near the surface by Coulombic attraction to their image charges in the surface. These ions equilibrate with the surface from which only that small fraction with sufficient thermal energy to escape leave to be collected. The yield of ions begins to rise steeply for $E>E_{th}$ because then the ions rebound with enough energy to escape directly from the Coulombic barrier. According to a simple model, the faster the rate of rise of the yield above E_{th} the more nearly elastic is the collision with the surface, and the value of E_{th} gives a measure of the distance at which the original ionization occurs.

In the other experiment a molecular beam of variable energy impinges on the surface of a thermocouple. The temperature rise recorded by the thermocouple varies with the angle from the axis of the beam thus providing a beam profile. In addition, the magnitude of the rise measures the energy transferred from the molecules to the surface.

Publications:

A. D. LeGrand and E. F. Greene, "The Nearly Elastic Scattering of Ne and Ar from LiF(100)," *Journal of Chemical Physics*, 84, p. 6483 (1986).

K. G. Glogovsky and E. F. Greene, "The Effect of a Beam of Electrons on a Beam of Alkali Halide Molecules Effusing from a Source," *Journal of Chemical Physics*, 85, p. 199, (1986).

P. J. Estrup, E. F. Greene, M. J. Cardillo and J. C. Tully, "Influence of Surface Phase Transitions on Desorption Kinetics: the Compensation Effect," *Journal of Physical Chemistry*, 90, p. 4099 (1986).

Laser Probe of Surface Scattering

Principal Investigator: G. J. Diebold, Associate Professor, Chemistry Department

Personnel: P. R. Muessig, Graduate Student, Chemistry Department
C. E. Shannon, Graduate Student, Physics Department

Source of Support: MRL

Objectives and Approaches:

This research has focussed on three objectives, laser detection of the velocity distribution of atoms scattered from crystal surfaces, study of the probability for internal energy relaxation of optically pumped atoms (i.e., atoms with non-Boltzmann hyperfine state population distributions), and a theoretical study of the use of laser induced fluorescence for determining state multipoles of the atomic angular momentum in scattering experiments. We have constructed a new ultra high vacuum apparatus for scattering atomic Na from crystal surfaces. The high resolution of a continuous dye laser is being used to determine the Doppler shifts on scattered atoms with laser induced fluorescence detection. The distribution of Doppler shifts can then be converted to a velocity distribution. The velocity distribution of scattered atoms has been the subject of theoretical research for a number of years. We seek to measure the distribution of Na atoms for comparison with theory. In the optical pumping experiments we measure the probability for equilibration of the non-Boltzman population distribution produced by optical pumping. The subject of quenching probabilities has not been investigated extensively. We seek to determine the temperature dependence of the quenching probability and the effect of different surfaces on the rate.

Research Achievements:

We have made progress in construction and operation of the new scattering apparatus. Atomic beams of Na have been produced and Doppler shifted velocity distributions measured. Much theoretical work has been done to determine what can be learned in a laser induced fluorescence experiment. That is, the incident pumping beam produces non-equilibrium population distributions in the atomic ground state. This is described in terms of a hyperfine state disequilibrium and a disequilibrium between the magnetic sublevels of each state. The latter can be described in terms of statistical tensors (state multipoles). Each multipole relaxes independently in surface scattering. The question we have addressed is how many tensor components can be measured in a laser induced fluorescence experiment In general, several incident light beams and detection geometrics are required, each with a definite laser polarization and detector polarization. We have focussed in our experiments on measuring the monopole and quadrupole terms. The theory gives a complete analysis of the geometries and experiments necessary to determine the relaxation of the various state multipoles

Publications:

P. R. Muessig and G. J. Diebold, "Optical Determination of Atomic State Multipoles in surface Scattering Experiments," (in preparation)

Chemisorption on Metal Surfaces

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

Personnel:
J. A. Prybyla, Graduate Student, Chemistry Department
J. Meyer, Graduate Student, Physics Department
M. Altman, Graduate Student, Physics Department
M. Hildner, Graduate Student, Physics Department

Sources of Support: NSF and NSF/MRL

Objectives and Approaches:

The main objective of this research is to establish improved microscopic models of surface interactions, particularly those that govern chemisorption phenomena, i.e. adsorbate-substrate forces and adsorbate-adsorbate forces. A major part of the research is focussed on the effects of substrate changes on properties of the adsorbate or, more generally, the participation of the substrate degrees of freedom in adsorption processes. Such effects may be ubiquitous but they are especially large when the surface undergoes reconstruction. In order to study them, the occurrence and origin of reconstruction on metal surfaces are explored experimentally. This is done by determining the surface structure as a function of temperature and coverage by means of low energy electron diffraction (LEED) and, recently, by glancing incidence X-ray diffraction. Additional characterization of the surface phases is carried out by reflection infrared absorption spectroscopy and by electron energy loss spectroscopy.

In other experiments, done in parallel with the structural studies, the kinetics of adsorption, dissociation and desorption on these substrates is investigated and the results correlated with the data on the surface geometry. The techniques used in this work include photoelectron spectroscopy and work function measurements, as well as mass-spectroscopy for temperature programmed desorption and measurements of adsorption isobars.

Research Achievements

Surface structural studies have been done for a series of adsorbate substrate combinations, consisting of hydrogen or oxygen on molybdenum or tungsten surfaces having (100), (110) or (211) orientation. In collaboration with Ying, the effects of adsorbates on the W(100) surface reconstruction have been explored both experimentally and theoretically, and the importance of the adsorbate site geometry for the stabilization of the reconstruction has been demonstrated. The phase diagrams of H/W(110) and H/Mo(110) have been obtained. They show interesting differences and in a collaboration with Ying and Kosterlitz it has been concluded that the most likely reason is a coupling between the substrate reconstruction and the adsorbate ordering which occurs on H/W(110) but not on H/Mo(110). LEED studies of the H/Mo(100) surface have been continued and have been complemented by infra-red measurements for each of the many phases formed by this system. The results show that the adatom-adatom interactions are attractive at low coverage, that Mo(100) reconstruction occurs at low but not at high coverage, and that many of the 2D phase transitions are first order in this system. The highly complex kinetics of the H/Mo(100) system observed in measurements of the electron stimulated disorption of H, the work function variation, the sticking probability and the desorption rate (see Fig. 41), can be explained by the adsorbate-induced reconstructed phases. As in the case of W(100), the desorption kinetics for H/Mo(100) exhibit a pronounced compensation effect: the preexponential factor A and the activation energy, E, in the Arrhenius expression for the rate constant, simultaneously decrease as the reconstruction disappears at higher hydrogen coverage. In a collaboration with Greene, a general explanation for the compensation effect has been given on the basis of an equilibrium model in which the rate constant is related to the free energy of the system which must be continuous across a phase boundary.

Publications:

J.W. Erickson and P.J. Estrup, "The Dissociation of CO on Modified Mo(110) Surfaces," *Surface Science*, 167, 519 (1986). NSF/MRL

L.D. Roelofs, J.W. Chung, S-C. Ying and P.J. Estrup, "Effects of Adsorbate Binding Site on Surface Reconstruction Phase Diagrams: O/W(100) and H/W(100)," *Physical Review* B 33, 6537 (1986). NSF

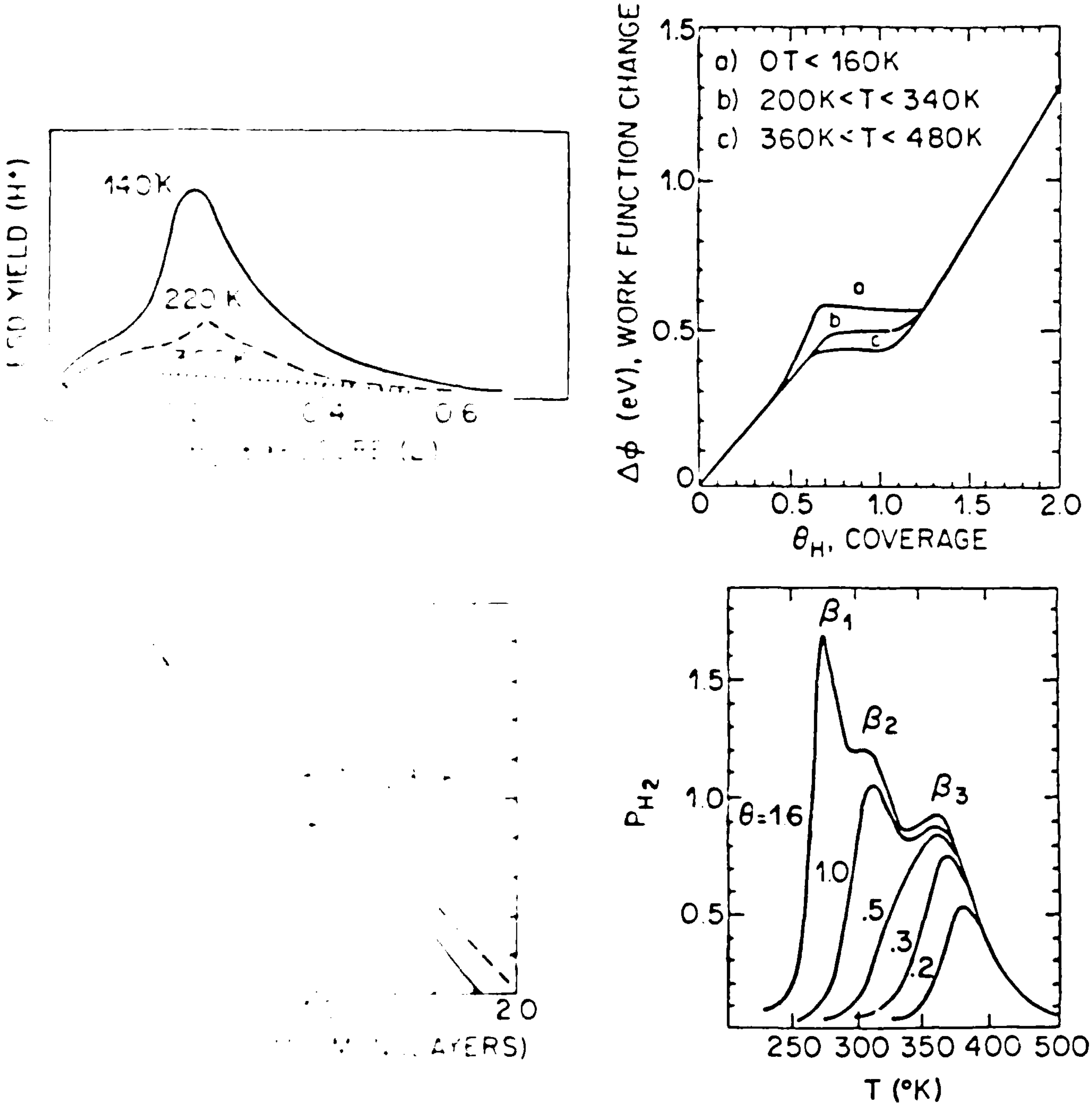
P.J. Estrup, E.F. Greene, M.J. Cardillo and J.C. Tully, "Influence of Surface Phase Transitions on Desorption Kinetics: The Compensation Effect," *Journal of Physical Chemistry* 90, 4099 (1986). NSF/MRL

J.W. Chung, S-C. Ying and P.J. Estrup, "Reconstruction of the W(110) Surface Induced by Hydrogen Adsorption," *Physical Review Letters* 56, 749 (1986). NSF and NSF/MRL

M. Altman, J.W. Chung, P.J. Estrup, J.M. Kosterlitz, J.A. Prybyla, D. Sahu and S-C. Ying, "Phase Transformations of the H/W(110) and H/Mo(110) Surfaces," *Journal of Vacuum Science Technology* A5 1045 (1987). NSF/MRL and NSF

J.A. Prybyla, P.J. Estrup, S-C. Ying, Y. Chabal and S.B. Christman, "Reconstructive Phase Transitions and Effective Adsorbate-Adsorbate Interactions: H/Mo(100) and H/W(100)," *Physical Review Letters* 58, 1877 (1987). NSF and NSF/MRL

J.A. Prybyla, P.J. Estrup and Y.J. Chabal, "Reconstruction, Adsorbate Bonding and Desorption Kinetics of H/Mo(100)," *Journal of Vacuum Science Technology* A5, 791 (1987). NSF and NSF/MRL.



[illegible] Experimental results for the adsorption of hydrogen on molybdenum [illegible] highly complex behavior due to substrate reconstruction. Coverage and temperature dependence for a) electron stimulated desorption, b) work function change, and c) sticking probability. The last panel shows the temperature programmed desorption of H_2.

Theoretical Studies of Kinetic Process on Solid Surfaces

Principal [illegible] Physics Department

Per[illegible] Physics Department
[illegible] Physics Department
[illegible] Physics Department

S[illegible]

Ob[illegible]

The [illegible] at a microscopic understanding of the kinetic processes [illegible] an understanding of the surface dynamics and the exchange [illegible] the adatom and the vibrational excitations of the substrate. [illegible] and their detailed temperature variations can serve a[illegible] for higher coverage or more complicated situations [illegible] complementary to the numerical simulation studies [illegible] two parallel directions. The first is to develop a general theoretical approach [illegible] the kinetic process on surfaces. The second is to study the surface vibrational properties of specific systems and then use the vibrational quantities as an input in the general theoretical approach. In this way we can have an evaluation of the validity of the general theoretical results for the kinetic coefficients as well as determining which results are system specific and which results have wide ranging applications for all adsorption systems.

Research Achievements

We have made a detailed study of the lattice dynamics of the (2×1) dimer reconstructed Si(100) surface and C(2×2) W(100) surface as an example of realistic reconstructed semiconductor and metal surfaces. Aside from their importance in studying adatom kinetic processes, the surface vibrational excitations and correlation functions are also of intrinsic interest. For example, the surface excitations depend sensitively on the surface geometry and hence provide an additional valuable piece of information in the determination of surface structure.

The vibrational correlation functions enter in the determination of a number of important quantities for kinetic processes. For example, it determines the modification of diffusion barriers due to substrate relaxation. The substrate relaxation also modifies the adatom-adatom interaction. The order of magnitude of this elastic mediated interaction is as large as an electronic mediated one and could be of crucial importance in determining the initial stages of diffusion and nucleation.

As the temperature or adatom coverage is varied, a surface can undergo transition from one structure to another. By now it is known that most semiconductor surfaces and a large number of metallic surfaces undergo structural transition. The surface reconstruction is intimately related to growth and kinetic processes. It has been found that epitaxial growth of Si and Ge on Si surfaces depends crucially on the reconstructed ordered surface structure. Also, near a displacive reconstruction phase transition, there are large vibrational fluctuations leading to possible anomalies in the rate processes. Therefore another important part of our program is to understand the surface reconstruction on various metal and semiconductor surfaces. We have developed theories to explain the reconstruction of C/Ni(100), H/W(100), H/W(110) and H/Mo(110).

