

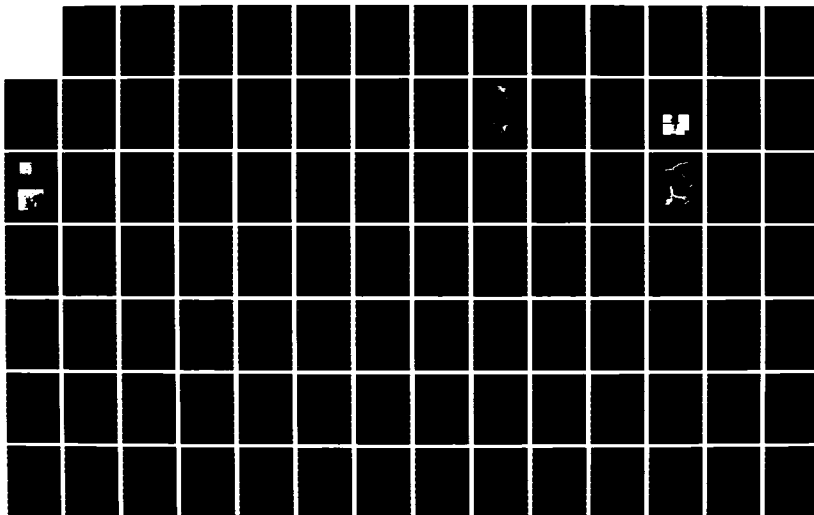
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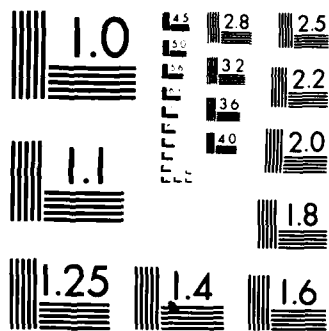
ANNUAL TECHNICAL REPORT MATERIALS RESEARCH LABORATORY 1 1/2
JULY 1984 - 30 JUNE 1986(U) BROWN UNIV PROVIDENCE RI
MATERIALS RESEARCH LAB 30 JUN 86 NSF-DNR83-16893

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MATERIALS RESEARCH LABORATORY
July 1, 1984-June 30, 1985

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**ANNUAL TECHNICAL REPORT
MATERIALS RESEARCH LABORATORY**

**BROWN UNIVERSITY
PROVIDENCE, RHODE ISLAND 02912**

A Report on Grant No. DMR-8316893

from the

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Washington, D.C. 20550

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TABLE OF CONTENTS

| | <u>Page</u> |
|--|-------------|
| Preface | 1 |
| Section 1 - Plasticity and Fracture | |
| Introduction | 2 |
| Research Results | 4 |
| Section 2 - Inorganic Glasses | |
| Introduction | 54 |
| Research Results | 56 |
| Section 3 - Solid Surfaces | |
| Introduction | 86 |
| Research Results | 87 |
| Section 4 - New Initiatives | |
| Introduction | 100 |
| Research Results | 101 |
| Section 5 - Materials Preparation | |
| Introduction | 109 |
| Research Results | 110 |
| Section 6 - Selected Materials Research at Brown University Outside the MRL Program | |
| Introduction | 116 |
| Research Results | 118 |
| Lectures in the Materials Research Laboratory Program, 1984-85 | 139 |
| List of Staff in the Materials Research Laboratory Program | 150 |
| Index of Principal Investigators | 151 |

PREFACE

In 1984/85, the main thrusts of interdisciplinary research supported by the Materials Research Laboratory at Brown University 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, MRL supported three New Initiatives:

Physical and Electronic Properties of Ge_3N_4 -Ge Interfaces (J. Rosenberg)
Surface Modification of Polymers (J. W. Suggs)
Conformational and Electronic Transitions in Macromolecular Systems
(R. Stratt and J. H. Weiner)

The MRL research was supported by six Central Facilities:

Materials Preparation Facility (directed by A. Wold)
Facility for Mechanical Testing (R. J. Clifton)
Electron Microscopy Facility (M. H. Richman)
Optical Facility (J. Tauc and W. M. Risen, Jr.)
Electron Spectroscopy Facility (P. J. Estrup)
Microelectronics Facility (P. J. Stiles and W. R. Patterson)

These Facilities provided supportive services for the MRL program and were also active in research on new techniques or new materials. The Materials Preparation Facility was involved in activities supporting some research programs on a national scale and we report on this Facility in a separate section.

In an attempt to make this report more useful we include also some selected materials research programs at Brown outside the MRL. These are an extended interdisciplinary program on Interfaces and Superlattices, studies of Ionomers and Molecular Complexes, Materials Properties at Low Temperatures and Transport of Material Through Membranes.

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, L. N. Cooper, P. J. Estrup, A. Houghton and P. J. Stiles).

SECTION 1 PLASTICITY AND FRACTURE

Introduction

The research program at Brown in the area of mechanics-of-materials is concerned with the study of phenomena occurring over a broad spectrum of size scales, from atomic, to microstructural, to continuum. In fact, a major objective of the program has been the development of a comprehensive understanding of the relationship of chemistry, material microstructure and microscale phenomena to macroscopic behavior. Major themes of the research conducted this past year have included: 1) the effects of strain rate dependence on elastic-plastic response, 2) unstable and localized plastic flow, 3) ultra high rate plastic flow at strain rates of up to 10^7 s^{-1} , 4) dynamic crack propagation, in particular as related to cleavage crack propagation and 5) the development of micromechanical and macromechanical models for plasticity and fracture. In addition, as should be clear from the research descriptions that follow, the projects typically involve combined experiment and theoretical analysis. In recent years much of this theoretical work has involved a good deal of computer computations and in the past year, in particular, a good deal of supercomputing. During the past year our work on the micromechanics of fracture and localized plastic flow has involved analytic electron microscopy.