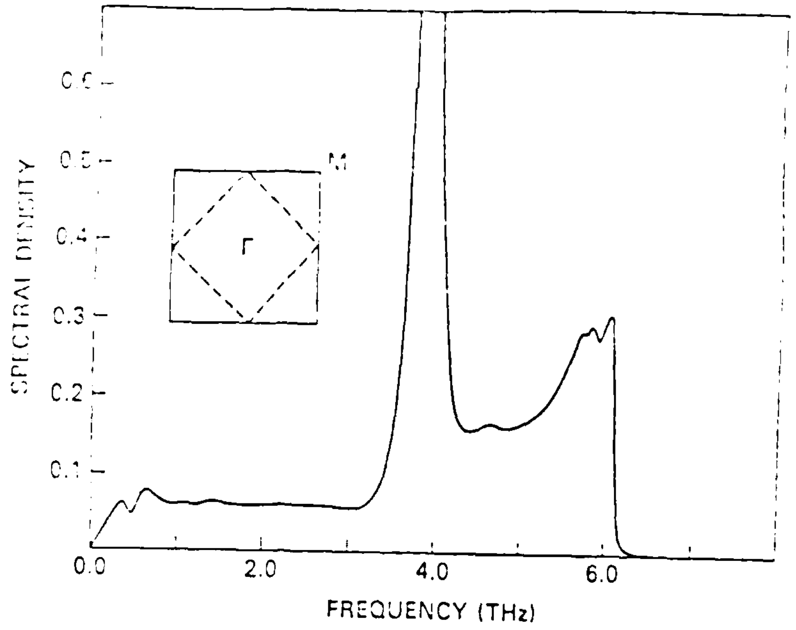


Figure 42(a) Spectral density vs. frequency for the reconstructed W(100) surface for vibration perpendicular to the surface ρ_{xx}. Insert shows the surface Brillouin zone of the unreconstructed surface (solid lines).

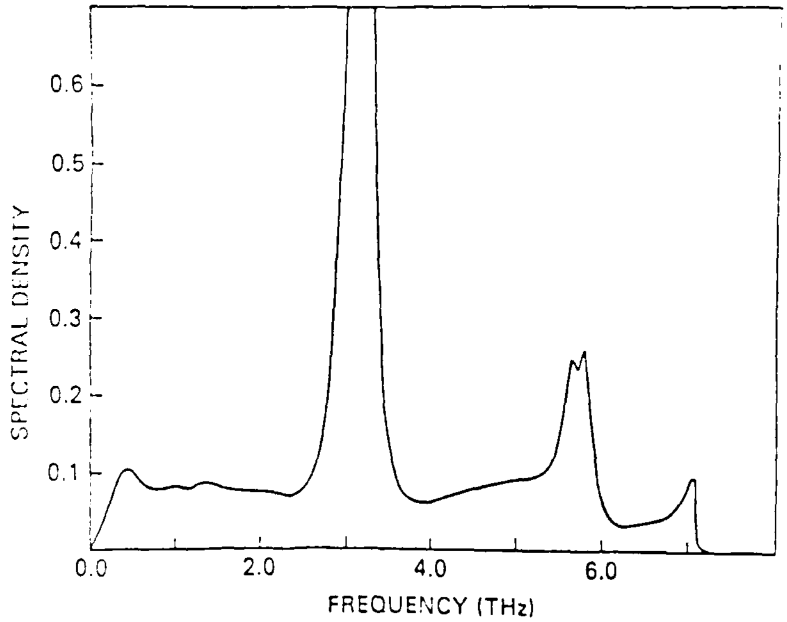


Figure 42(b) Spectral density vs. frequency for vibration parallel to the surface ρ_{yy}.

Publications:

S-C. Ying, "Soft Phonon of Ni(100) Surface," Proceedings of Fourth International Conference on Vibrational Properties of Surfaces," eds. King, Richardson and Holloway (Elsevier, 1986).

T.L. Reinecke and S-C. Ying, "Vibrational Properties of the ($\sqrt{2} \times \sqrt{2}$) R45° W(100) Surface," Proceedings of Fourth International Conference on Vibrational Properties of Surfaces," eds. King, Richardson and Holloway (Elsevier, 1986).

S. Tiersten, S-C. Ying and T.L. Reinecke, "The Vibrational Properties of the Si(100) (2×1) Surface," *Physical Review B* 33, p. 4062 (1986).

J.W. Chung, S-C. Ying and P.J. Estrup, "Reconstruction of the W(110) Surface Induced by Hydrogen Adsorption," *Physical Review Letters*, 56, p. 749 (1986).

S-C. Ying, "Adsorbate-Induced Reconstruction of Ni(100) Surface," *Physical Review Letters*, 56, p. 536 (1986).

L. Roelofs, S-C. Ying, P.J. Estrup and J.W. Chung, "Effect of Adsorbate Binding Sites on Surface Reconstruction Phase Diagrams: O W(001) and H W(001)," *Physical Review B*, 33, 6537 (1986).

A. Steif, S. Tiersten and S-C. Ying, "Vibrational Correlation Function for Si and Gi," *Physical Review B*, 355, p. 857 (1987).

T.L. Reinecke and S-C. Ying, "Vibrational Properties of the Reconstructed W(100) Surface," *Physical Review Letters*, 58, p. 242 (1987).

G.Y. Hu and S-C. Ying, "Monte-Carlo and Coarse Graining Renormalization Studies for the X-Y Model with Cubic Anisotropy," *Physica*, 140A, p. 585 (1987).

J. Prybyla, P.J. Estrup, S-C. Ying, Y. Chabal and S.B. Christman, "Reconstructive Phase Transitions and Effective Adsorbate-Adsorbate Interactions: H/Mo(100) and H/W(100)," *Physical Review Letters*, 58, p. 1877 (1987).

Transitions at Surfaces and Growth of Interfaces

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

Personnel: J-M. Kim Graduate Student, Physics Department
D. Sahu, Research Assistant, Physics Department

Sources of Support: MRL, NSF

Objectives and Approaches:

Growth of Interfaces:

The objective was to study driven growth at low temperatures by, for example. ballistic aggregation of particles on the surface. A simply dynamical model of growth was used

$$\frac{\partial h}{\partial t} = \eta \nabla^2 h - A \sin 2\pi h + \lambda (\nabla h)^2 + \mu(t) + \eta(t)$$

where $h(\vec{r},t)$ is the local height of the interface assuming no overhangs. $\mu(t)$ is the driving force and $\eta(t)$ is a random variable measuring the deviations from a uniform deposition rate. The methods used are numerical and mapping onto a simple dynamical map in certain limits of interest.

Transitions at Surfaces:

The systems of interest are chemisorbed H/W(110) and H/Mo(110). These are modeled by a lattice gas on a deformable substrate and studied by analytic methods (mean field theory and renormalization group) and by Monte Carlo. The objective is to understand the experimental observations and why the two systems behave so differently.

Research Achievements:

Growth of Interfaces:

This work is still in progress but some preliminary results have been obtained. The temperature range of interest is far below the roughening temperature so one assumes $A >> 1$ so that the local heights are integers. Under these circumstances, growth takes place when $M > A$ so we are far from equilibrium. In the special case where $\mu(t)$ is a periodic function of time, this model can be mapped into

$$h_i(n+1) - h_i(n) = \text{nint}[\nu(h_{i+1}(n) + h_{i=1}(n) - 2h_i(n)) + \lambda(h_{i+1} - h_i)^2 + \eta_i(n)]^2$$

where now the $h_i(n)$ are integers. We have shown that the interface grows but remains flat provided the noise (measured by $\eta_i(n)$) is below a critical value and the surface becomes less well organized as the noise increases. In fact, for intermediate noise levels the distribution of cluster sizes, a cluster being defined as a connected region of flat surface, is a fractal up to a certain length scale and above this the density of large clusters decays rapidly (probably exponentially). This is of interest in studying the distribution of steps during growth. We are in the process of carrying out more extensive simulations and analysis of the data.

Transitions at Surfaces

In the H/W(110) and H/Mo(110) systems a model was developed to account for the loss of mirror plane symmetry observed by LEED, photoemission and EELS. This is interpreted as a uniform shift of the top layer of W atoms without change of structure. The model developed to describe this is a lattice gas model on a deformable substrate. The mean field analysis accounted rather well for the observed features on the two systems. On H/Mo(110) the sequence disorder → (2×2) → order → disorder was observed whereas in H/W(110) a shift of the substrate was observed at both high and low temperatures. At fixed T, the sequence disorder → (2×1) → (2×2) → shift → disorder + shift was seen. The details of the phase diagram and the orders of the transitions were elucidated by extensive Monte Carlo simulations for both systems and good agreement with experiment found. Further work on other possible phase diagrams with different values of lattice gas parameters is in progress.

Publications:

D. Sahu, S. C. Ying and J. M. Kosterlitz, "Theory of Phase Transitions on H/W(110) and H/Mo(110)," to be published.

M. Altman, J.W. Chung, P.J. Estrup, J.M. Kosterlitz, J.A. Prybyla, D. Sahu and S.C. Ying, "Phase Tranformations of the H/W(110) and H/Mo(110) Surfaces," *Journal of Vacuum Science and Technology* A5, 1045 (1987).

Probes of Surface Modification by Interface Studies

Principal Investigator: P. J. Stiles, Professor, Physics Department

Personnel:
- A. Dabiran, Graduate Student Physics Department
- H. Fang, Graduate Student Physics Department
- J. Luo, Graduate Student Physics Department
- D. Popovic, Graduate Student Physics Department
- E. E. Crisman, Senior Research Engineer
- R. Zeller, Senior Research Engineer

Sources of Support: MRL, NSF, ONR, ARO, MRL Facilities

Objectives and Approaches:

The aim of the research is to understand the electronic properties of interfaces, i.e. at terminations of bulk materials. Of particular interest is the modification of electronic properties due to the preparation of the interface. The long term approach has been to study not only the electronic properties at the interface of a MOSFET structure as in the well known Si MOS transistor, but to look for ways that other semiconductors can be prepared with the same beneficial effect on properties, as well as looking for the modification due to a single atom on a clean surface.

Research Achievements:

The approach of using a free surface at which one could terminate an electric field applied externally perpendicular to the surface as a probe was thought to be worthwhile. Two groups external to our MRL have successfully utilized this approach to determine some of the properties that we were aiming to determine. However, they have not taken full advantage of the opportunity to study the effect of the electric field in the presence of the foreign atom and the ability to probe the system with light. We still have that as one of our goals.

We have initiated a program trying to passivate the surface of other semiconductors. We have had success on germanium and gallium arsenide. For the former, we developed a technique that employed high pressure oxidation. This has the advantage of undergoing moderate surface reactions at a low temerature. At higher temperatures than we employed, GeO sublimes off the surface very rapidly. Surface properties were explored with modifications of these oxides by reacting with flowing ammonia and converting them to oxy-nitrides. Both these passivating layers have reasonable properties which allow one to fabricate fair quality transistors.

For the case of GaAs, we utilized plasma oxidation to form the oxide. Both this technique and the one emloyed for Ge grow the oxide from bulk material at the itnerface. This has the effect of self leveling the interface and self purifying the region of the interface. The interface obtained with the plasma oxidation was good enough to allow us to fabricate the world's best transistor on GaAs with a native oxide. Still the surface mobility was about three times lower than an ideal surface. We have also fabricated native oxides on InP, InAs, InSb and (Pb,Sn)Te. In fact we feel that this technique is applicable for many such systems. We are in the process of comparing the results for all the In III-V compounds.

Other projects have dealt with the electronic properties of the Si MOSFET and (Ga,Al)As:GaAs heterostructures. Both of these systems are well studied now and the general characteristics are in the textbooks. We have been exploring new probes that can be developed or applied to these and similar systems. The most promising technique is one that we call the "floating gate" technique. It is a modification of the technique for measuring work functions. By creating a capacitive structure with one interface of the capacitor controlled and then varying one external parameter, one can obtain the changes of the electrochemical otential of the interface under investigation. We have successfully applied the technique to the systems above and are in the process of testing intercalated graphite and some conducting organic compounds.

Publications

P.J. Stiles, B.B. Goldberg, T.P. Smith, III and M. Heiblum, "AC Conductivity of (AlGa)As-GaAs Heterostructures and Silicon MOSFETs in the Quantum Hall Regime," Page 180, Proceedings of the Sixth International Conference on the Electronic Properties of Two-Dimensional Systems (edited by T. Ando, North Holland 1986) and *Surface Science* 170, p. 154 (1986).

P.J. Stiles, T.P. Smith, III, B.B. Goldberg and M. Heiblum, "Magnetocapacitance Measurements in GaAs Heterostructures," Page 304 Proceedings of the Electronic Properties of a Two-Dimensional System, (Sixth International Conference) (ed. by T. Ando, North Holland 1986) and *Surface Science* 170, p. 154 (1986).

P.J. Stiles, T.P. Smith, III, J.M. Phillips, R. People, J.M. Gibson and L. Pfeiffer, "Electronic Properties of Epitaxial Calcium Floride-Silicon Structures," published in the Mat. Rec. Soc. Sym. Proc (1986).

P.J. Stiles, J.E. Furneaux, D.A. Syphers, J.S. Brooks, G.M. Schmiedeshoff and R.G. Wheeler, "Studies of the Fractional Quantum Hall Effect in a Silicon MOSFET," Page 154 Proceedings of the Yamada Conference XIII on Electronic Properties of Two-Dimensional Systems (Sixth International Conference) (ed. by T. Ando, North Holland 1986) and *Surface Science* 170, p. 154 (1986).

P.J. Stiles, E.E. Crisman and O.J. Gregory, "Microstructures and Properties of Native Insulators on Single Crystal Germanium," the Mat. Res. Soc. Sym. Proc. 54, p. 593 (1985).

P.J. Stiles, R.T. Zeller, F.F. Fang, B.B. Goldberg and S.L. Wright, "The Floating Gate Technique Applied to Two-Dimensional Systems," *Physical Review*. 33, p. 1529 (1986).

P.J. Stiles and D.A. Syphers, "The Quantum Hall Effect and Macroscopic Inhomogeneities," submitted to *Solid State Communications*.

P.J. Stiles, J.E. Furneaux, D.A. Syphers, J.S. Brooks, G.M. Schmiedeshoff, R.G. Wheeler, G. Dorda and R.P. Smith, "The Fractional Quantum Hall Effect in Si MOSFETs: New Results," *Surface Science*. 170 p. 154 (1986).

P.J. Stiles, T.P. Smith, III and W.I. Wang, "The Two-Dimensional Density of States in the Extreme Quantum Limit," to be published in the Proceedings of the Conference of the Applications of High Magnetic Fields in Semiconductor Physics.

P.J. Stiles, T.P. Smith, III and W.I. Wang, "Density of States Measurements in the Extreme Quantum Limit," *Physical Review*. B34, p. 2995 (1986).

P.J. Stiles and R.P. Smith, "Temperature Dependence of the Conductivity in High Mobility N-Channel Silicon MOSFETs," *Solid State Communications*. 56 (1986).

P.J. Stiles, E.E. Crisman, J.I. Lee and O.J. Gregory, "Characterization of N-Channel Germanium MOSFET with Gate Insulator Formed by High Pressure Thermal Oxidation," *Electronics Letters*. 23, p. 8 (1987).

P.J. Stiles and J. Lee, "The Frequency Dependence of the Diagonal Conductivity of a 2DEG in GaAs Heterostructure in the Quantum Hall Regime," submitted to *Solid State Communications*.

P.J. Stiles, A.M. Dabiran, R.T. Zeller, F.F. Fang and S. Wright, "Electrochemical Potential Oscillations of the Two-Dimensional Electron Gas in GaAs:(Al,Ga)As Heterostructures in High Magnetic Fields," to be published in the proceedings of EP2DS VII.

Solid-Liquid Interface Mobility in Helium

Principal Investigator: C. Elbaum, Professor, Department of Physics and Division of Applied Mathematics

Personnel: M. B. Manning, Graduate Student, Department of Physics
M. J. Moelter, Graduate Student, Department of Physics

Sources of Support: NSF

Objectives and Approaches:

The solid-liquid interface of helium provides unique opportunities for studies of crystal growth. For an ordinary solid, crystal growth is greatly influenced by thermal processes, i.e., by the latent heat of fusion, which is released when liquid is converted into solid. In most situations the rate at which a crystal grows is determined by the rate at which this heat can be removed from the interface by thermal conduction, rather than by the microscopic kinetic processes which occur at the interface. For ^{4}He at temperatures below 1 K the latent heat of fusion is extremely small. In addition, heat is transported away from the interface very rapidly, either as second sound, or as freely propagating ballistic phonons. The consequence is that, at least below 1 K the latent heat does not usually limit the growth rate of helium crystals, and one can study growth kinetics without interference from this effect.

In general, crystal growth from its liquid can be described phenomenologically by a relation $v = K\Delta\mu$, where v is the growth rate of the solid, $\Delta\mu$ is the difference in chemical potential between the liquid and the solid, and K is a kinetic coefficient. For a classical system in which the growth process is diffusion and/or nucleation dependent, K increases with temperature, usually according to an Arrhenius law. For quantum solids (such as helium) it has been proposed that crystal growth proceeds in an entirely different way, that the solid-liquid interface has very high mobility and that at $T = 0K$ the process is continuous and reversible, i.e., without dissipation. As the temperature increases, thermal excitations in the liquid and in the solid interact with the solid-liquid interface and cause dissipation. Consequently, unlike in classical systems, the coefficient K <u>decreases</u> with increasing temperature. It was realized, in this context, that pressure changes associated with a sound wave propagating from liquid to solid would be taken up by the advancing or receding interface, where the pressure would be near or at the equilibrium melting value. Thus sound transmission between the two media would be substantially reduced or even suppressed. This reduction in transmission provides a method of studying growth kinetics used here.

Research Achievements:

We have measured the reflection and transmission of 10 MHz ultrasonic waves at the solid-liquid interface of ^{4}He, in the temperature range $0.8 < T < 1.4$ K. From these measurements we determined that the freezing-melting process is accompanied by a temperature dependent energy dissipation from the ultrasonic waves. The total relative acoustic energy absorption at the interface was then obtained as a function of temperature. In order to account for these results we developed two separate models of energy absorption. One of these is based on a vacancy diffusion process at the interface and the other on the pressure contribution of second sound. The predictions of both models agree equally well with the experimental results. In order to distinguish between the two models, the dependence of the dissipation on ultrasonic frequency will be measured.

Publications:

M.B. Manning, M.J. Moelter and C. Elbaum, "Ultrasonic Studies of ^{4}He Solid-Liquid Interface Mobility," *Journal de Physique*. C10, 46, p. 801 (1985).

M.B. Manning, M.J. Moelter and C. Elbaum, "^{4}He Solid-Liquid Interface Mobility and Ultrasonic Energy Absorption Mechanisms," *Journal of Low Temperature Physics*. 61, p. 447 (1985).

M.J. Moelter, M.B. Manning and C. Elbaum, "Effects of Second Sound on the Acoustic Transmission at the Solid-Liquid ^{4}He Interface," *Physical Review*. B 33, p. 1634 (1986).

SECTION 4

NEW INITIATIVES

Introduction

The four research areas in which the MRL has initiated support are: Layered Synthetic Microstructures; Surface Modification of Hydrocarbons; Physical and Electronic Studies of Ge Passivation; and both the development of the Laboratory for Lightwave Technology and its use for the incorporation of novel dopants in optical fibers. Even in these early stages, the work has lead to interesting advances, which are reported here.

Suggs has discovered a new way to treat hydrocarbon surfaces to activate them for adhesion or chemical modification. The key to this is the use of Mn(TDCPP)Cl, which gives the mildest yet most surface sensitive treatment of those known to date. In studies reported here, he has shown how this treatment and another developed in this work, with chromoyl chloride, compare with standard chromic acid oxidations.

Rosenberg has developed a thermal, atmospheric pressure process for the formation of insulating films on Ge which are MOSFET compatible. He has characterized these stable, insoluble films containing Ge_2N_2O by electrical and spectroscopic techniques. and has shown that these films result in sufficient interfacial quality for MOS and junction passivation applications. Moreover, in conjunction with Ge_3N_4, films were produced which result in passivation of Ge p-n junctions with dark currents that are improved over reported structures.

Morse has continued the development of the Laboratory for Lightwave Technology with the installation of new characterization facilities and a fiber draw tower, with which high quality optical fibers have been drawn. Complementing the successful effort to bring the laboratory to full operational status, Morse has completed theoretical and experimental studies of the parameters affecting the incorporation of phosphorous dopants in optical fiber preforms. This has lead to a theoretical description of the index of refraction variations in cladding layers produced by the MCVD process.

Nutt has made detailed microstructural investigations of multilayer synthetic films. The objective is to correlate their X-ray and UV optical properties with their microstructures. Of particular interest is his observation of nanocrystallinity within tungsten layers in the longer period films of W-C multilayers studied with periods ranging from 1.4 to 8 nm. These and additional features, including periodic oxide channels in electrochemically anodized multilayer films, are reported.

W. M. Risen, Coordinator

Layered Synthetic Microstructures

Principal Investigator: S. R. Nutt, Assistant Professor, Division of Engineering

Personnel: T. Marieb, Undergraduate Research Assistant, Division of Engineering
O. Soldes, Undergraduate Research Assistant, Division of Engineering

Sources of Support: MRL and use of Electron Microscopy Facility

Objectives and Approaches:

One of the most successful applications of metallic multilayer structures has been as Bragg reflectors (mirrors) for X-rays and extreme ultraviolet radiation. Multilayer films that are periodic reflect X-rays of a specific wavelength, since the refractive index varies periodically with depth. In order to maximize X-ray reflectivity, multilayer components are selected with widely different atomic scattering amplitudes (e.g., W-Si, W-C, and Mo-Si). The wavelength of the reflected X-radiation can be controlled by simply varying the bilayer thickness in the structure.

The optical performance characteristics depend critically on the sharpness and smoothness of the interfaces, variations in layer thickness, and the presence or absence of crystallinity within the layers. A primary objective of the new initiative is to correlate these microstructural characteristics with measured optical properties. The approach involves direct observations of the layers by high resolution electron microscopy coupled with reflectivity measurements using low-angle X-ray diffraction. Initial attention is focussed on effects of bilayer thicknesses in the range of 1-4 nm.

The chemical and mechanical properties of synthethic multilayers can be expected to differ significantly from bulk materials. Anodic oxidation behavior and the elastic-plastic behavior of multilayer films is being studied in an effort to understand fundamental mechanisms controlling the observed phenomena.

Research Achievements:

We have made detailed microstructural observations in as-deposited W-Si and W-C multilayer (ML) films ranging in period from 1.4-8 nm. Of particular interest is the observation of nanocrystallinity within W layers in longer period films of W-C. Optical diffractractograms reveal lattice spacings consistent with W and WC. Shorter period MLs on the other hand are amorphous. A second observation is that interfaces tend to be more diffuse as the period is decreased below 2 nm. A computer model has been developed to simulate the diffracted X-ray intensity for graded and sharp interfaces in MLs of different periods and constituent materials. We would like to be able to correlate observed interface characteristics with their effect on X-ray optical behavior.

We have also eletrochemically anodized ML films of W-Ti and W-Si. We find that an unusual structure develops as a result of a Rayleigh-Taylor instability. Beneath a surface layer of homogenized (unlayered) oxide, the layers develop a wavy profile with periodic channels of oxide penetrating tens of layers deep. The observations are interpreted in terms of an instability caused by a less resistive oxide developing beneath a more resistive oxide, and accelerated oxidation occurring at sites of layer imperfections. (See Figure 43).

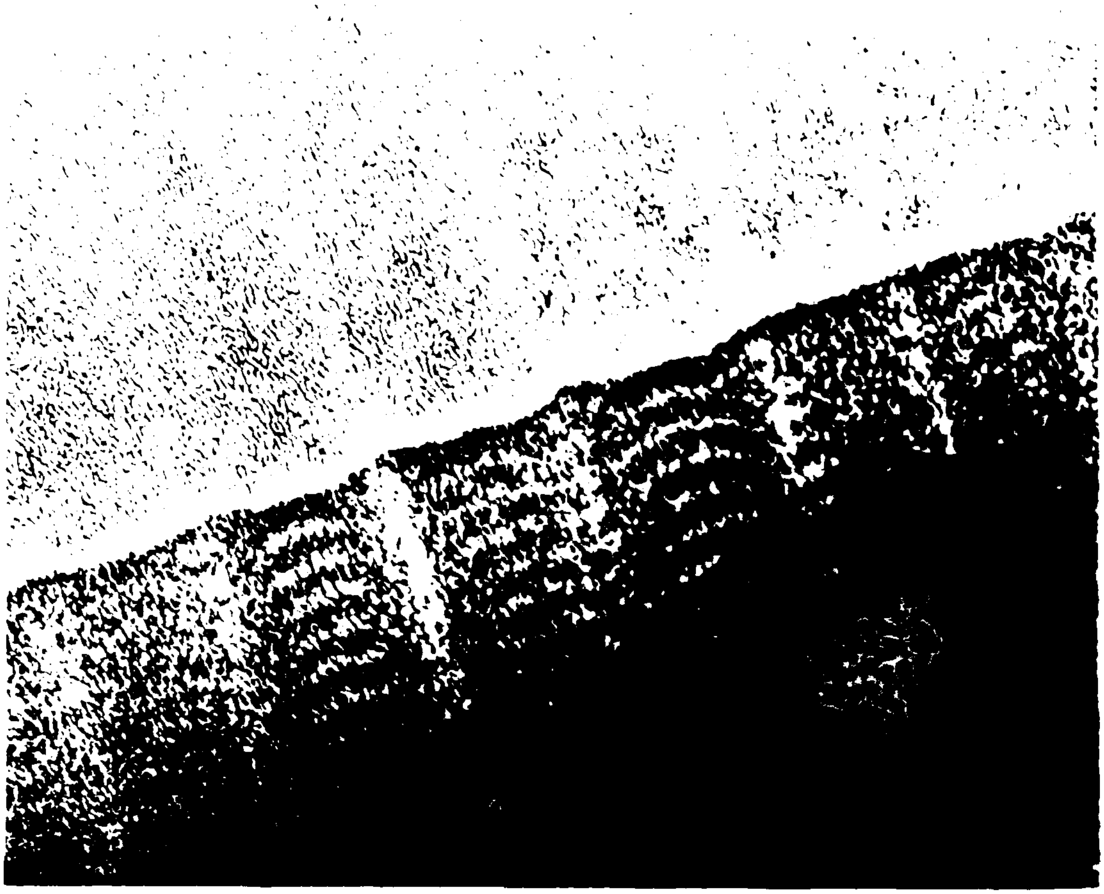


Figure 43 Anodically oxidized W-Si multilayer [illegible]

Publications

A.K. Petford-Long, M.B. Stearns, C.H. Chang, S.R. Nutt, D.G. Stearns, N.M. Ceglio and A.M. Hawryluk, "High-Resolution Electron Microscopy Study of X-ray Multilayer Structures," *Journal of Applied Physics* 61, p. 1422 (1987)

Physical and Electronic Properties of the Germanium Oxynitride/Germanium System

Principal Investigator: J. J. Rosenberg, Assistant Professor, Division of Engineering

Personnel: D. J. Hymes, Graduate Student, Division of Engineering

Sources of Support: MRL, PYI, IBM and use of the Microelectronics Facility

Objectives and Approaches:

The objective of this study was an investigation of physical and electronic properties of native germanium oxynitrides on germanium with the goal of developing a fabrication technique for an insulating film on germanium having sufficient interfacial quality for MOS and junction passivation applications. We have developed a thermal reaction process for this study, in which atmospheric pressure oxidation of germanium substrates is followed by atmospheric pressure nitridation. Physical characterization has been carried out using infra-red transmission spectroscopy, ESCA and Auger electron spectroscopy. Electrical characterization by capacitance-voltage measurement and channel mobility measurements in MOSFETs have been carried out as well.

Research Achievements:

The thermal reaction process developed for this study, atmospheric pressure oxidation followed by atmospheric pressure nitridation yields smooth, uniform, native germanium oxynitride films which have high interfacial quality and which are MOSFET process compatible. Physical characterization using infra-red transmission spectroscopy, ESCA and Auger electron spectroscopy indicates that the thermal oxidation of germanium at 600°C results in a vitreous film of essentially stoichiometric GeO_2. By considering the results of all three techniques together, this study shows that the nitridation of vitreous thin films of GeO_2 for long times at 600°C results in the formation of a thermodynamically stable stoichiometric oxynitride, Ge_2N_2O (rather than causing complete conversion to Ge_3N_4, which occurs only at higher temperatures). An infra-red absorbance peak at 800 cm^{-1} has been identified and attributed to a vibrational mode of germanium bound in the stoichiometric oxynitride structure. Intermediate nitridation times result in a glassy network of germanium, nitrogen, and oxygen in which germanium is bound to both oxygen and nitrogen, but nitrogen and oxygen are not found bonded to each other. These films are water insoluble (unlike vitreous GeO_2) and are MOSFET process compatible. Electrical characterization by capacitance-voltage measurement and channel mobility measurements in MOSFETs indicates that appropriate nitridation conditions result in an interface state density of $\sim 10^{11}/cm^2$-eV and a channel mobility of 1200 cm^2/V-sec. In addition, these films in conjunction with chemically deposited Ge_3N_4 films result in passivation of ion-implanted planar germanium p-n junctions which exhibit dark currents which are four times lower than reported for comparable structures.

Surface Modification of Hydrocarbons

Principal Investigator: J. W. Suggs, Associate Professor, Chemistry Department

Personnel: L. Ytuarte, Graduate Student, Chemistry Department

Sources of Support: MRL, NSF, NIH, Governors' Cancer Research Fund

Objectives and Approaches:

Many of the properties of solid organic polymers (such as electrostatic charging, wettability and adhesion, degradation and biocompatability) are surface properties. We have studied the surface modification of low density polyethylene using chemical oxidants to introduce new functional groups onto the surface. These new groups are a function of which oxidant was used.

Three techniques have been used to study the oxidized polymer surface. Scanning electron microscopy was used to see the extent of surface roughening. Contact angle measurements were used to measure the work of adhesion, adhesion tension, and critical surface tension. The change of contact angle with pH was used to probe for the presence and surface density of surface carboxylic acid groups. The contact angle measurements are sensitive only to groups within ca. 10Å of the surface. Attenuated total reflectance infrared (ATR-IR) was used to study the functional groups introduced upon oxidation, It penetrates up to 11,000Å into the surface. Extensive oxidation is required before ATR-IR picks up surface charges.

Research Achievements:

A number of chemical oxidants were found to oxidize the surface of low density polyethylene. The contact angle data for these oxidants are summarized below. Mn(TDCPP)Cl is manganese(III)tetra-2,6-dichlorophenyl-porphyrin-H_2O_2 and Fenton's reagent is Fe(III)-H_2O_2.

Each oxidant shows a unique behavior. Chromic acid produces a carboxylic acid surface density of 10^{17} COOH/cm^2. Chromyl trifluoracetate produces the largest Wa, but very little acid groups. Ketone groups are the major surface species, as seen by ATR-IR.

Chromyl acetate produces mostly ester groups on the surface, as well as unsaturated C-C groups. It leaves Cr(III) residues on the surface which can be removed by acid washes. Mn(TDCPP)Cl is the mildest and most surface sensitive method. Hydroxyl groups are produced which can be modified by cyclic anhydrides to give surface acid groups. Fenton's reagent seems to crosslink the surface and deposits iron complexes on the surface.