Research at Brown has led to unique experimental and theoretical work on dynamic plasticity and crack growth. During the past year these techniques have been used to study the formation of shear bands during dynamic loading and crack propagation under conditions of stress wave loading. This work has been combined with fundamental experimental studies of dislocation generation and motion at plastic strain rates of order 10^7 s^{-1} . The experimental work on shear bands is particularly concerned with the measurement of the highly nonuniform temperature distribution that is associated with localized deformation occurring at ultra high strain rates. Very new experimental work has been concerned with electron microscopy studies of the internal structure of shear bands and with using TEM observations to correlate the micromechanisms with macroscopic behavior. The theoretical work, on the other hand, has been aimed at understanding the influence of material strain rate sensitivity and temperature dependence of inelastic response, in general, and in particular on the development of nonuniform and localized deformation. These analyses, which are accomplished by combined numerical and analytical methods, are directly compared to the experimental observations.

Experimental work on fracture in plain carbon steels this past year has led to detailed correlations of microstructures and observed micromechanisms of quasi-static and dynamic fracture and macroscopic fracture toughness behavior. This work has been combined with novel theoretical studies of crack tip behavior carried out by computer methods. In particular, finite element studies of crack tip deformation have been carried out using constitutive models that account for void initiation and growth which lead to a loss in strength and ultimately to material failure. Other work on fracture during cyclic loading has led to correlations between chemistry,

microstructure and fracture behavior in 'new generation' Al-Li alloys. In this work, which has now been extended to other alloys as well as ceramics, compressive testing techniques have been developed which allow study of crack growth and fracture mechanisms in more brittle materials. Other studies of crack tip behavior include dynamic and high strain rate effects which are similarly used to analyze the dynamic fracture experiments. In this work novel 3-dimensional numerical methods have been developed which have led to a relatively complete understanding of the process of crack tip behavior in materials which are nearly strain rate insensitive and only weakly strain hardening; these methods are being used to describe crack tip behavior and crack propagation in materials that are strain rate dependent. These analyses are also being used to interpret experiments on dynamic crack propagation in high strength steels. New work has been concerned with theoretical analysis of crack tip behavior in high rate atomically sharp cracks. These analyses provide an emerging framework for new types of analysis of the ductile-to-brittle transition.

Theoretical work on localized deformation has demonstrated quite clearly that many of the most fundamental features of deformation, in particular the stability of homogeneous patterns of deformation versus tendencies toward the development of localized and unstable deformation, depend sensitively on the details of constitutive description. For example, stress and strain state and stress-strain path dependent strain hardening properties have been shown to be pivotal in the prediction of localized shearing. On the other hand, phenomenological theories which are in widespread use in the engineering literature do not account for these critical dependencies. A major thrust the past 2-3 years has been the development of large strain, strain rate dependent models for polycrystals. Specific aims of these models are: 1) to describe large strain, path dependent strain hardening, 2) to predict the formation of deformation textures and anisotropy along with the effect of texture on constitutive behavior, 3) to interpret and guide experiments on large strain, strain hardening behavior, and 4) to guide the development of analytically tractable large strain constitutive models which can then be used in the numerical simulation of specific deformation processes.

The research summaries that follow describe projects concerned with the above mentioned topics along with research on a series of closely related phenomena in two-phase polycrystalline materials, single crystals and metallic glasses. Although these research descriptions are not arranged in any particular order, the links between them and how they address the major themes listed above should be clear.

R. J. Asaro, Coordinator

Research Results

Fracture of 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:

A new dynamic fracture experiment has been developed for imposing crack-tip loading rates as high as $K_I = 10^8 \text{ MPa m}^{1/2} \text{ s}^{-1}$ under well characterized conditions. These loading rates are comparable to those that occur under impact loading of structures containing pre-existing cracks. The experiment involves the impact of a circular disc with a mid-plane, prefatigued, edge crack that has propagated halfway across the diameter. (See Fig. 1). A compressive pulse propagates through the specimen, reflects from the rear surface, and subjects the crack plane to a step tensile pulse. The motion of the rear surface of the specimen is monitored with a laser interferometer. Analytical solutions for the diffraction of the loading wave by the crack, as well as numerical solutions for the waves radiated from the crack-tip as the crack begins to advance, are used to compare predictions based on various crack propagation models with the measured motion at the rear surface.

Research Achievements:

During the past year this experiment has been extended to low temperatures in order to study fracture in the cleavage mode. Tests on a 4340 VAR steel have been conducted at temperatures down to -110°C . Cleavage is observed to occur across grains, but fracture due to ductile hole growth occurs near grain boundaries. At these low temperatures, crack extensions are relatively large - - as large as 6 mm - - for tensile pulse durations of only 1.0×10^{-6} sec. Through integration of the equations of motion for a crack in an elastic solid, the velocity-time profile for the crack tip has been related to the applied loading and a material-specific value of the stress intensity factor that must be sustained by the applied loading in order to sustain crack growth. Based on this analysis it is evident that the duration of crack extension is considerably larger than that of the incident pulse. As a result, the maximum crack velocity in the high velocity experiments is less than the change in length of the fracture divided by the duration of the incident stress pulse. The maximum crack-tip velocity is, however, relatively high (greater than 90% of the Rayleigh surface wave speed in some cases). Inferred values for the critical stress intensity factor are comparable to those expected for cleavage fracture. Further interpretation of the experiments through numerical solutions of the corresponding mixed initial and boundary value problem is continuing. Overall, it appears that the change in crack length is quite a sensitive indicator of the susceptibility of the material to dynamic fracture.

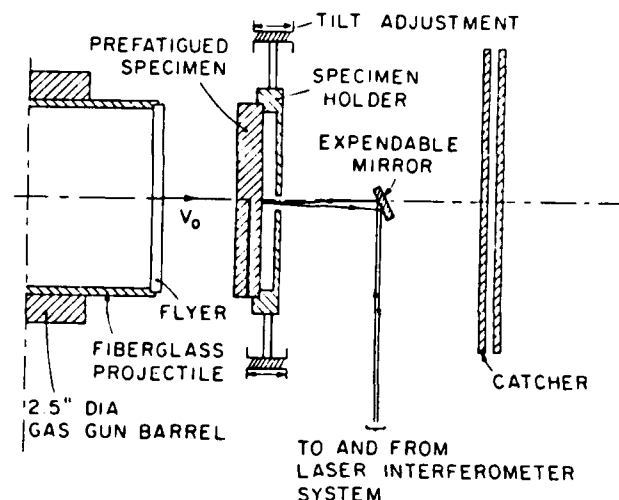


Figure 1: Schematic of dynamic fracture experiment

Plastic Flow of Metals at Strain Rates up to 10^7 sec^{-1}

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

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

Sources of Support: ARO, NSF and MRL

Objectives and Approaches:

The plastic response of metals at high strain rates is important in such applications as high speed machining, high rate forming and high velocity impact. In these applications, failure often occurs by the formation of bands of localized shearing deformation or by the high speed propagation of cracks. Within shear bands, as well as in the immediate neighborhood of the tips of propagating cracks, the strain rate is greatly intensified, resulting in plastic strain rates of 10^4 sec^{-1} to 10^7 sec^{-1} , using Kolsky bar techniques. We introduced the pressure-shear plate impact experiment and obtained the flow stresses of several metals up to strain rates of approximately 2×10^5 . Recently we extended the range of strain rates up to 10^7 sec^{-1} by reducing the specimen thickness to approximately $3 \mu\text{m}$. Such very thin specimens of iron and aluminum were prepared by vapor deposition.

Research Achievements:

During the past year the dynamic plastic response of high purity copper has been investigated at strain rates from approximately 10^5 sec^{-1} to 10^7 sec^{-1} . However, the microstructures of the lapped specimens strained at 10^5 sec^{-1} and the vapor-deposited specimens strained at $10^6 - 10^7 \text{ sec}^{-1}$ are markedly different. Thus, there is uncertainty as to whether the large increase in flow stress is due primarily to differences in microstructure or to increased strain rate. Preparation of $3 \mu\text{m}$ -thick specimens by either vapor deposited or rf-sputtering resulted in the same values for the measured flow stress at strain rates of approximately $7 \times 10^6 \text{ sec}^{-1}$. On the other hand, essentially the same flow stress was obtained at a strain rate of $5 \times 10^5 \text{ sec}^{-1}$ for a $38 \mu\text{m}$ -thick specimen prepared by rf-sputtering. This relative lack of strain rate sensitivity for the same microstructure suggests that a significant part of the large increase in flow stress at high strain rates may be due to differences in microstructure.

Progress has also been made in the inclusion of temperature changes in the interpretation of high strain rate pressure-shear experiments. Inclusion of heat generation due to plastic working, and inclusion of heat conduction, leads to the conclusion that tests at strain rates of 10^5 sec^{-1} , for specimen thicknesses of approximately 0.3 mm, are essentially adiabatic. However, in the tests at strain rates above 10^6 sec^{-1} and specimen thicknesses below $40 \mu\text{m}$, significant fractions of the heat are conducted into the bounding elastic plates. Corrections for this heat loss have been introduced in determining phenomenological constitutive relations from measured stress-time and strain-time histories.

Publications:

R. W. Klopp, R. J. Clifton and T. G. Shawki, "Pressure-Shear Impact and the Dynamic Viscoplastic Response of Metals," (to appear in Mechanics of Materials).

T. G. Shawki, J. P. Yang and R. J. Clifton, "Calculation of the Visco-Plastic Response of Polycrystals from Slip Theory for f.c.c. Single Crystals," (Preprint), 22nd Annual Meeting, Society of Engineering Science, held at Penn State University, October, 1985.

S. Huang and R. J. Clifton, "Dynamic Plastic Response of OFHC Copper at High Shear Strain Rates," Proceedings of the IUTAM Symposium on Macro- and Micro-Mechanics of High Velocity Deformation and Fracture, held in Tokyo, Japan, August, 1985.

R. J. Clifton, "Stress Wave Experiments in Plasticity," International Journal of Plasticity 1, 1985, 289-302.

Dislocation Dynamics of Plastic Flow

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

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

Sources of Support: MRL and NSF

Objectives and Approaches:

Fundamental understanding of the plastic flow of crystalline solids requires an understanding of the motion and generation of dislocations due to applied stresses. An attractive experiment for advancing this understanding for high stress levels is a plate impact experiment for determining changes in dislocation configurations in a single crystal due to a single passage of a known stress pulse. This "soft-recovery" experiment provides fundamental information on the mobility and generation of dislocations. In this experiment a square single crystal is impacted by a thin plate to generate a plane stress pulse with a duration of $0.25 \mu\text{sec}$ or less. The longitudinal momentum of the pulse is trapped by a plate behind the specimen so that the stress pulse caused by impact passes through the crystal only once. Also, the face of the plate impacting the specimen is star-shaped to prevent lateral unloading waves from propagating through a central region of the crystal. In this way, such a central region is subjected to a known stress pulse. Differences between the dislocation configurations in the crystal before and after the test can be used with the known stress history to assess the validity of proposed models for dislocation mobility and generation.