Contact Angle Data for Oxidized Polyethylene Films

Method	θ°	Wa (erg/cm^2)	Hysteresis (deg)	$\Delta\theta$pH
Untreated	100	59.7	3	0
Chromic Acid (72° 605°C)	92	70	27	32
(25°, 1 hr.)	84	80	--	20
(25°, 18 hr.)	81	83	--	33
Chromyl trifluoroacetate (0.5 M, 10 min.)	74	92	20	0
(0.25 M, 5 min.)	77	88	--	0
Chromyl acetate	90	72	22	0
Mn(TDCPP)Cl	90	72	23	0
Fenton's reagent	108	49.9	22	33

θ = water contact angle

Wa = work of adhesion

Hysteresis = difference between advancing and receeding contact angle

$\Delta\theta$pH = difference in contact angle between acidic and basic drop

Publications:

J.W. Suggs and L. Ytuarte, "Hydrocarbon Oxidations with $CrO_2(O_2CCF_3)_2$, *Tetrahedron Letters*, 27, p. 437 (1986).

Incorporation of Novel Dopants into Silica based Glasses, Development of Facilities of Laboratory for Lightwave Technology

Principal Investigator: T. F. Morse, Professor, Division of Engineering

Personnel: P. Beade, Graduate Student, Division of Engineering

Sources of Support: MRL, NSF, AFOSR

Objectives and Approaches:

Much of the effort spent in the past year has been applied toward the establishment of a unique university facility for the fabrication of state-of-the-art optical fibers. With a value of equipment in our laboratory of the order of one million dollars (NSF, DOD, Bell Research Corporation), this facility consists of an MCVD (Modified Chemical Vapor Deposition) optical fiber preform capability, with gas purifying systems, computer controlled flow delivery system (PDP 11/23), and a double burner glass lathe. The second component of the laboratory is a preform and fiber characterization laboratory with a York Technology Preform Analyzer and a York Technology FCM1000 fiber analyzer (recently donated by the Bell Research Corporation). The final component of our laboratory is a Special Gas Control Optical Fiber draw facility. These three components provide an ability to design, fabricate, and dope silica based preforms with a host of materials for special applications. Research in conjunction with the expertise of faculty in the inorganic glass thrust area, allows the characterization of how the processing can influence the incorporation of dopants. This is done by using NMR and micro-Raman analysis.

Research Achievements:

As noted above, much of our recent activity has been associated with the establishment of the three individual facilities within the Laboratory for Lightwave Technology. These consist of the MCVD deposition laboratory that has been operational for one year, the fiber characterization laboratory, and the draw tower that is now operyational. Fibers have been fabricated with losses of .353 dB/bm at 1.3μ, and .28 dB/bm at 1.55μ. Fibers have been drawn with a tolerance of $\pm1.0\mu$ at a mean diameter of 125μ.

A theoretical and experimental program has been in progress to determine the effects of various process parameters on the incorporation of P_2O_5 into a silica based matrix. This reaction is of importance for several reasons. First, $POCl_3$ is one of the dopants used in optical fiber preforms, and the chemistry at elevated temperatures is quite simple. Recent work also has indicated that P_2O_5 in the fiber is responsible for some potentially interesting nonlinear phenomena. Above 900°K we need consider only PO_2 in gaseous form. We have considered a model in which SiO_2 particles are produced in the MCVD process, and in which a specified amount of P_2O_5 dopant is found. These particles, that comprise the flocculated aerosol, are then sintered in a background gas of PO_2. As these particles are heated, they melt, and fuse together, into a vitreous, pore-free layer. As they are heated, the pore fraction decreases, the dopant incorporation is effected, thus changing the viscosity of the fusing material, which in turn, affects the rate at which dopant is driven off. This has led to a theoretical description of the index of refraction variations in the cladding layers in the MCVD process, and this work is forming the basis for further studies in gradient index optical materials. Publication in progress.

SECTION 5

MATERIALS PREPARATION

Introduction

The solid state chemistry laboratories at Brown University have been engaged in the preparation and characterization of new materials suitable for various electronic or catalytic applications. The facilities at Brown are unique in that equipment capable of preparing a wide range of materials has been assembled in one laboratory. As a result, a number of new materials can be prepared which are not available from any commercial source. Among such materials are the II-Vi semiconductors doped with transition metals. Such compounds show interesting electronic properties as a result of the interaction of the 3^d electrons of the transition metal with the semiconductor.

In addition to the preparation of the semi-magnetic semiconductors which are part of the cooperative program with the National Magnet Laboratory at M.I.T., two industrial programs have been ongoing for a number of years. One is with the Exxon Research Laboratories in which new transition metal sulfides are being synthesized for potential hydrodesulfurization catalysis. The new compounds prepared at Brown are available for their catalytic activity at Exxon, and a number of publications have appeared between the two laboratories. Another industrial program is with GTE Labs in Waltham, MA, and this program has now begun to study the preparation of aluminum oxide thin films.

Finally there has been a program with the Army Materials and Mechanics Research Center in Watertown, MA, and this program has concentrated on the examination of the preparation and characterization of unusual vanadium oxides such as V_3O_5. These oxides show large charges in resistivity as a function of temperature and this unusual property can be correlated with corresponding changes in crystal structure.

A. Wold

Physics and Chemistry of Semimagnetic Semiconductors
(NSF-MRL-MIT Cooperative Research Program)

Principal Investigator: Aaron Wold, Vernon K. Krieble, Professor of Chemistry

Personnel: (at Brown University)
D. H. Ridgley, Research Associate, Chemistry Department
E. D. Honig, Research Associate, Chemistry Department
R. Kershaw, Senior Research Engineer, Division of Engineering
K. Dwight, Professor (Research), Chemistry Department

(at M.I.T. Francis Bitter National Magnet Lab)
D. E. Heiman, Research Staff Member
R. L. Aggarwal, Senior Research Scientist
Y. Shapira, Senior Research Scientist
P. A. Wolff, Director

Sources of Support: NSF, MRL-Brown, ONR

Objectives and Approaches:

Attempts were made during the past year to grow single crystals of several materials crystallizing with the stannite structure. The first method was a modofied Bridgman technique in which growth of members of the systems $Cu_2Zn_{1-x}M_xGeS_4$ (M = Fe,Mn) as well as $Cu_xZn_{1-x}Mn_xSiSe_4$ were attempted. In no case could single crystals of reasonable quality be grown from the melt. The products, for the most part, indicated that at the melting point some slow decomposition occurred.

A more successful method appears to be chemical vapor transport in which the crystals are grown below the melting point. Unfortunately, for many products, some halogen (the transport agent) appears to be incorporated into the crystals which results in large absorption or scattering of light when optical measurements are attempted. However, the compositions $Cu_2ZnSiSe_4$ and Cu_2CdSiS_4 result in the formation of transparent orange and green crystals, respectively. Recent crystal growth experiments using iodine as a transport agent resulted in the growth of $Cu_2Zn_{.82}Mn_{.18}SiSe_4$ single crystals which were transparent and red-orange in color. The concentration of manganese established in the production of preliminary growth runs was 18 mole % from magnetic susceptibility measurements. There was no correction made for core diamagnetism. The manganese concentration was established from magnetic susceptibility measurements assuming the moment for spin only Mn(II).

These crystals were grown at Brown University and sent to the National Magnet laboratory at M.I.T. where they were further characterized. The M.I.T. physicists also continued their studies on crystals grown at Brown on the system $Cd_{1-x}MnSe$ and a number of papers appeared on this work.

Publications:

J. Warnock, R. Kershaw, D. Ridgley, K. Dwight, A. Wold and R. R. Galazka, "Localized Excitons and Magnetic Polaron Formation in (Cd,Mn)Se and (Cd,Mn)Te," *Journal of Luminescence* 34, 25 (1985).

J. Warnock, D. Heiman, P. A. Wolff, R. Kershaw, D. H. Ridgley, K. Dwight, A. Wold and

R. R. Galazka, "Optical Pumping and Polarized Photoluminescence in (Cd,Mn)Se," Proceedings of the XVII International Conference on the Physics of Semiconductors, D. Chadi and W. A. Harrison, Eds. (Springer-Verlag, NY, 1985) p. 1407.

R. L. Aggarwal, S. N. Jasperson, Y. Shapira, S. Foner, T. Sakakibara, T. Goto, N. Miura, K. Dwight, and A. Wold, "Determination of the Antiferromagnetic Exchange Coupling Constant between Nearest-Neighbor Mn^{++} Ions in $Cd_{0.95}Mn_{0.05}Se$," ibid., p. 1419.

D. Heiman, R. Kershaw, D. Ridgley, K. Dwight, A. Wold, R. R. Galazka, "Magnetic Polarons in (Cd,Mn)Te and (Cd,Mn)Se," *Bulletin of the American Physics Society* 30, 216 (1985).

D. Heiman, P. Becla, R. Kershaw, D. Ridgley, K. Swight, A. Wold, R. R. Galazka, "Field Induced Exchange Effects in (Cd,Mn)Te and (Cd,Mn)Se from Photoluminescence Measurements," *Physics Review B* 15, (1986).

Y. Shapira, N. F. Oliveira, Jr., D. H. Ridgley, R. Kershaw, K. Dwight and A. Wold, "Magnetoresistance and Hall Effect near the Metal-Insulator Transition of $Cd_{1-x}Mn_xSe$," *Physical Review B* 34, p. 4187 (1986).

Preparation and Characterization of New Semiconductor Chalcogenides
(NSF-GTE-MRL Cooperative Research Program)

Principal Investigator A. Wold, Vernon K. Krieble, Professor of Chemistry

Personnel (at Brown University)
R. Brusasco, Research Assistant (Full Support) Chemistry Department
W. DeSisto, Research Assistant, Chemistry Department
J. Massoyan, Research Assistant, Chemistry Department
J. A. Fournier, Research Associate, Chemistry Department
R. Kershaw, Senior Research Engineer, Division of Engineering
K. Dwight, Professor (Research), Chemistry Department

(at GTE Laboratories, Inc.)
J. A. Baglio, Senior Research Chemist

Sources of Support NSF, GTE Labs, Inc., MRL-Brown University, ONR

Objectives and Approaches

During this period we completed our initial work on the preparation and characterization of alumina films by the sol-gel method. A large problem which was unsolved by our investigation was the porosity of the films. As a result of this porosity, there was a small breakdown potential which indicated that the films would not have the high insulating capability which we required. The results of this work were published in the Materials Research Bulletin. This work is being continued in an effort to reduce porosity of the films.

In addition, growth of Al_2O_3 has also been started by the technique of metalorganic chemical vapor deposition (MOCVD) The results of our investigation over the past year indicate that the films are much denser, do not shrink, and from I-V measurements, breakdown voltages were shown to exceed 4 volts. This work has been in close collaboration with the GTE Labs, Waltham, MA.

Publications

R. Brusasco, R. Kershaw, J. Baglio, K. Dwight, A. Wold, "Preparation and Characterization of Alumina Films by Sol-Gel Method," *Materials Research Bulletin*. 21(3), p. 301 (1986)

J. Fournier, W. DeSisto, R. Brusasco, J. Baglio, K. Dwight and A. Wold, "Preparation and Characterization of Thin Films of Alumina by Metal-Organic Chemical Vapor Deposition," to be published.

New Synthetic Techniques for the Optimization of Transparent Far Infrared Chalcogenides and Phosphides

Principal Investigator: A. Wold, Vernon K. Krieble, Professor of Chemistry

Personnel: (at Brown University)
H-S. Shen, Research Associate, Chemistry Department
G-Q. Yao, Research Associate, Chemistry Department
E. D. Honig, Research Associate, Chemistry Department
K. Kourtakis, Research Associate, Chemistry Department
R. Kershaw, Senior Research Engineer, Division of Engineering
K. Dwight, Professor (Research), Chemistry Department

(at Naval Weapons Laboratory)
R. Schwartz, NWL, China Lake

Sources of Support: ONR, MRL-Brown University

Objectives and Approaches:

The objective in this program has been to prepare materials which transmit in the far infrared, i.e. beyond 10 microns, are relatively hard -- i.e., the hardness of tool steel, and can withstand temperatures up to 800°C. These materials would be of use to the Office of Naval Research. The program has been carried out with the collaboration of the Naval Weapons Laboratory in China Lake. The program at Brown primarily has been concerned with methods of preparation and characterization of such materials. Among the compounds prepared and studied are the *phosphides* $ZnSiP_2$ *and* $ZnGeP_2$./ The latter compound transmits to 12.5 microns, decomposes above 650°C when heated in air and had a hardness greater than that of tool steel. The compound is being evaluated for the possibility of making domes by the Navy.

Publications:

G-Q. Yao, H-S. Shen, R. Kershaw, K. Dwight and A. Wold, "Preparation and Characterization of $ZnSiP_2$ and $ZnGeP_2$ Single Crystals," *Materials Research Bulletin*, 21, p. 653 (1986).

H-S. Shen, G-Q. Yao, R. Kershaw, K. Dwight and A. Wold, "Preparation and Characterization of Several II-IV-V_2 Chalcopyrite Single Crystals," accepted for publication in the *Journal of Solid State Chemistry*.

G-Q. Yao, H-S. Shen, E. D. Honig, R. Kershaw, K. Dwight, A. Wold, "Preparation and Characterization of the QuaternaryChalcogenides $Cu_2B(II)C(IV)X_4$ [B(II) = Zn,Cd; C(IV) = Si,Ge, X = S,Se], to be published in the *Journal of Solid State Ionics*.

New Electronic Materials and CO_2 Reduction

Principal Investigator: A. Wold, Vernon K. Krieble, Professor of Chemistry

Personnel (at Brown University)
M. Schwartz, Research Associate, Chemistry Department
Z-D. Zhang, Research Associate, Chemistry Department
S. Davison, Research Assistant, Chemistry Department
K. Smith, Research Assistant, Chemistry Department
Y-C. Zhang, Research Assistant, Chemistry Department
J. Yu, Research Assistant, Chemistry Department
P. Wu, Research Assistant, Chemistry Department
R. Kershaw, Senior Research Engineer, Division of Engineering
K. Dwight, Professor (Research), Chemistry Department

Sources of Support: ONR, Exxon Research & Engineering, Eastman Kodak Company, MRL-Brown University, NSF

Objectives and Approaches:

Research in the area of catalysis at Brown deals with the development of low temperature synthetic methods for the preparation of well-dispersed catalysts (Fe_2O_3, Cr_2O_3 and NiO) on several oxide supports (ZrO_2, TiO_2). Physical methods, such as x-ray diffraction, magnetic susceptibility and temperature programmed reduction, are used to study the interaction between the dispersed metal oxide and the support. For the specific system Rh_2O_3/ZrO_2, the solubility of rhodium oxide in the support was followed as a function of the structural changes of the ZrO_2 as well as the stabilization of the Rh_2O_3 towards reduction.

The extent of substitution of nickel into Fe_5C_2 was also studied since both nickel and iron are Fischer-Tropsch catalysts. The limit of substitution was determined for samples prepared under actual reactor conditions and was determined from both magnetic and x-ray analysis.

Finally, a thermomagnetic balance has been constructed and is being used to determine the nucleation and growth of catalytically active magnetic phases which can be correlated at the same time with the temperature programmed data.

During the past year it was shown that nickel can be substituted into Fe_5C_2 to the extent of 20 atomic percent. Samples were prepared by codecomposition of mixed nitrates followed by reduction at 290 °C in a 9:1 H_2:CO atmosphere. Confirmation of the limit of substitution was made by both magnetic and x-ray analysis.

Samples of well-dispersed hexagonal Rh_2O_3 on tetragonal ZrO_2 have been prepared by the codecomposition of the nitrates at 900 °C. An increase in the stability of dispersed Rh_2O_3 compared to bulk Rh_2O_3 demonstrates that a solid solution was formed between the two oxides.