Research Achievements:

Significant progress was made during the past year in understanding the effect of temperature on dislocation mobility and generation. The impact configuration was modified to that shown in Fig. 2 in order to allow the specimen temperature to be reduced to approximately 100°K . Results of such experiments on high purity LiF show that the mobility of dislocations is enhanced at low temperatures. In particular, at the lowest temperatures, no fractures are found in the recovered samples. Furthermore, the attenuation of stress pulses due to plastic flow increases monotonically with decreasing temperature. However, the increased mobility of dislocations is considerably less than that predicted by phonon drag models in which the drag coefficient is commonly regarded as being proportional to the absolute temperature. Dislocation generation at low temperatures is similar to that at room temperature except that, at higher impact velocities, there appears to be an instability in which bands of intense shear develop and run through the full thickness of the crystal. Understanding these observations is expected to contribute to overall improvement in the understanding of the mobility and generation of dislocations.

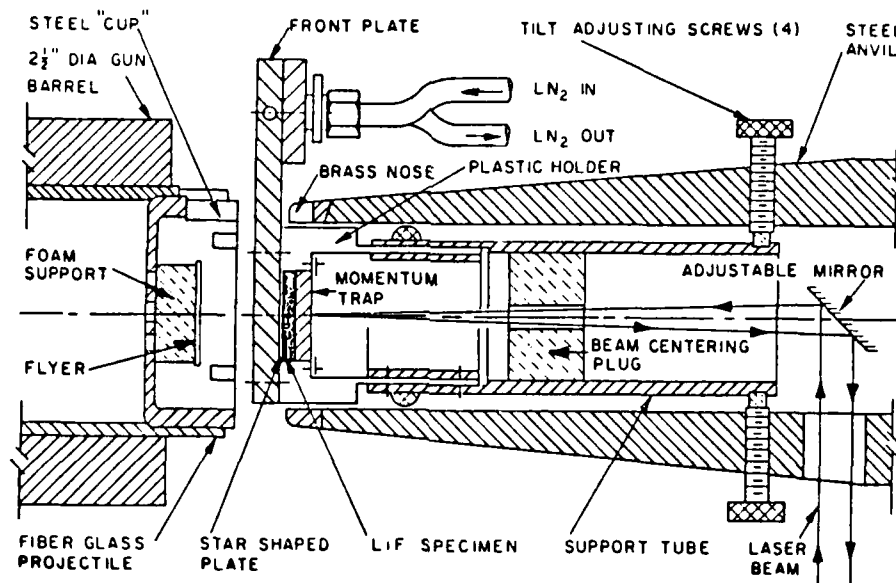


Figure 2: Experimental configuration for recovery experiment with cooling capability

Publications:

G. Meir and R. J. Clifton, "The Effect of Dislocation Generation at Surfaces and Subgrain Boundaries on Precursor Decay in High Purity LiF," J. Appl. Phys. 59, 1986, pp. 124-148.

G. Meir and R. J. Clifton, "Temperature Effects on Dislocation Nucleation and Mobility in Shocked Single Crystals of Pure LiF," (in press).

G. Meir, "Dislocation Mobility in Pure LiF Under Shock Loading," Ph.D. Thesis, Brown University, June, 1985.

Quantum Rate Processes

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

Personnel: K. F. Lau, Graduate Student, Department of Physics

Sources of Support: MRL and Gas Research Institute

Objectives and Approaches:

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

An important open question is the appropriate domain of application of two types of approaches to tunneling calculations, namely the energy-splitting method and the transmission function method. It might be thought that comparison of theoretical predictions with experiment should provide decisive discrimination between the theories, and such comparisons have been attempted. The results of such comparisons are far from conclusive because tunneling rates are sensitively dependent upon the effective potential employed, and it is difficult to determine this potential for a given system from first principles in an unequivocal manner. In fact, one important use of a reliable theory would be to determine the potential from experimentally measured tunneling rates in an inverse manner.

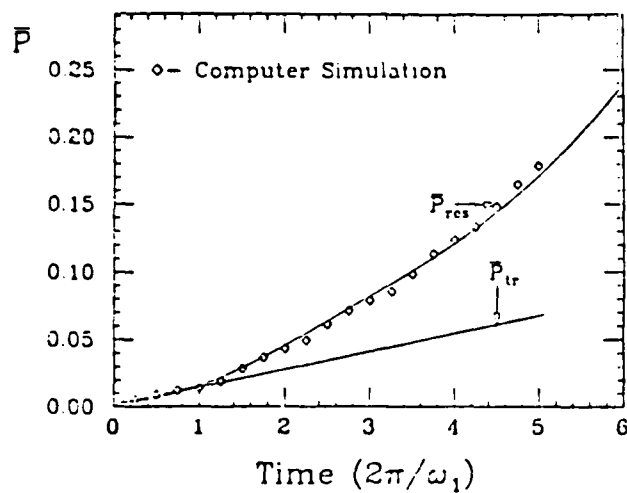
Research Achievements:

We have attempted to gain insight into the domains of validity of the energy-splitting method and the transmission function method by the computer simulation of a coupled quantum-classical model of two degrees of freedom. The former may be regarded as representing, for example, a light impurity atom in a lattice while the latter represents a massive neighboring host atom. A double-well potential couples the two. To introduce thermal effects, the classical particle is described by a Langevin equation.