During the next year our studies on catalyst support interactions will be extended to the following systems: Fe_2O_3-Rutile TiO_2, Fe_3O_3-ZrO_2, NiO-ZrO_2, Rh_2O_3-La_2O_3/ZrO_2. The successful synthesis of rutile TiO_2 at low temperatures (to be published) enables us now to compare the dispersion and properties of the Fe_2O_3-TiO_2 vs. Fe_2O_3-ZrO_2 systems. It is anticipated that the catalyst support interaction for the rutile system will be dependent upon the rate of formation of the ilmenite $FeTiO_3$ under reducing conditions. No such phase forms in the Fe_2O_3-ZrO_2 system.

The NiO-ZrO_2 system is ideal for initial studies with our new thermomagnetic balance. Bulk NiO reduces at about 300 °C and the Curie temperature of metallic nickel is 350 °C. We should be able to determine the exact temperature at which various stabilized nickel oxide samples dispersed on ZrO_2 begin to be reduced.

Finally, our reactor experiments contrasting the reduction of CO with H_2 using a Rh_2O_3-ZrO_2 catalyst will be compared to those containing varying amounts of La_2O_3. *The quantity of oxygenated products will be compared to the amount of perovskite* ($LaRhO_3$) formed and its effect on rhodium III stabilization.

Publications:

Y-C. Zhang, S. Davison, R. Brusasco, Y-T. Qian, K. Dwight and A. Wold, "Preparation and Characterization of Tetragonal ZrO_2," *Journal of Less-Common Metals*, 116(1), p. 299 (1986).

Y-C. Zhang, K. Dwight and A. Wold, "Preparation and Characterization of Dispersed Rh_2O_3 on Tetragonal ZrO_2," *Materials Research Bulletin*, 21, p. 853 (1986).

Y-C. Zhang, R. Kershaw, K. Dwight and A. Wold, "Preparation and Characterization of Nickel Substituted Fe_5C_2," *Materials Research Bulletin*, 21, p. 979 (1986).

Y-C. Zhang, R. Kershaw, K. Dwight and A. Wold, "Stabilization of Cubic ZrO_2 with Rh(III) and/or La(III)," accepted by *Journal of Solid State Chemistry*..

J. Yu, R. Kershaw, K. Dwight and A. Wold, "Preparation and Properties of Dispersed Iron (III) Oxide on Rutile," accepted by *Journal of Solid State Chemistry*.

P. Wu, R. Kershaw, K. Dwight and A. Wold, "Preparation and Characterization of Members of the chromium Zirconium Oxide, accepted by *Journal of Materials Science Letters*.

M. Schwartz, R. Kershaw, K. Dwight and A. Wold, "An Examination of the Relative Stabilities of $Mg_xNi_{x-1}O$ and NiO on Spherical Carbon Particles," accepted for publication, *Materials Research Bulletin*.

S. Davison, R. Kershaw, K. Dwight and A. Wold, "Preparation and Characterization of Cubic ZrO_2 Stabilized be Fe(III) and Fe(II)," submitted for publication in *Journal of Solid State Chemistry*.

K. Smith, R. Kershaw, K. Dwight and A. Wold, "Preparation and Properties of Cubic ZrO_2 Stabilized with Ni(II)," submitted for publication in *Materials Research Bulletin*.

Additional Programs:

U.S./Israel Joint Research Program
Preparation and Characterization of Gamma Alumina Particles and Alumina Films
Preparation and Characterization of Iron Oxide Catalysts

Additional Personnel:

K. Doverspike, Research Assistant, Chemistry Department
J. DiCarlo, Research Assistant, Chemistry Department
X-C. He, Research Associate, Chemistry Department
Y-C. Long, Research Associate, Chemistry Department

Additional Publications:

R. Tenne and A. Wold, "Passivation of Recombination Centers in n-WSe_2 Yields High Efficiency (>14%) Photoelect5rochemical Cell," *Applied Physics Letters*, October, 1985.

R. Tenne and A. Wold, "Photoelectrochemical Etching of n-$MoSe_2$," *Ber. Bunserges. Phys. Chem.*, 90, p. 545 (1986).

Preprints:

R. Coehoorn, C. Haas, J. Dijkstra, C.J.F. Flipse, R.A. deGroot and A. Wold, "The Electronic Structure of $MoSe_2$, MoS_2 and WSe_2: I: Band Structure Calculations and Photoelectron Spectroscopy," to be published.

LECTURES IN THE MATERIALS RESEARCH LABORATORY PROGRAM, 1985-87

September 9, 1985
Physics Colloquium: Professor John Imbrie, Brown University, *"ASTRONOMICAL THEORY OF THE ICE AGES."*

September 23, 1985
Physics Colloquium: Professor Zeev Vardeny, Technion - Israel Institute of Technology and Brown University, *"ELECTRONIC PROPERTIES OF CONDUCTING POLYMERS."*

September 26, 1985
Inorganic Seminar: Dr. Efi Honig, Brown University, *"NUDIOPHILIC ADDITIONS TO COORDINATED CYCLIC π-HYDROCARBONS."*

September 26, 1985
Chemistry Colloquium: Professor Kit Bowen, John Hopkins University, *"PHOTOELECTRON SPECTRA OF NEGATIVE CLUSTER IONS."*

September 27, 1985
Chemistry Colloquium: Professor James F. Rusling, University of Connecticut, *"ELECTROCATALYTIC DEHALOGENATION REACTIONS."*

September 30, 1985
Physics Colloquium: Professor R. V. Tensen, Yale University, *"CLASSICAL CHAOS IN QUANTUM SYSTEMS."*

September 30, 1985
Solid Mechanics Seminar: Professor Arun Shukla, University of Rhode Island, *"DYNAMIC PHOTOELASTIC STUDIES OF FRACTURE."*

October 3, 1985
Physical Tea Session: Tony DeSimone, Brown University *"CONTINUUM PERCOLATION IN AN INTERACTING SYSTEM: COORDINATION VERSUS CORRELATION."*

October 3, 1985
Condensed Matter Seminar: Professors J. Quinn, P.J. Stiles et al., Brown University, *"REPORT ON THE 6TH INTERNATIONAL CONFERENCE ON ELECTRONIC PROPERTIES OF 2D SYSTEMS."*

October 4, 1985
Chemistry Colloquium: Professor Derek Lindsay, City College of New York, *"METAL CLUSTERS IN MATRICES."*

October 7, 1985
Physics Colloquium: Professor J.P. Harrison, Queen's University, *"COOLING* ^{3}*He TO BELOW 1 mK - ACOUSTIC HEAT TRANSFER."*

October 9, 1985
Condensed Matter Physics Discussion Group and Journal Club: Dr. T.C. Choy, University of Rhode Island, Imperial College, London, England, *"STRUCTURE AND ELECTRONIC PROPERTIES OF 2-DIMENSIONAL PENROSE LATTICES."*

October 15, 1985
Solid Mechanics Seminar: Professor T.H.H. Pian, MIT, *"EVOLUTION OF ASSUMED STRESS HYBRID FINITE ELEMENT."*

October 16, 1985
Chemistry Colloquium: Professor L. F. Dahl, University of Wisconsin, *"SMALL TO GIANT SIZE TRANSITION METAL CLUSTERS: SYNTHESIS, STRUCTURE AND BONDING FEATURES AND CHEMICAL/ELECTROCHEMICAL REACTIVITY FEATURES."*

October 17, 1985
Inorganic Seminar: Yunchang Zhang, Brown University, *"PREPARATION AND CHARACTERIZATION OF TETRAGONAL* ZrO_2*."*

October 17, 1985
Physical Chemistry Tea Session: Robert Stewart, Brown University, *"QUANTUM BEAT SPECTROSCOPY - A DYNAMICAL VIEW."*

October 18, 1985
Chemistry Colloquium: Dr. Chuck Doubleday, Columbia University, *"NANOSECOND TIME-RESOLVED STUDIES OF BIRADICAL DYNAMICS."*

October 21, 1985
Solid Mechanics Seminar: Dr. Roshdy Barsoum, Army Materials & Mechanics Research Center, *"FRACTURE ASPECTS OF DUCTILE COMPOSITES."*

October 21, 1985
Physics Colloquium: Dr. A. Gossard, ATT Bell Labs, *"ARTIFICIAL QUANTUM WELL STRUCTURE BY MOLECULAR BEAMS."*

October 21, 1985
Condensed Matter Seminar: L. B. Kadanoff, University of Chicago, *"MEASURING THE PROPERTIES OF FRACTALS."*

October 23, 1985
Chemistry Colloquium: Professor J. Barrie Raynor, University of Leicester, *"ENDOR STUDIES ON SOME COPPER COMPLEXES AND COPPER-CONTAINING ENZYMES."*

October 23, 1985
Condensed Matter Physics Discussion Group and Journal Club: Dr. Nicholas Read, *"ON A NEW THEORY OF THE FRACTIONAL QUANTIZED HALL EFFECT BY KIVELSON, KALLIN, AROVAS AND SCHRIEFFER."*

October 24, 1985
Condensed Matter Seminar: Professor Y. Abe, Hokkaido University, Japan, *"INTERFEROMETRIC MEASUREMENT OF HIGHER-ORDER ELASTIC CONSTANTS OF GERMANIUM AND GALLIUM ARSENIDES."*

October 28, 1985
Physics Colloquium: Dr. D. Friedan, Enrico Fermi Institute, University of Chicago, *"TWO DIMENSIONAL CRITICAL PHENOMENA AND STRINGS."*

October 28, 1985

Solid Mechanics Seminar: Professor Lalit Anand, MIT, *"ADVANCES IN CONSTITUTIVE EQUATIONS AND ANALYSIS PROCEDURES FOR HOT FORGING METALS."*

October 31, 1985

Condensed Matter Physics Discussion Group and Journal Club: Professor A. Houghton, Brown University, *"ULTRASONIC ATTENUATION IN STRONGLY DISORDERED ELECTRONIC SYSTEMS."*

October 31, 1985

Condensed Matter Seminar: Professor Sankar Das Sarma, University of Maryland, *"PROPOSED EXPERIMENTAL REALIZATION OF ANDERSON LOCALIZATION IN RANDOM AND INCOMMENSURATE ARTIFICIALLY STRUCTURED SYSTEMS."*

October 31, 1985

Physical Chemistry Tea Session: Professor Frank Levin, Brown University, *"EFFECTS OF REACTION CHANNELS IN SOME SIMPLE MOLECULAR SYSTEMS:* H_2 H_3+ *AND* H_2+ *GROUND STATES.* $H+HF$, $H+H_2$ *AND* $D+H_2$ *COLLINEAR COLLISIONS."*

October 31, 1985

Inorganic Seminar: Janice DeGray, Brown University, *"LOW TEMPERATURE ESR OF SOME TRANSITION METAL COMPLEXES."*

November 4, 1985

Solid Mechanics Seminar: Professor Kenneth W. Neale, University of Sherbrooke, Canada, *"NECKING IN POLYMERIC MATERIALS."*

November 6, 1985

Condensed Matter Discussion Group and Journal Club: James T. Daly, Brown University, *"III-V SEMICONDUCTOR MATERIALS AND DEVICES: AN OVERVIEW OF THE TECHNOLOGY."*

November 7, 1985

Condensed Matter Seminar: Professor G. Kotliar, MIT, *" 'ANDERSON LOCALIZATION' AND THE THEORY OF DIRTY SEMICONDUCTORS."*

November 7, 1985

Physical Chemistry Tea Session: Dr. Jeffery P. Perl, Brown University, *"MICROWAVE INTERFEROMETRIC DETERMINATION OF COMPLEX DIELECTRIC CONSTANTS IN SOLIDS, LIQUIDS AND GASSES."*

November 8, 1985

Chemistry Colloquium: Professor Erwin D. Poliakoff, Boston University, *"RESONANCE PHENOMENA IN MOLECULAR PHOTOIONIZATION."*

November 11, 1985

Solid Mechanics Seminar: Professor Subra Suresh, Brown University, *"MECHANICS AND MICROMECHANICS OF FAILURE IN NEW GENERATION AEROSPACE MATERIALS."*

November 13, 1985
Condensed Matter Physics Discussion Group and Journal Club: Professor H. J. Maris, Brown University, *"VERY STRANGE ATTRACTORS FOR HYDROGEN DROPLETS."*

November 14, 1985
Inorganic Seminar: Jung-Mi Ha, Brown Univeristy, *"OBSERVATIONS OF HYSTERESIS AND RELAXATION IN POLY3BCMU."*

November 15, 1985
Physical Chemistry Tea Session: Mark Sigrist, ETH - Zurich, *"LASER ENERATED SOUND IN LIQUIDS."*

November 15, 1985
Chemistry Colloquium: Dr. L. C. Pitchford, GTE - Waltham, *"NON-EQUILIBRIUM EFFECTS IN GAS DISCHARGES."*

November 20, 1985
Condensed Matter Physics Discussion Group and Journal Club: Professor A.M.M. Pruisken, Columbia University, *"QUANTUM HALL EFFECT - THEORY AND EXPERIMENT."*

November 21, 1985
Inorganic Seminar: Ashfaq Mahmood, Brown University, *"KENETICS AND ELECTROCHEMISTRY OF MATALLOPHORPHYRINS."*

Novmeber 21, 1985
Physical Chemistry Tea Session: Tania Didascalou, Brown University, *"THE INVERSE OPTOACOUSTIC EFFECT."*

November 21, 1985
Condensed Matter Seminar: Professor J. Worlock, Bell Communication Laboratories, *"PHONONS IN SUPERCONDUCTOR SUPERLATTICES."*

November 22, 1985
Chemistry Colloquium: Professor Bruno M. Vittimberga, University of Rhode Island, *"PHOTO-INITIATED ELECTRON TRANSFER REACTIONS OF NITROGEN HETEROCYCLES: A TEST OF THE REHN-WELLER EQUATION."*

November 25, 1985
Solid Mechanics Seminar: Professor P. S. Symons, Brown University, *"PATHOLOGICAL CASES IN ELASTIC-PLASTIC RESPONSE TO PULSE LOADING."*

November 25, 1985
Physics Colloquium: Professor Henry Tye, Cornell University, [illegible] *SUPERSTRING."*

Novmeber 26, 1985
Solid Mechanics Seminar: Professor [illegible] Appliquees, France *"BU[illegible]*

December 4, 1985

Condensed Matter Physics Discussion Group: Ji-Wei Wu, Brown University, *"MAGNETIC POLARON EFFECTS IN $CdTe/Cd1\text{-}x\ Mn^{x}Te$ QUANTUM WELL SYSTEMS."*

December 5, 1985

Condensed Matter Seminar: Dr. D. Haldane, Bell Labs, *"FRACTIONAL QUANTUM HALL EFFECTS."*

December 5, 1985

Physical Chemistry Tea Session: Judith Prybla, Brown University, *"H/Mo(100): PHASE DIAGRAM, SURFACE STRUCTURE AND DESORPTION KINETICS."*

December 5, 1985

Inorganic Seminar: Kang Sun, Brown University, *"RARE EARTH GLASSES."*

December 6, 1985

Chemistry Colloquium: Professor Jan Northby, University of Rhode Island, *"CHARGED RARE-GAS CLUSTER BEAMS."*

December 9, 1985

Joint Chemistry and Physics Colloquium: Professor Thomas Engel, University of Washington, Seattle, *"SURFACE STUDIES BY HELIUM ATOM DIFFRACTION: STRUCTURE AND ROUGHENING TRANSITION."*

December 10, 1985

Solid Mechanics Seminar: Professor J. W. Hutchinson, Harvard University, *"SOME SPECIAL PROBLEMS RELATED TO DELAMINATION AND SPALLING OF BRITTLE MATERIALS."*

December 12, 1985

Condensed Matter Seminar: Professor H. Schulz, Orsay University and Bell Labs, *"QUANTUM SPIN CHAINS: PHASE DIAGRAMS AND CRITICAL PROPERTIES."*

December 12, 1985

Physical Chemistry Tea Session: Professor Gene Carpenter, Brown University, *"CRYSTAL STRUCTURE DETERMINATION BY DIRECT METHODS."*

January 23, 1986

Condensed Matter Seminar: Professor Jon Machta, University of Massachusetts, *"LOCALIZATION OF CLASSICAL WAVES IN DISORDERED SYSTEMS."*

January 30, 1986

Physical Chemistry Tea Session: Vladimir Dobrosavljevic, Brown University, *"ELECTRONIC STRUCTURE OF CONFORMATIONALLY DISORDERED CONJUGATED POLYMERS."*

February 4, 1986

Solid Mechanics Seminar: Gregory N. Brooks, Georgia Institute of Technology, *"ELASTIC-PLASTIC ANALYSIS OF AXISYMMETRIC SHELLS AND BOUNDARY INTEGRAL ANALYSIS OF SHELLS."*

February 5, 1986

Condensed Matter Physics Discussion Group and Journal Club: Dr. C. Thomsen, Brown Unviersity, *"PICOSECOND HIGH FREQUENCY ULTRASONIC MEASUREMENTS IN GLASSES."*

February 6, 1986

Physical Chemistry Tea Session: Seung Min Park, Brown University, *"ELECTRO-ACOUSTIC MEASUREMENT OF DIELECTRIC CONSTANT."*

February 7, 1986

Chemistry Colloquium: Professor Jack Saltiel, Florida State University, *"THE EFFECT OF SPIN STATISTICAL FACTORS ON DIFFUSION CONTROLLED REACTIONS."*

February 7, 1986

Solid Mechanics Seminar: Janet A. Blume, California Institute of Technology, *"SOME ISSUES IN THE KINEMATICS OF FINITE DEFORMATIONS."*

February 10, 1986

Solid Mechanics Seminar: Stewart A. Silling, California Institute of Technology, *"NUMERICAL STUDIES OF LOSS OF ELLIPTICITY IN ELASTOSTATICS."*

February 12, 1986

Condensed Matter Physics Discussion Group and Journal Club: C. Stanton, Cornell University, *"NON-EQUILIBRIUM CURRENT FLUCTUATIONS IN SEMICONDUCTORS: A BOLTZMAN EQUATION APPROACH."*

February 13, 1986

Condensed Matter Seminar: Dr. G. Grinstein, IBM, Yorktown Heights, *"SOME STATISTICAL MECHANICS OF PROBABILISTIC CELLULAR AUTOMATA."*

February 13, 1986

Inorganic Seminar: Raymond Brusasco, Brown University, *"ALUMINUM OXIDE ACICULAR PARTICLES AND THIN FILMS."*

February 13, 1986

Chemistry Colloquium: Professor Herbert Strauss, University of California - Berkeley, *"ELUCIDATION OF THE DISORDERED SOLID PHASES OF N-ALKANES BY VIBRATIONAL SPECTROSCOPY."*

February 14, 1986

Chemistry Colloquium: Professor Udayan Mohanty, Boston College, *"LATTICE MODEL FOR SELF-AVOIDING POLYMERS: CORRECTIONS TO FLORY-HUGGINS THEORY."*

February 17, 1986

Physics Colloquium: Professor Sidney Nagel, University of Chicago, *"SPECIFIC HEAT SPECTROSCOPY OF THE GLASS TRANSITION."*

February 19, 1986

Condensed Matter Physics Discussion Group and Journal Club: Dr. Pawel Hawrylak, Brown University, *"SCREENED COULOMBIC IMPURITY BOUND STATES IN SEMI-INFINITE MULTIPLE QUANTUM WELL SYSTEMS."*

February 20, 1986

Condensed Matter Seminar: Professor Charles N. Archie, SUNY - Stonybrook, *"POLARIZED ^3He LIQUID PROPERTIES FROM MELTING EXPERIMENTS: THE PROS AND CONS FOR A NEW METAMAGNETIC PHASE."*

February 20, 1986

Inorganic Seminar: Steve Davison, Brown University, *"MAGNETIC PROPERTIES OF THE DISPERSED TRANSITION METAL OXIDE SYSTEM: FE_2O_3/ZRO_2."*

February 20, 1986

Physical Chemistry Tea Session: David Cannon, Brown University, *"ELECTRO-ACOUSTIC EFFECTS IN AQUEOUS ELECTROLYTE SOLUTIONS AND COLLOIDAL DISPERSIONS."*

February 21, 1986

Solid Mechanics Seminar: Thomas N. Farris, Northwestern University, *"ON POSSIBLE MECHANISMS FOR THE TRANSITION FROM SHELLING TO DETAIL FRACTURE IN RAILS."*

February 24, 1986

Solid Mechanics Seminar: Peter A. Matage, Harvard University, *"DYNAMIC CRACK GROWTH IN RATE-SENSITIVE MATERIALS."*

February 27, 1986

Inorganic Seminar: Tim Alavosus, Brown University, *"SUCCESSIVE ADDITIONS OF CARBON-DONOR NUCLEOPHILES TO MAGANESE-COORDINATED n^6 AND n^5 RING SYSTEMS."*

February 27, 1986

Physical Chemistry Tea Session: John Tanner, Brown University, *"THE DISTORTED WAVE APPROACH TO ROTATIONALLY AND VIBRATIONALLY INELASTIC SCATTERINTG."*

February 28, 1986

Chemistry Colloquium: Professor Keith Nelson, MIT, *"ULTRAFAST TIME-RESOLVED SPECTROSCOPY OF STRUCTURAL PHASE TRANSITIONS. VIBRATING CRYSTALS AND MOLECULES AND CHEMICALLY REACTING MOLECULES."*

February 28, 1986

Solid Mechanics Seminar: Leonidas Paparizos, California Institute of Technology, *"SOME OBSERVATIONS ON THE RANDOM RESPONSE OF HYSTERETIC SYSTEMS."*

March 3, 1986

Physics Colloquium: Professor B. I. Halperin, Harvard University, *"FRACTIONAL QUANTUM HALL EFFECTS."*

March 4, 1986

Organics Seminar: Karen Inman, Brown University, *"IN VIVO APPLICATIONS OF HIGH FIELD NMR."*

March 6, 1986
Inorganic Seminar: Guang-Qing Yao, Brown University, *PREPARATION AND CHARACTERIZATION OF $ZnSiP_2$ AND $ZnGeP_2$ SINGLE CRYSTALS."*

March 6, 1986
Physical Chemistry Tea Session: Paul Muessig, Brown University, *"LASER PROBE OF SPIN RELAXATION AT SOLID SURFACES: THE HOLY GRAIL AND THE LAST HURRAH."*

March 6, 1986
Chemistry Colloquium: Professor Gideon Frankel, Ohio State University, *"STRUCTURE IN DYNAMIC BEHAVIOR OF ORGANOLITHIUM COMPOUNDS."*

March 6, 1986
Condensed Matter Seminar: Professor T. Lubensky, University of Pennsylvania, *"ELASTICITY, HYDRODYNAMICS AND DEFECTS IN QUASI-CRYSTALS."*

March 10, 1986
Solid Mechanics Seminar: Professor J. L. Bassani, University of Pennsylvania, *"MECHANICS OF CRACK GROWTH AT ELEVATED TEMPERATURES."*

March 10, 1986
Physics Colloquium: Professor T. A. Witten, Exxon Research & Engineering Co., *"TENUOUS STRUCTURES BY DISORDERLY GROWTH: NEW STRUCTURE AND PROPERTIES."*

March 12, 1986
Chemistry Colloquium: Professor Peter T. Wolczanski, Cornell University, *"PROGRESS IN EARLY TRANSITION METAL ORGANOMETALLIC CHEMISTRY."*

March 12, 1986
Condensed Matter Physics Discussion Group and Journal Club: Tony DeSimone, Brown University, *"THE ROLE OF INTERACTIONS IN CONTINUUM PERCOLATION."*

March 13, 1986
Physical Chemistry Tea Session: Diane Stewart, Brown University, *"SURFACE IONIZATION OF HYPERTHERMAL SODIUMA TOMS FROM Si(111) AND Pt."*

March 13, 1986
Inorganic Seminar: Karen Hagen, Brown University, "^{57}*Fe NMR."*

March 14, 1986
Chemistry Colloquium: Professor Myron Rosenblum, Brandeis University, *"VINYL ETHER IRON COMPLEXES. NEW STEREO AND ENANTIOSELECTIVE REGENTS FOR CARBON-CARBON BOND FORMATION."*

March 20, 1986
Inorganic Seminar: Cathy Camaioni, Brown University, *"ELECTROCHEMISTRY OF SOME MANGANESE CYCLOPENTADIENYL COMPLEXES - EFFECTS AT LOW TEMPERATURES."*

March 20, 1986

Physical Chemistry Tea Session: Professor Theodore F. Morse, Brown University, *"RESEARCH IN OPTICAL FIBERS."*

March 20, 1986

Condensed Matter Seminar: Dr. Larry Schwartz, Schlumberger-Doll Research, *"VIBRATIONAL AND ELECTRICAL PROPERTIES OF GRANULAR MATERIALS."*

March 21, 1986

Chemistry Colloquium: Drs. R. L. Taylor and M. A. Pickering, CVD Incorporated, *"CHEMICAL VAPOR DEPOSITION APPLIED TO PRODUCING NOVEL OPTICAL MATERIALS."*

March 27, 1986

Inorganic Seminar: Joyhn Cyr, Brown University, *"17-ELECTRON CENTERS AND ELECTRON-TRANSFER CHAIN CATALYSIS IN ORGANOMETALLIC SYSTEMS."*

March 31, 1986

Solid Mechanics Seminar: Dr. Shamita Das, Columbia and Harvard Universities, *"NUMERICAL STUDIES OF DYNAMIC SHEAR CRACK PROPAGATION."*

April 1, 1986

Solid Mechanics Seminar: Dr. Gilles Canova, Metz University, France, *"GRAIN SHAPE EFFECTS ON SLIP SYSTEM ACTIVITY AND ON LATTICE ROTATIONS."*

April 3, 1986

Physical Chemistry Tea Session: Elizabeth Rinden, Brown University, *"VIBRATIONAL PREDISSOCIATION OF NEGATIVE CLUSTER IONS."*

April 3, 1986

Inorganic Seminar: Chul Ho Jun, Brown University, *"HOMOGENEOUS C-C BOND ACTIVATION BY ORGANOMETALLIC COMPOUNDS."*

April 7, 1987

Solid Mechanics Seminar: Professor Alan Needleman, Brown University, *"ANALYSIS OF DUCTILE RUPTURE AT A CRACK TIP."*

April 8, 1986

Organic Seminar: Elizabeth West, Brown University, *"CAN METAL ALKOXIDES BE USED IN ORGANIC SYNTHESIS."*

April 10, 1986

Inorganics Seminar: Dr. John Bixler, State University of New York, *"ULTRAMICROELECTRODES: SMALLER CAN BE BETTER."*

April 10, 1986

Physical Chemistry Tea Session: Tao Tao, Brown University, *"ACTIVATION OF CHEMICAL REACTION BY IMPACT OF MOLECULES ON A SURFACE."*

April 16, 1986

Condensed Matter Physics Discussion Group and Journal Club Matthew J. Moelter, Brown University, *"He-4 SUPERFLUID-SOLID INTERFACE: ULTRASONICS AND SECOND SOUND"*

April 17, 1986
Inorganic Seminar: Anthi Kotsiliou, Brown University, *"SPECTRA STUDIES OF $TCNQF_4$ COMPLEXES."*

April 17, 1986
Physical Chemistry Tea Session: Laura Cooley, Brown University, *"ESR OF METHYL RADICALS IN SOLUTION."*

April 17, 1986
Condensed Matter Seminar: Dr. A. H. MacDonald, National Research Council, Canada, *"COLLECTIVE EXCITATIONS IN THE FRACTIONAL QUANTUM HALL REGIME."*

April 18, 1986
Chemistry Colloquium: Professor Anthony Haymet, University of California - Berkeley, *"FREEZING OF SIMPLE LIQUID."*

April 21, 1986
Physics Colloquium: Dr. Ravin Bhatt, ATT Bell Laboratories, *"THE ISING SPIN GLASS."*

April 23, 1986
Condensed Matter Physics Discussion Group and Journal Club: Dr P Hawrylak, Brown University, *"PLASMONS OF A QUASIPERIODIC SUPERLATTICE: A QUASIPERIODIC POISSON EQUATION. CHAOS AND CRITICALITY."*

April 24, 1986
Physical Chemistry Tea Session: Julie Child, Brown University, *"TRANSPORT OF NEGATIVE IONS IN ION BEAMS."*

April 24, 1986
Inorganic Seminar: Catherine Schwab, Brown University, *"COBALT PORPHYRINS: ELECTRONIC EFFECTS AS OBSERVED BY ^{59}Co NMR."*

April 25, 1986
Chemistry Colloquium: Professor Paul Barbara, University of Minnesota, *"SMALL-BARRIER ISOMERIZATION IN SOLUTION AND IN THE GAS PHASE."*

April 28, 1986
Solid Mechanics Seminar: Professor Kyung-Suk Dim, University of Illinois-Urbana, *"DYNAMIC BRITTLE FRACTURE PROCESSES IN 4-POINT BENDING EXPERIMENTS."*

April 28, 1986
Physics Colloquium: Dr. Gordon Thomas, ATT Bell Laboratories and Harvard University, *"METAL-INSULATOR TRANSITION."*

April 29, 1986
Organic Seminar: George Whitesides, Appleton Lecturer, *"THE PHYSICAL ORGANIC CHEMISTRY OF SURFACE AND THIN FILMS."*

May 1, 1986
Physical Chemistry Tea Session: Huy-Zu Cheng, Brown University, *"PHOTOACOUSTIC EFFECT IN KENETIC STUDY."*

May 1, 1986
Inorganic Seminar: Wendy Halpin, Brown University, *"ALKENE COMPLEXES FROM (ARENE) MANGANESE TRICARBONYL CATIONS: PRECURSORS TO FUNCTIONALIZED ARENES."*

May 1, 1986
Condensed Matter Seminar: Professor M. N. Silver, University of North Carolina, *"ELECTRONIC TRANSPORT IN AMORPHOUS SEMICONDUCTORS."*

May 2, 1986
Condenseed Matter Seminar: Dr. Stephen Bishop, Naval Research Laboratory, *"OPTICAL STUDIES OF III-IV SEMICONDUCTOR QUANTUM WELL STRUCTURES."*

May 5, 1986
Physics Colloquium: Dr. V. Narayanamurti, ATT Bell Laboratories, *"SEMICONDUCTOR SUPERLATTICES: WHAT GALLIUM ARSENIDE IC'S HAVE IN COMMON WITH THE QUANTUM HALL EFFECT."*

May 6, 1986
Solid Mechanics Seminar: Professor John J. Jonas, McGill University, Canada, *"A SIMPLIFIED DESCRIPTION OF PLASTIC ANISOTROPY OF TEXTURED POLYCRYSTALS."*

May 8, 1986
Inorganic Seminar: Larry Ytuarte, Brown University, *"CHROMYL TRIFLUOROACETATE AND THE ACTIVATION OF C-H BONDS."*

May 8, 1986
Physical Chemistry Tea Session: Jeony Sook Ha, Brown University, *"TEMPERATURE DEPENDENCE OF SURFACE STRUCTURES."*