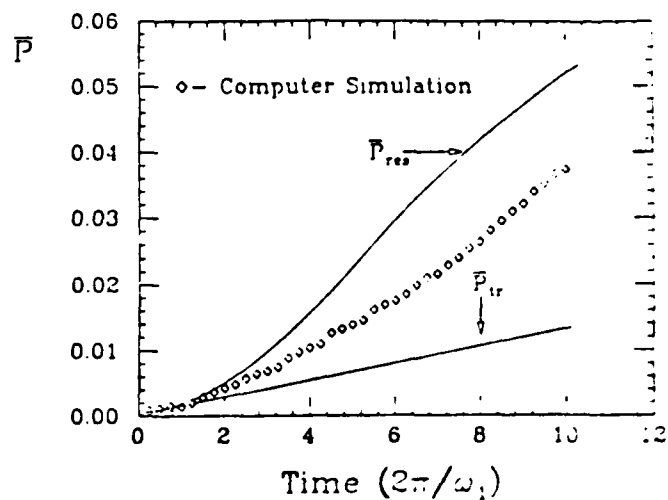
The computer simulation results show that, with all other parameters held fixed, tunneling through low energy barriers is governed by energy-splitting while for high energy barriers the transmission approach agrees well with simulation results. Examples of the transition in behavior is shown in the accompanying figure. Furthermore, when the transmission approach is applicable, the computer simulation results agree very well with the predictions of the form of the theory¹ developed earlier under this program.

References:

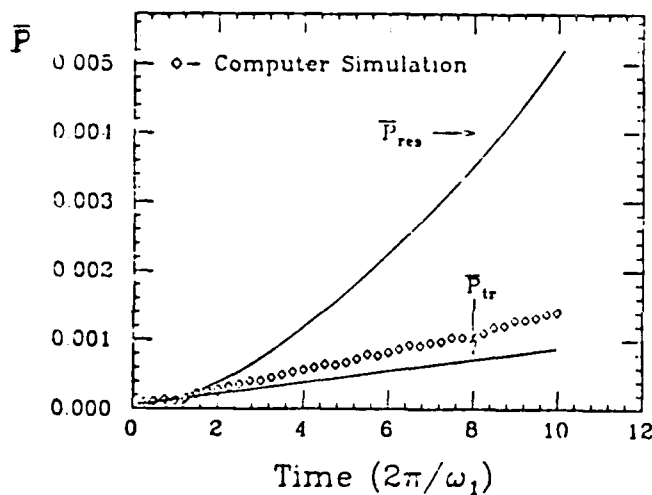
J. H. Weiner, J. Chem. Phys. 68, 2492 (1978).



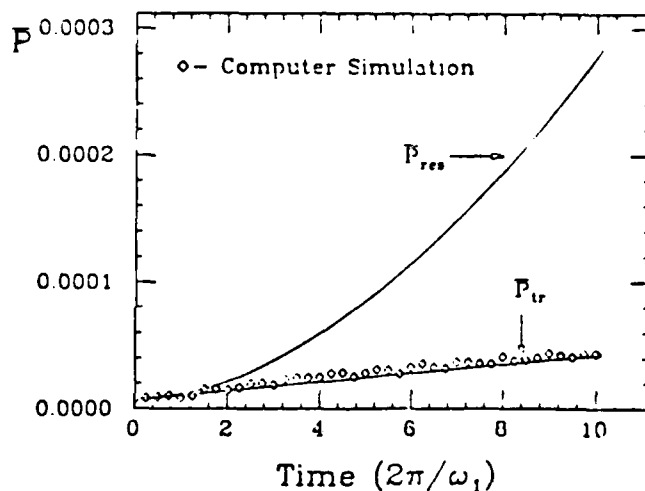
(a)



(b)



(c)



(d)

Figure 3: Change in character of tunneling history, $\bar{P}(t)$, as barrier height, E_b , is increased with all other parameters held fixed. (a) $E_b/\hbar\omega_1 = 2.25$ (b) $E_b/\hbar\omega_1 = 3.06$ (c) $E_b/\hbar\omega_1 = 4.00$ (d) $E_b/\hbar\omega_1 = 5.06$ with ω_1 the classical circular frequency of light particle in its potential well. Solid curve, \bar{P}_{res} , is theory based on energy-splitting while solid curve, \bar{P}_{tr} , is based on transmission function theory.

Publications:

K. F. Lau and J. H. Weiner, "Computer Simulation of Temperature Effects on Tunneling Rates," Chem. Phys. Lett. 114, 261 (1985).

K. F. Lau and J. H. Weiner, "Transmission Function vs. Energy Splitting in Tunneling Calculations. II. Computer Simulation Results," J. Chem. Phys. 83, 1567-1572 (1985).

Tunneling Motion of Dislocation Kinks

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

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

Sources of Support: MRL

Objectives and Approaches:

This investigation is a part of our research program on the microscopic mechanisms that govern the motion of dislocations and of kinks in crystalline solids. We are using an approach developed in the context of studying low temperature properties of amorphous solids and adapting it to the case of kink motion, as follows.

A phenomenological model for two-level tunneling systems (TLS) was worked out in considerable detail to explain experimentally observed low-temperature thermodynamic and transport properties of amorphous materials. The model assumes that low-energy excitations arise from the quantum mechanical tunneling of some entity (an atom or group of atoms) between the two minima of an asymmetric double-well potential. In addition, the model assumes a broad and smooth distribution in the energy of the tunneling states. While the model was initially developed in connection with the properties of amorphous solids, it also proved to be applicable in explaining observations on crystals containing various amounts of disorder, which result in TLS. Among the other features, the TLS model accounts well for the observed "anomalous" temperature dependence, at low temperatures ($T \ll 1K$), and ultrasonic velocity change, $\Delta V/V$, in amorphous and disordered materials. This dependence consists of a linear increase of $\Delta V/V$ with $\ln T$ at low temperatures, followed by a maximum and a rapid decrease as the temperature increases further. Here we report results on the temperature dependence of ultrasonic velocity in an aluminum single crystal in the superconducting state, which also has the above characteristics ($\ln T$ dependence, etc.). This behavior is induced by the application of a small bias stress and is suppressed when the sample is put in the normal state. We interpret these results in terms of tunneling of TLS associated with kinks on dislocations and we provide evidence of the suppression of tunneling in the presence of dissipation.

Research Achievements:

We have observed unusual behavior of the temperature dependence of sound velocity and amplitude dependence of attenuation in an aluminum single crystal when the sample is in the superconducting state and is subjected to a bias stress. The observed behavior is similar to that found in metallic glasses at low temperatures ($T < 1\text{K}$), where it has been explained in terms of two level tunneling systems (TLS). We interpret our results on aluminum in terms of tunneling of dislocations (kinks between the two levels of adjacent potential wells) produced by the bias stress. In the normal state, the effect of damping on the observed tunneling due to electrons, is to suppress the process.

Publications:

A. Hikata and C. Elbaum, "Tunneling of Dislocation Kinks and the Effect of Dissipation," Phys. Rev. Letters 54, 2418 (1985).

A. Hikata and C. Elbaum, "Ultrasonic Studies of Dislocation TLS in Aluminum Single Crystals," Journal de Physique 46, C10-293 (1985).

Ultrasonic Studies of Materials during Deformation

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

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

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 frequency ultrasonic wave attenuation and velocity changes concurrently (i.e., in real time) with application of the 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:

We have been able to separate, for the first time, the effects of mobile dislocations from those of immobile dislocations, in a crystal undergoing plastic deformation. This is accomplished by an analysis of changes in ultrasonic attenuation measured simultaneously with strain and strain rate, while a stress pulse propagates through the sample. An extension of the attenuation measurements beyond the time of stress pulse passage allows us to determine the ratio of mobile to "stationary" dislocations. These studies have been conducted at room temperature and will be extended to lower temperatures.

Crystal Defects and Deformation Studies in Quantum Solids

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

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

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 ^3He in ^4He . In this case the motion of the ^3He 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 to 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 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 kinks³), where unambiguous evidence of such delocalization effects from 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 ⁴He, plastic flow appears to proceed by thermally activated dislocation motion. Plastic flow in the bcc phases of ³He and ⁴He, however, has been both less thoroughly investigated and less readily attributable to dislocation slip than in the case of the hcp ⁴He. In fact, we proposed, on the basis of the small ultrasonic attenuation increases and evidence for localized deformation in bcc ⁴He 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 ⁴He 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:

One of the objectives of the present study was to investigate plastic flow in bcc ³He in a manner similar to our earlier bcc ⁴He plasticity experiments. In the present experiment it was found that stress-strain curves of bcc ³He were quite distinct from those of hcp ⁴He and very similar to those of bcc ⁴He. It was not possible, however, to satisfactorily account for the relationship between the flow stress and the strain rate in bcc ³He over the temperature range investigated by either a vacancy diffusion mass transport or by classical dislocation slip motion alone. Instead, a model involving both of these mechanisms gives good agreement with the experimental results and yields a value for the bandwidth of delocalized vacancies.

Localized Shearing in Crystalline Materials

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

Personnel: H. Deve, Graduate Student, Division of Engineering
C. McCullough, Research Associate and Lecturer, Division of Engineering
S. Harren, Graduate Student, Division of Engineering

Sources of Support: Metallurgy Section DMR, NSF, MRL, Office of Advanced Scientific Computing

Objectives and Approaches:

Localization of deformation into shear bands is a common mode of ductile rupture that limits ductility and toughness in plastically deformable materials. During the past several years we have developed experimental techniques and theoretical (computational) methods to study the microstructural and crystallographic aspects of shear band formation and to link these with macroscopic behavior. Past experimental work led to an understanding of the effects of precipitate type, strength and strain hardening on shear localization which was compared to the results of computational (finite element) studies of necking and shear localization in tension tests of single crystals. Experiments were performed on relatively strain rate insensitive single crystals of Al-Cu and Cu-Co alloys in addition to crystals of pure, single phase Cu. More recent work, again both experimental and theoretical, has been concerned with more strain rate sensitive BCC crystals, in particular Fe and Fe-Ti-Mn alloys. The experimental work has involved extensive amounts of transmission and scanning/transmission electron microscopy whereas the theoretical work involves supercomputing.

Research Achievements:

Experimental studies of necking and localized shearing in single crystals of Fe-Ti-Mn have documented the conditions under which localized shearing develops during uniaxial tension. Critical conditions of stress and strain hardening rate have been measured and detailed transmission electron microscopic observations have been made of the internal structure of shear bands. These observations have been compared to the results of recent numerical (i.e. finite element) computations of localized shear in the single crystal test. The computations used the actual specimen geometry, crystallography, and material properties as measured experimentally. Our experimental observations indicated that the slip mode which prevailed was primarily a *planar* mode of symmetric double slip on slip systems of the type $\{112\} \langle 111 \rangle$. Localized shearing began shortly after necking while the material continued to strain harden without evidence for microfractures 'in progress'.

Thin foil specimens were prepared which contained the interface between shear bands and the adjacent matrix. An example of this is shown in Fig. 4. Uniform plastic strains of the order of 8 percent occurred in the matrix up to the maximum load point where shear bands initiated and propagated across the gage section. Matrix regions are indicated by region 'a' in Fig. 4 whereas shear band regions are designated 'b'. The material plane of the band was inclined

about 45° to the tensile axis. Shear band interfaces were quite sharp as can be easily seen in Fig. 4. The matrix substructure consisted of arrays of screw dislocations arranged in a 'lozenge' pattern whereas the shear band microstructure consisted of highly elongated cellular regions aligned in the direction of shear. Matrix and shear band regions are separated by extremely sharp boundaries, less than $0.5 \mu\text{m}$ wide, across which strain gradients of up to 10^6 cm^{-1} occur.