May 15, 1986
Physical Chemistry Tea Session: Normand Tanquay, Brown University, *"ELECTRON DETACHMENT SPECTROSCOPY OF NEGATIVE IONS."*

June 23, 1986
Solid Mechanics Seminar: Professor M. Predeleanu, Universite of Paris, *"FINITE PLASTICITY ANALYSIS OF DAMAGE EFFECTS IN METAL FORMING PROCESSES."*

July 9, 1986
Solid State Seminar: Dr. E. Batke, Bell Laboratories, *"CYCLOTRON RESONANCE IN LAYERED TWO DIMENSIONAL ELECTRON GAS."*

July 9, 1986
Solid Mechanics Seminar: Professor B. Raniecki, Institute of Fundamental Technological Research, Polish Academy of Science, *"ASPECTS OF FINITE STRAIN PLASTICITY."*

July 11, 1986

Solid Mechanics Seminar: Professor K. L. Johnson, F.R.S., University of Cambridge, *"PLASTIC DEFORMATION, RESIDUAL STRESS AND SHAKEDOWN IN ROLLING CONTACT."*

July 17, 1986

Solid State Discussion Group Seminar: Dr. N. Read, Brown University, *"SCALING THEORY OF THE ELECTRON GLASS MODEL OF DISORDERED INSULATORS."*

July 18, 1986

Seminar: Dr. D. King-Smith, Exeter University, *"PLASMONS AND PHOTONS IN SUPERLATTICES."*

August 12, 1986

Solid Mechanics Seminar: Professor J. Zarka, Laboratoire de Mecanique des Solids, Ecole Polytechnique, France, *"MODELLING GLOBAL BEHAVIOR OF AGGREGATES."*

August 12, 1986

Solid State Seminar: Dr. Zhu, University of Toronto, *"PARAMAGNON CONTRIBUTION TO THE BANDWIDTH NARROWING IN SIMPLE METALS."*

August 14, 1986

Solid State Seminar: Dr. Grabowski, University of Colorado, *"NON-CONVENTIONAL MECHANISMS FOR SUPERCONDUCTIVITY IN HEAVY FERMION SYSTEMS."*

August 19, 1986

Solid Mechanics Seminar: Gerald N. Nurick, University of Capetown, *"LARGE PERMANENT DEFLECTIONS OF THIN PLATES SUBJECTED TO IMPULSIVE LOADING."*

September 5, 1986

Chemistry Colloquium: Brian Robinson, University of Otago, New Zealand, *"ELECTRON TRANSFER IN METAL CLUSTERS."*

September 11, 1986

Condensed Matter Seminar: Dr. Gunther Bauer, University of Leoben, Austria and Brown University, *"NARROW BAND GAP SEMICONDUCTOR SUPERLATTICES."*

September 24, 1986

Condensed Matter Physics Discussion Group and Journal Club: Professor A. Nurmikko, Brown University, *"RECENT RESULTS ON MAGNETIC SEMICONDUCTOR SUPERLATTICES."*

September 25, 1986

Physical Chemistry Tea Session: John Tanner, Brown University, *"THE EFFECT OF POTATIONS ON VIBRATIONAL ENERGY TRANSFER."*

September 25, 1986

Solid Mechanics Seminar: Professor James Dally, University of Maryland, *"DYNAMIC CRACK INITIATION."*

September 25, 1986

Condensed Matter Seminar: Dr. Allen Bray, Manchester University, England and Schlumberger-Doll Research Lab, *"THE ORDERED PHASE OF SPIN GLASSES."*

September 25, 1986

Inorganic Seminar: John O. Edwards, Brown University, *"A COMMON MECHANISTIC PATTERN FOR THE RADICAL DECOMPOSITIONS OF PEROXYMONOSULFATE ION."*

October 1, 1986

Condensed Matter Physics Discussion Group and Journal Club: Professor S-C Ying, Brown University, *"STRAINED LAYER EPITAXY."*

October 2, 1986

Condensed Matter Seminar: Professor M. Kardar, MIT, *"INTERFACES. QUENCHED IMPURITIES AND GROWTH."*

October 2, 1986

Inorganics Seminar: Professor Aaron Wold, Brown University, *"COOPERATIVE VENTURES IN SOLID STATE CHEMISTRY."*

October 2, 1986

Physical Chemistry Tea Session: Professor Edward F. Greene, Brown University, *"INTERACTION OF ALKALI ATOMS WITH SILICON SURFACES - EQUILIBRIUM AND DYNAMICS."*

October 3, 1986

Chemistry Colloquium: M. Matti Maricq, Brown University, *"SPIN THERMODYNAMICS. RELAXATION. AND THE MAGNUS PARADOX."*

October 6, 1986

Physics Colloquium: Dr. J. Demuth, IBM Research Laboratory, *"IMAGING OF SURFACE ATOMS AND THEIR WAVE FUNCTIONS WITH SCANNING TUNNELING MICROSCOPY."*

October 6, 1986

Solid Mechanics Seminar: Dr. Brice Cassenti, United Technologies Research Center, *"PHYSICAL CONCEPTS IN THE DEVELOPMENT OF CONSTITUTIVE EQUATIONS."*

October 8, 1986

Condensed Matter Seminar: Professor Patrick Lee, MIT, *"CONDUCTANCE FLUCTUATIONS IN DISORDERED METALS."*

October 16, 1986

Condensed Matter Seminar: Dr. Stroscio, IBM Watson Laboratories, *"RECENT DEVELOPMENTS IN SCANNING TUNNELING MICROSCOPY."*

October 16, 1986

Inorganics Seminar: Georgios D. Chryssikos, Brown University, *"SYNTHESIS AND STUDY OF NOVEL SEMICONDUCTING OXIDE GLASSES."*

October 17, 1986
Chemistry Colloquium: Peter Mazur, Leiden University, The Netherlands. *"ANAMALOUS LIGHT SCATTERING FROM A GROWING ICE CRYSTAL."*

October 23, 1986
Condensed Matter Seminar: Dr. A. T. Fiory, Bell Laboratories, *"STRAINED LAYER EPITAXY."*

October 24, 1986
Chemistry Colloquium: Thomas G. Spiro, Princeton University, *"HEMOGLOBIN STRUCTURE AND DYNAMICS FROM RESONANCE RAMAN."*

October 27, 1986
Physics Colloquium: Professor George Watkins, Lehigh University, *"ELECTRON-ELECTRON ATTRACTION NEAR A DEFECT IN A SOLID."*

October 27, 1986
Solid Mechanics Seminar: Professor J. Prevost, Princeton University, *"COMPUTATIONAL METHODS FOR THE ANALYSIS OF TWO-PHASE SOIL SYSTEMS.:*

October 30, 1986
Condensed Matter Seminar: Professor A. M. Tremblay, Cornell University, *"THE INFINITE SET OF EXPONENTS OF FRACTAL OBJECTS."*

October 30, 1986
Physical Chemistry Tea Session: Bret E. Jackson, University of Massachusetts, Amherst. *"THE DYNAMICS OF* H_2 *DISSOCIATION ON Ni(100): A QUANTUM MECHANICAL STUDY."*

October 31, 1986
Chemistry Colloquium: M-H. Whangbo, North Carolina State, *"STRUCTURAL AND ELECTRONIC PROPERTIES OF ORGANIC METALS."*

October 31, 1986
Condensed Matter Seminar: F. de la Cruz, San Carlos de Bariloche, Argentina, *"SUPERCONDUCTIVITY AS A TOOL TO STUDY DEFECTS IN AMORPHOUS MATERIALS."*

November 6, 1986
Inorganic Seminar: John D. Higgins, Brown University, *"AN ORGANIC CHEMIST VISITS THE THIRD FLOOR: STUDIES ON THE SYNTHESIS AND CHEMISTRY OF CYCLIC PALLADIUM COMPLEXES."*

November 6, 1986
Physical Chemistry Tea Session: John Schotland, Brown University, *"THE SOLVATED ELECTRON: SOME NEW APPROACHES TO AN OLD PROBLEM."*

November 7, 1986
Joint Electrical Sciences and Solid State Seminar: Professor Klaus Klingshirn, University of Frankfurt and Bell Laboratories, *"NONLINEAR AND DYNAMICAL OPTICAL BEHAVIOR IN COMPOUND SEMICONDUCTORS."*

November 12, 1986
Condensed Matter Physics Discussion Group and Journal Club: Professor R. [illegible], Brown University, *"QUASI-CRYSTALS."*

November 13, 1986
Condensed Matter Seminar: Dr. J. Smith, Los Alamos National Laboratory, *"HEAVY ELECTRON METALS."*

November 13, 1986
Inorganics Seminar: Michael Schwartz, Brown University, *"A STUDY OF METAL SURFACE INTERACTIONS."*

November 14, 1986
Chemistry Colloquium: G. Doyle Daves, Lehigh University, *"PALLADIUM-MEDIATED ARYLATION REACTIONS OF ENOL ETHERS."*

November 20, 1986
Special Chemistry Seminar: Alan Jacobson, Exxon Research & Engineering, Allendale, NJ, *"LOW TEMPERATURE SOLID STATE CHEMISTRY."*

November 20, 1986
Inorganics Seminar: Nancy Stone, Brown University, *"ELECTROCHEMISTRY OF (BENZENE) TRICARBONYLCHROMIUM AND OTHER π-HYDROCARBON COMPLEXES."*

November 20, 1986
Condensed Matter Seminar: Professor David Ronis, Harvard University, *"EQUILIBRIUM & NONEQUILIBRIUM PROPERTIES OF DILUTE COLLOIDAL SUSPENSION."*

November 20, 1986
Physical Chemistry Tea Session: Tim Su, Southeastern Massachusetts Institute, *"THE MAGIC OF ION MOLECULE CLOSE ENCOUNTERS."*

November 21, 1986
Chemistry Colloquium: Joseph Dinnocenzo, University of Rochester, *"CATION RADICAL EXPLORATIONS."*

November 25, 1986
Solid Mechanics Seminar: Mr. Donald E. Hawk, University of Pennsylvania, *"CRACK GROWTH IN SMALL SCALE CREEP."*

December 1, 1986
Solid Mechanics Seminar: Professor Walter Bradley, Texas A&M University, *"FRACTURE TOUGHNESS CHARACTERIZATION OF POLYETHYLENE USING A J-INTEGRAL APPROACH."*

December 1, 1986
Physics Colloquium: Professor Robert Westervelt, Harvard University, *"CHAOTIC DYNAMICS IN SEMICONDUCTORS."*

December 3, 1986
Chemistry Colloquium: Steve Bertz, ATT Bell Laboratories, *"NEW ORGANCOPPER CHEMISTRY."*

December 4, 1986
Physical Chemistry Tea Session: Robert Harris, University of California, Berkeley, *"PARITY VIOLATION IN HANDED MOLECULES AND THE DYNAMICS OF CHIRALITY."*

December 4, 1986
Condensed Matter Seminar: Professor P. Eklund, University of Kentucky, *"OPTICAL PROPERTIES OF INTERCALATED GRAPHITE."*

December 4, 1986
Solid Mechanics Seminar: Professor John C. Lambropoulos, University of Rochester, *"THE MICROMECHANICS OF INELASTIC DEFORMATION DURING THE GROWTH OF SEMICONDUCTOR MATERIALS IN BULK AND THIN FILM FORM."*

December 8, 1986
Solid Mechanics Seminar: Professor A. Chudnovsky, University of Illinois at Chicago, *"THE ROLE OF MICROEFFECTS IN FRACTURE."*

December 10, 1986
Condensed Matter Seminar: Dr. Gerald Iafrate, U.S. Army Electronics Technology and Devices Laboratory, *"BLOCH ELECTRON DYNAMICS & QUANTUM TRANSPORT IN ELECTRIC FIELDS."*

December 16, 1986
Solid State Seminar: Dr. J. Shacham, Technion, Israel, *"RECOMBINATION MECHANISM IN HgCdTe."*

December 17, 1986
Condensed Matter Physics Discussion Group and Journal Club: Dr. B. Minchau, K.F.A. Julich, Germany, *"GROWING QUASI-CRYSTALS IN 2 DIMENSIONS."*

January 12, 1987
Special Chemistry Seminar: Mark Hollingsworth, Cambridge University, Cambridge, England, *"STRESS AND MECHANISM IN SOLID STATE PHOTOCHEMISTRY."*

January 22, 1987
Inorganics Seminar: Cathy Schwab, Brown University, *"ELECTRONIC EFFECTS OF COBALT (III) PORPHYRINS AS OBSERVED BY* ^{59}*Co NMR."*

January 12, 1987
Special Chemistry Seminar: Lothar Brixner, E. I. DuPont de Nemours & Co., *"RECENT RESULTS ON THERMOLUMINESCENCE OF X-RAY IRRADIATED PHOSPHORS."*

January 25, 1987
Special Chemistry Seminar: Arnold Migus, Ecole Polytechnique at Palaiseau, France, *"FEMTOSECOND SPECTROSCOPY OF CHARGE TRANSFER IN PHOTOSYNTHETIC REACTION CENTERS AND ELECTRON SOLVATION IN WATER."*

January 26, 1987
Physics Colloquium: Professor R. B. Hallock, University of Massachusetts, Amherst, *"EXPERIMENTS IN SUPERFLUID FILMS - MAGIC IN 2 DIMENSIONS."*

January 29, 1987
Physical Chemistry Tea Session: Colman Shannon, Brown University, *"VELOCITY DISTRIBUTION OF ATOMS SCATTERED FROM SURFACES."*

January 29, 1987
Inorganics Seminar: Hyochon Bang, Brown University, *"OXYGEN DONATION TO MANGANESE (III) TETRAPHENYL PORPHYRIN."*

January 29, 1987
Condensed Matter Seminar: Dr. S. Teitsworth, Harvard University, *"NONLINEAR DYNAMICS. DETERMINISTIC NOISE AND HIGH FIELD DOMAINS IN SEMICONDUCTORS."*

January 30, 1987
Chemistry Colloquium: Lloyd Jackman, Pennsylvania State University, *"CARBANION REACTIONS: STRUCTURE AND MECHANISM."*

February 2, 1987
Solid Mechanics Seminar: Dr. Olaf Storaasli, NASA Langley Research Center, *"STRUCTURAL ANALYSIS METHODS FOR PARALLEL COMPUTERS."*

February 5, 1987
Physical Chemistry Tea Session: Yue Bu, Brown University, *"THE IONIZATION OF Na ON Si(111) SURFACE."*

February 5, 1987
Condensed Matter Seminar: Dr. B. Abeles, Exxon, *"AMORPHOUS SEMICONDUCTOR SUPERLATTICES."*

February 5, 1987
Inorganics Seminar: Jay Fournier, Brown University, *"PREPARATION AND INTERCALATION OF* TiS_2*."*

February 6, 1987
Chemistry Colloquium: Kenneth Schweizer, Sandia National Laboratories, *"PHASE TRANSITION AND OPTICAL PROPERTIES OF FLEXIBLE CONJUGATED POLYMERS."*

February 9, 1987
Solid Mechanics Seminar: Professor Richard Gallagher, Worcester Polytechnic Institute, *"FINITE ELEMENT ANALYSIS OF THIN SHELLS."*

February 11, 1987
Condensed Matter Physics Discussion Group and Journal Club: P. Weir, Brown University, *"RANDOM FIELD MODELS IN LOW DIMENSIONS."*

February 12, 1987
Physical Chemistry Tea Session: Steve Adachi, Brown University, *"ON THE ORIGIN OF THE PHASE TRANSITIONS IN A CLASS OF MIXED-VALENCE COMPOUNDS."*