Previous theoretical analyses [Asaro, *Acta Met.*, 1979] showed that an important part of the micromechanics of shear band formation is the development of abrupt lattice misorientations across the shear band/matrix interface. These misorientations have been followed by the SAD diffraction patterns of the type shown in Fig. 4. SAD patterns as shown in Fig. 4 are taken at multiple locations approaching the shear band interface -- only two of these are shown in Fig. 4. These lattice misorientations led to a 'geometrical softening' of the active slip systems. Subsequent finite element studies [Peirce, Asaro and Needleman] analyzed this process in more detail. The most recent work by Harren, Asaro and Deve has been concerned with specific numerical (finite element) analyses of necking and shear localization in these iron-alloy crystals. Numerical results have been obtained for the full uniaxial tension test, which follow the crystal through necking and shear localization. The results are in excellent agreement with the experiments, including their descriptions of the localized lattice rotations described by the diffraction patterns of Fig. 4. Several of the calculations were performed by S. Harren while attending the Summer Institute for Supercomputing sponsored by NSF at the Boeing Computational Center.

Other work by McCullough, Deve and Asaro is concerned with the micro and macromechanics of shear band formation in Al alloy single crystals subject to deformation states such as plane strain compression. This work includes detailed transmission electron microscopic observation of the internal structure of shear bands and their correlation with the macromechanical analyses.

Publications:

H. Deve, C. McCullough, S. Harren and R. J. Asaro, "Micro- and Macromechanics of Shear Localization in Single Crystals of Internally Nitrided Fe-Ti-Mn Alloys," in preparation.



An Experimental Study into the Development of Shear Bands During Dynamic Deformation of Metals

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

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K. A. Hartley, Graduate Student, Division of Engineering
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G. J. LaBonte, Jr., Technical Assistant, Division of Engineering

Sources of Support: MRL, ARO, ONR

Objectives and Approaches:

The purpose of our research is the development of an understanding of the factors leading to and causing inhomogeneous deformation, or shear bands, during dynamic deformation. Shear bands are important in material behavior since they constitute a failure process in themselves and since they also frequently precede fracture, Figure 5. Our experimental approach involves (1) measuring the temperature profile across a shear band during its formation and (2) obtaining high speed photographs of shear bands during their formation. The experiments are difficult to perform because the event is brief (about 10 to 200 microseconds, depending on material and conditions), because the observed band is narrow (about 10 to 250 microns), and finally, because the location of the shear band on the specimen's surface is unknown before the experiment is performed and hence frequently lies entirely outside the field of view.

Temperature Profile Across a Shear Band during its Formation

An important part of this research involves the measurement of the temperature rise in steel specimens resulting from the very large plastic deformation that takes place within the shear band. For this purpose thin-walled tubular specimens are subjected to dynamic loading in a torsional Kolsky bar at strain rates of about $2 \times 10^3 \text{s}^{-1}$. An advantage in using the Kolsky bar is that we obtain simultaneously with the temperature measurement a stress-strain curve for the specimen material through a measurement of the stress and of the average strain across the specimen, both as functions of time, Figure 6. In the present tests to measure the surface temperature, we employ a linear array of ten infrared radiation detectors focussed on the specimen. These detectors measure temperature at ten points arranged axially, thus providing a thermal map across the specimen's gage length throughout the deformation process, Figure 7. These experimental data are essential to analyses into the mechanisms of shear band initiation and growth. In addition, metallurgical evidence suggests that the temperature reached within some shear bands is great enough to cause a material phase transformation which results in a much narrower shear band. In our experiment the size of the area observed by the detectors can be controlled by adjusting the optics. Thus, to observe the temperature profile across the entire 2.5 mm gage length, a spot size of 0.25 mm per detector element was chosen. This is the approximate width of a deformed shear band. On the other hand, temperature measurements of the narrower transformed shear bands, which are only about 10 microns wide, requires a much

smaller spot size. At the present time we are limited to a minimum spot size of 20 microns so it is not yet possible to measure the peak temperature within a transformed shear band. This technique has been used to measure the temperature profile across deformed shear bands in 1018 cold rolled steel and 1020 hot rolled steel. Temperature measurements also have been made of transformed shear bands in 4340 VAR steel. Our present efforts are directed toward improving and refining the measurements, in particular with the aim of a more accurate measurement of temperature in the narrow transformed bands.

Photographic Study of Shear Band Formation

To further our understanding of the formation of shear bands a photographic study of shear band development has been initiated. As a first step, we plan to take still photographs of short exposure times (less than one microsecond) using three cameras aimed at the specimen gage section from three different radial directions 90 degrees apart. Short duration light sources will be used and timed to flash at a pre-set instant during the process of the shear band formation. In different tests, the flash will be timed to occur earlier or later during the shear band formation process to provide photographs of the strain distribution nearer or further from the start of the instability process, as indicated by the stress-strain curve. A fine axial grid, applied photographically to the specimen gage section, will show clearly the strain distribution along the gage section. The purpose of these experiments is to determine the evolution of the shear band. Later experiments of this nature will attempt high speed photographic recording of the complete evolution process using an ultra high speed camera system still under development.