February [illegible]
[illegible]
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February [illegible]
[illegible]
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February [illegible]
Chem[illegible]
[illegible]

February [illegible]
S[illegible]
Ca[illegible]

February [illegible]
Condensed Matter [illegible]
H[illegible]
SUPERCON[illegible]

February 19, 1987
Inorganic Seminar: [illegible]
REDUCTION PROPERT[illegible]

February 19, 1987
Joint Condensed Matter: H. [illegible]
University, *"QUANTUM SPIN C[illegible]*

February 19, 1987
Physical Chemistry Tea Session: N[illegible]
RESOLUTION DIODE LASER SPECTROSCOPY[illegible]

February 19, 1987
Solid Mechanics Seminar: Dr. M. A. Crisfield, Transport & Road Research Laboratory, Bridge Design Division, Berkshire, England, *"NONLINEAR FINITE ELEMENT ANALYSIS OF STRUCTURES."*

February 23, 1987
Chemistry Colloquium: Bruce Foxman, Brandeis University, *"SINGLE CRYSTAL REACTIONS OF METAL COMPLEXES."*

February 25, 1987
Solid Mechanics Seminar: Professor Mahir Sayir, E.T.H., Switzerland, *"HIGH-SPEED DEEP DRAWING OF HARDENING AND RATE-SENSITIVE SOLIDS."*

February 26, 1987
Solid Mechanics Seminar: Professor Rohan Abeyaratne, MIT, *"SOME OBSERVATIONS ON THE RESPONSE OF AN ELASTIC BAR WITH A NON-MONOTONE STRESS-STRAIN CURVE."*

[illegible] Seminar: Dr S. Bishop, Naval Research Laboratory, *"NMR [illegible] DOPED GALLIUM ARSENIDE."*

[illegible] Smith, Brown University, *"STABILIZATION OF Ni(II) VIA FORMATION OF A SOLID SOLUTION WITH* ZrO_2*."*

[illegible]: Professor Nick Aravas, University of Pennsylvania, *"THE [illegible] GROWTH THAT LEADS TO CENTRAL BURSTS DURING*

[illegible] Physics Discussion Group and Journal Club: Professor A. [illegible], Brown University *"MIXED VALENCE, KONDO-LATTICE, 1/N AND ALL THAT"*

[illegible] Seminar: Dr. Andre Mysyrowicz, Ecole Normale and Brown *"FEMTOSECOND SPECTROSCOPY OF GaAs MULTIPLE-QUANTUM WELLS"*

[illegible] Chemistry Tea Session: Huy-Zu Cheng, Brown University, *"CHEMICAL [illegible] IN DILUTE SOLUTION: PHOTOACOUSTIC DETECTION OF SMALL [illegible] CHANGES."*

[illegible] Seminar: Ping Wu, Brown University, *"CHARACTERIZATION OF CHROMIUM AND COBALT OXIDES IN THEIR SOLID SOLUTION WITH* ZrO_2*."*

[illegible] 1987
Physical Chemistry Tea Session: **Seung Min Park**, Brown University, *"ELECTRON IMPACT IONIZATION OF LASER EXCITED ATOMS."*

March 12, 1987
Condensed Matter Seminar: **Dr. J. Gunton**, Temple University, *"THE KINETICS OF ORDERING OF ADATOMS ON SURFACES."*

March 13, 1987
Chemistry Colloquium: **A. Welford Castleman, Jr.**, Pennsylvania State University, *"SHINING A LITTLE LIGHT ON CLUSTERS: IONIZATION, REACTIONS, AND DYNAMICS OF DISSOCIATION."*

March 13, 1987
Inorganics Seminar: **John Williams**, Brown University, *"ELECTROCHEMICAL REDUCTION OF PHOSPHONIUM SALTS HETEROCYCLES: MECHANISM AND pH DEPENDENCE."*

March 19, 1987
Physical Chemistry Tea Session: **Tao Tao**, Brown University, *"GAS-SURFACE INTERACTIONS: WITH THERMOCOUPLE AS A DETECTOR."*

March 19, 1987

Solid Mechanics Seminar: Professor B. Budiansky, Harvard University, *"MECHANICS OF TOUGHENED CERAMICS."*

March 19, 1987

Inorganics Seminar: Wendy Halpin, Brown University, *"SYNTHESIS AND REACTIONS OF (ARENE) Mn* $(CO)_2$ *(ALKENE) CATIONS."*

March 20, 1987

Chemistry Colloquium: Gene G. Wubbels, Grinnell College, *"GENERAL BASE CATALYSIS, INCLUSION COMPLEXATION, AND BRONSTED PLOTS AS PROBES OF PHOTOCHEMICAL SMILES REARRANGEMENTS."*

March 25, 1987

Special Condensed Matter Seminar: Dr. Cai-Zhong Wang, I.C.T.P. Trieste, *"MOLECULAR DYNAMICS SIMULATION OF DISPLACIVE SURFACE RECONSTRUCTION."*

March 30, 1987

Physics Colloquium: Dr. Martin Blume, Brookhaven National Laboratory, *"SYNCHROTRON RADIATION - SCIENCE AND TECHNOLOGY."*

March 30, 1987

Solid Mechanics Seminar: Professor Ren Wang, Peking and Yale Universities, *"FRACTURE DEVELOPMENT PROCESS OF A SLOT IN A MARBLE PLATE - EXPERIMENT AND FINITE-ELEMENT SIMULATION."*

April 1, 1987

Special Chemistry Seminar: Donald Hilvert, Scripps Oceanographic Institute, La Jolla, CA, *"STUDY AND DESIGN OF ENZYMES."*

April 2, 1987

Physical Chemistry Tea Session: Vladimir Dobrosavljevic, Brown University, *"TUNNELING IN DISORDERED CRYSTALS."*

April 2, 1987

Condensed Matter Seminar: Professor David Mukammel, IBM and Weizmann Institute, Israel, *"STABILITY OF QUASI CRYSTALS."*

April 2, 1987

Inorganic Seminar: Karen Hagen, brown University, *"THE COBALNITROAMMINES: MORE COMPLEX THAN ONE MIGHT THINK."*

April 6, 1987

Solid Mechanics Seminar: Professor George J. Dvorak, Rensselaer Polytechnic University, *"A BIMODAL PLASTICITY THEORY OF FIBROUS COMPOSITE MATERIALS."*

April 9, 1987

Physical Chemistry Tea Session: Elizabeth Rinden, Brown University, *"RO-VIBRATIONAL SPECTROSCOPY OF NO AND ITS DIMER."*

April 9, 1987
Inorganics Seminar: Jie Yu, Brown University, *"A STUDY OF THE INTERACTION BETWEEN IRON (III) OXIDE AND RUTILE."*

April 9, 1987
Condensed Matter Seminar: Dr. Nicholas Read, MIT, *"ORDER PARAMETER: CHERN-SIMONS TERM AND GINZBERG-LANDAU THEORY FOR THE QUANTIZED HALL EFFECT."*

April 10, 1987
Solid Mechanics Seminar: Professor Morton E. Gurtin, Carnegie-Mellon University, *"ON SOLIDIFICATION WITH INTERFACIAL ENERGY AND ENTROPY."*

April 13, 1987
Special Chemistry Seminar: John MacChesney, AT&T Bell Labs, *"CASE HISTORIES OF THE DEVELOPMENT OF OPTICAL FIBER PROCESSING: FROM THE DOUBLE CRUCIBLE TO SOL-GEL TECHNIQUES."*

April 13, 1987
Physics Colloquium: Professor Paul Chaikin, University of Pennsylvania, *"CLASSICAL WIGNER CRYSTALS AND LOIQUID FROM POLYBALLS."*

April 16, 1987
Condensed Matter Seminar: Professor Toyoichi Tanaka, MIT, *"PHASE TRANSITION OF POLYMER GELS."*

April 17, 1987
Chemistry Colloquium: Todd B. Marder, Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Ontario, Canada, *"TRANSITION METAL CATALYZED C-C BOND FORMATION VIA C-H ACTIVATION."*

April 20, 1987
Solid Mechanics Seminar: Professor James R. Rice, Harvard University, *"CRACK TIP FIELDS IN DUCTILE CRYSTALS."*

April 20, 1987
Physics Colloquium: Professor D. Nelson, Harvard University, *"CRACK TIP FIELDS IN DUCTILE CRYSTALS."*

April 20, 1987
Physics Colloquium: Professor D. Nelson, Harvard University, *"STATISTICAL MECHANICS OF CRUMPLED SURFACES."*

April 23, 1987
Physical Chemistry Tea Session: Jeong Sook Ha, Brown University, *"TEMPERATURE DEPENDENT STRUCTURAL PHASE TRANSITION OF SILICON SURFACES."*

April 23, 1987
Inorganic Seminar: Timothy Alavosus, Brown University, *"FUNCTIONALIZATION OF ARENES MEDIATED BY COORDINATION TO TRANSITION METALS."*

April 27, 1987

Physics Colloquium: Professor P. Pershan, Harvard University, *"LIQUID LIQUID CRYSTAL AND SOLID SURFACES."*

April 29, 1987

Special Chemistry Seminar: Fred Basolo, Northwestern University, *"THE KINETICS AND MECHANISMS OF REACTIONS OF METAL CARBONYLS REVISITED."*

April 30, 1987

Physical Chemistry Tea Session: Julie Child, Brown University, *"THRESHOLD PHOTODETACHMENT SPECTROSCOPY OF NEGATIVE IONS."*

April 30, 1987

Condensed Matter Seminar: Dr. S. Jackson, ATT Bell Labs, *"SPIN FLUCTUATIONS AND MAGNETIC POLARON EFFECTS IN DILUTED MAGNETIC SEMICONDUCTORS AND THEIR SUPERLATTICES."*

April 30, 1987

Inorganic Seminar: Cathy Camaioni-Neto, Brown University, *"MANGANESE AND RHENIUM: REDUCTIVE ELECTROCHEMISTRY OF SOME* η^5*-RING NITROSYL COMPLEXES."*

May 4, 1987

Solid Mechanics Seminar: Professor Jwo Pan, University of Michigan, *"ASYMPTOTIC CRACK TIP FIELDS FOR PLASTICALLY DEFORMING ORTHOTROPIC MATERIALS."*

May 7, 1987

Condensed Matter Seminar: Dr. P. Horn, IBM Watson Research Lab, *"ARE QUASI-CRYSTALS, CRYSTALS?"*

May 19, 1987

Solid Mechanics Seminar: Professor Zdenek P. Bazant, Northwestern University, *"LOCALIZATION OF DISTRIBUTED DAMAGE AND NONLOCAL FRACTURE ANALYSIS."*

May 28, 1987

Solid Mechanics Seminar: Professor F. K. Carlos Tome, University of Rosario, Argentina, *"SIMULATION OF RESIDUAL STRESSES IN HEXAGONAL CRYSTALS."*

LIST OF STAFF IN THE MATERIALS RESEARCH LABORATORY PROGRAM

DIVISION OF APPLIED MATHEMATICS

C. Elbaum, Professor
A. Hikata, Professor (Research)

DEPARTMENT OF CHEMISTRY

R. Brusasco, Graduate Student
Y. Bu, Graduate Student
G. D. Chryssikos, Graduate Student
R. H. Cole, Professor
S. Davison, Graduate Student
W. DeSisto, Graduate Student
G. J. Diebold, Professor
K. Dwight, Professor (Research)
P. J. Estrup, Professor
J. A. Fournier, Graduate Student
E. F. Greene, Professor
J. S. Ha, Graduate Student
E. D. Honig, Research Associate
A. Koutsiliou, Graduate Student
K. Kourtakis, Research Associate
W-H. Lee, Graduate Student
J. Massoyan, Graduate Student
P. R. Mussieg, Graduate Student
J. Petit, Sr. Technical Assistant
J. Prybla, Graduate Studnet
R. H. Ridgley, Research Associate
W. M. Risen, Professor
M. Schwartz, Research Associate
H. S. Shen, Research Associate
D. K. Stewart, Graduate Student
R. M. Stratt, Associate Professor
K. Smith, Graduate Student
J. W. Suggs, Associate Professor
K. Sun, Graduate Student
T. Tao, Graduate Student
D. E. Turcotte, Graduate Student
A. Wold, Professor
P. Wu, Graduate Student
G-Q. Yao, Research Associate
L. Ytuarte, Graduate Student
J. Yu, Graduate Student
Y. C. Zhang, Graduate Student
Z. D. Zhang, Research Associate

DIVISION OF ENGINEERING

R. J. Asaro, Professor
P. Beade, Graduate Student
R. Becker, Graduate Student
J. R. Brockenbrough, Graduate Student
C. Bull, Research Engineer
C. Champion, Research Associate
K-M. Cho, Graduate Student
T. A. Christman, Graduate Student
R. J. Clifton, Professor
H. Couque, Graduate Student
E. E. Crisman, Sr. Research Engineer
H. E. Deve, Graduate Student
J. Duffy, Professor
L. Ewart, Graduate Student
L. B. Freund, Professor
A. Gianakopoulous, Graduate Student
R. Godse, Graduate Student
K. A. Hartley, Graduate Student
X. Han, Graduate Student
S. V. Harren, Graduate Student
R. H. Hawley, Sr. Research Engineer
L. A. Hermann, Sr. Research Engineer
S. Huang, Research Associate
J. Leighton, Graduate Student
Y. Leroy, Graduate Student
C. McCullough, Research Asociate
A. Marchand, Research Associate
T. Marieb, Undergraduate Student
H. Mei, Graduate Student
A. Molinari, Visiting Assistant Professor
B. Moran, Graduate Student
T. F. Morse, Professor
A. Needleman, Professor
S. R. Nutt, Assistant Professor
M. Ortiz, Professor
W. R. Patterson, Sr. Research Engineer
R. Paul, Technical Assistant
G. Povirk, Graduate Student
J. C. Ramirez, Graduate Student
G. Ravichandran, Graduate Student
J. J. Rosenberg, Assistant Professor
O. Soldes, Undergraduate Student
C. F. Shih, Professor
H. Stanton, Technical Assistant
S. Suresh, Professor
M. Symington, Graduate Student

D. J. Hymes, Graduate Student
R. J. Kershaw, Sr. Research Engineer
T. Kirst, Sr. Research Engineer
R. W. Klopp, Graduate Student
G. LaBonte, Technical Assistant
S. Lee, Graduate Student
J. Tauc, Professor
W. Tong, Graduate Student
V. Tvergaard, Visiting Professor
A. Varias, Graduate Student
J. H. Weiner, Professor
A. Wold, Professor

DEPARTMENT OF PHYSICS

M. Altman, Graduate Student
P. J. Bray, Professor
A. Dabiran, Graduate Student
P. De, Graduate Student
V. Dobrosavljevic, Graduate Student
C. Elbaum, Professor
P. J. Estrup, Professor
H. Fang, Graduate Student
J. Gao, Graduate Student
H. Grahn, Graduate Student
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J. Luo, Graduate Student
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M. B. Manning, Graduate Student
H. J. Maris, Professor
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M. J. Moelter, Graduate Student
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P. J. Stiles, Professor
H. Stoddart, Graduate Student
A. Sudbo, Graduate Student
S. P. Szu, Graduate Student
J. Tauc, Professor
S. Tiersten, Graduate Student
N. Thantu, Graduate Student
C. Thomsen, Graduate Student
P. Williams, Undergraduate Student
H. Won, Graduate Student
S. C. Ying, Professor
D. Young, Graduate Student
R. Zeller, Sr. Research Engineer
X. C. Zhang, Graduate Student
J. Zhong, Graduate Student
T. X. Zhou, Graduate Student

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