Research Achievements:

It was found as a result of this research that shear bands are accompanied by large temperature gradients within the gage section and that these gradients continue to grow with further deformation, often until fracture. For the deformed bands that form in 1018 cold rolled steel and 1020 hot rolled steel, temperatures as high as 440°C occur at the center of the band as measured over a 20 micron spot width. The temperature varies considerably across the width of the band. This is consistent with the inhomogeneous permanent strain profile made evident by the change in shape of a set of internal lines scribed on the specimen surface before loading. An analytical model by Clifton et al., using parameters derived from the stress-strain curves for these two steels, predicts quite accurately both the temperature profile across the gage section and the critical strain for shear localization in each of these steels. This is true despite their different strain hardening behavior and despite the fact that shear bands form in the 1018 CRS at about 10 percent strain while about 100 percent strain is required for strain localization in 1020 HRS.

For the transformed bands in the 4340 VAR steel, temperature measurements using a 20 micron spot width indicated a maximum shear band temperature of 410°C. Because this spot size is considerably wider than the transformed shear band, the actual maximum temperature within the band is no doubt considerably higher. Whether or not the shear band temperature exceeds the austenitizing temperature (about 900°C), however, cannot be determined conclusively from these experiments.

Early still photographs taken during the initial stages of shear band formation in 1018 CRS have shown that the experimental method outlined in the previous section will give clear photographic records of forming shear bands. This conclusion is based on the use of a spark-gap visible light source and macro lenses with high speed film. In the future we shall attempt to improve the quality of the photographs through the use of infrared laser light sources and infrared film.

Publications:

Clifton, R. J., Duffy, J., Hartley, K. A. and Shawki, T. G., "On Critical Conditions for Shear Band Formation at High Strain Rates," *Script Met.*, Vol. 18, pp. 443-448, 1984.

Hartley, K. A., "Temperature Profile Measurements During Shear Band Formation in Steels at High Strain Rates," Ph.D. Thesis, Brown University, May, 1986.

Duffy, J., "A Review of Some Recent Results in Dynamic Plasticity," Invited lecture presented at Army Symposium on Solid Mechanics, Newport, R.I., October 3, 1984.

Hartley, K. A. and Duffy, J., Editors, "High Strain Rate Shear Testing," Metals Handbook (Vol. 8), American Society for Metals, pp. 215-239, 1985, which includes an article by Hartley, K. A., Duffy, J. and Hawley, R. H., "The Torsional Kolsky (Split Hopkinson) Bar".

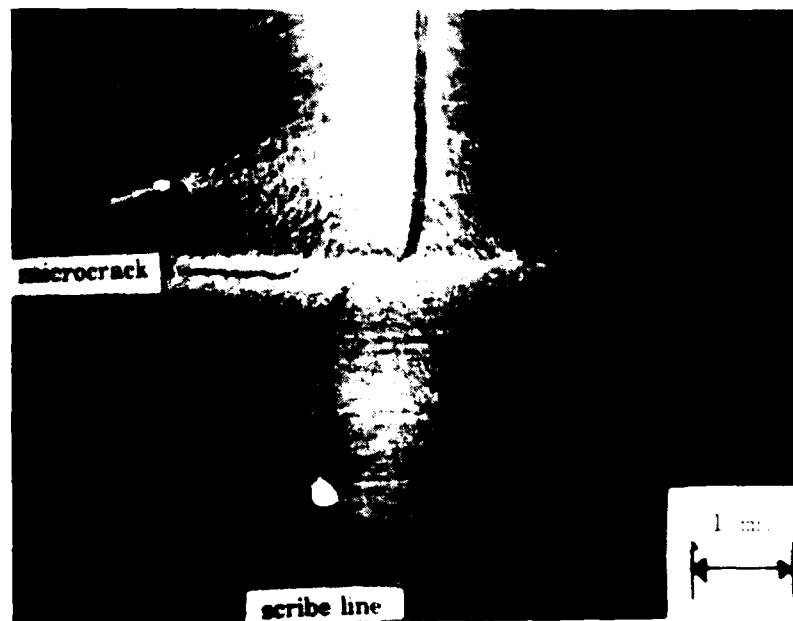


Figure 5

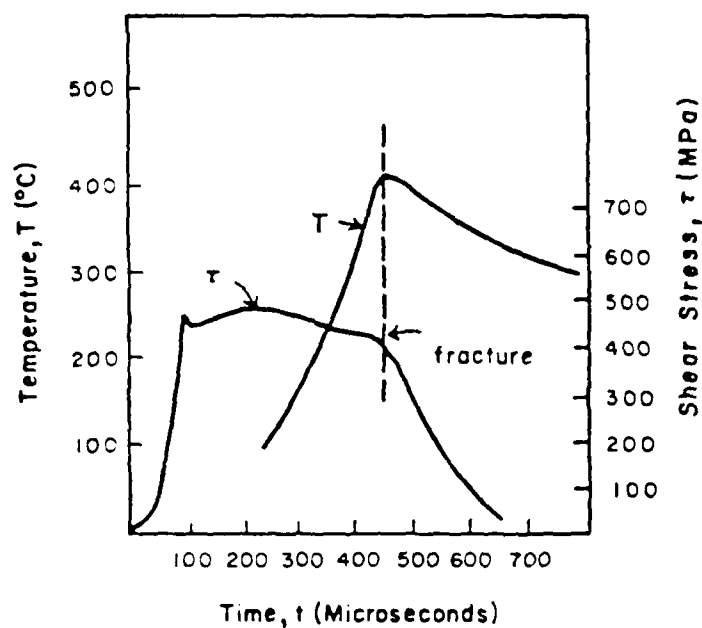


Figure 6: Shear Band Temperature and Stress As Functions of Time (20 Micron Spot, Specimen 165) in 1018 CRS.

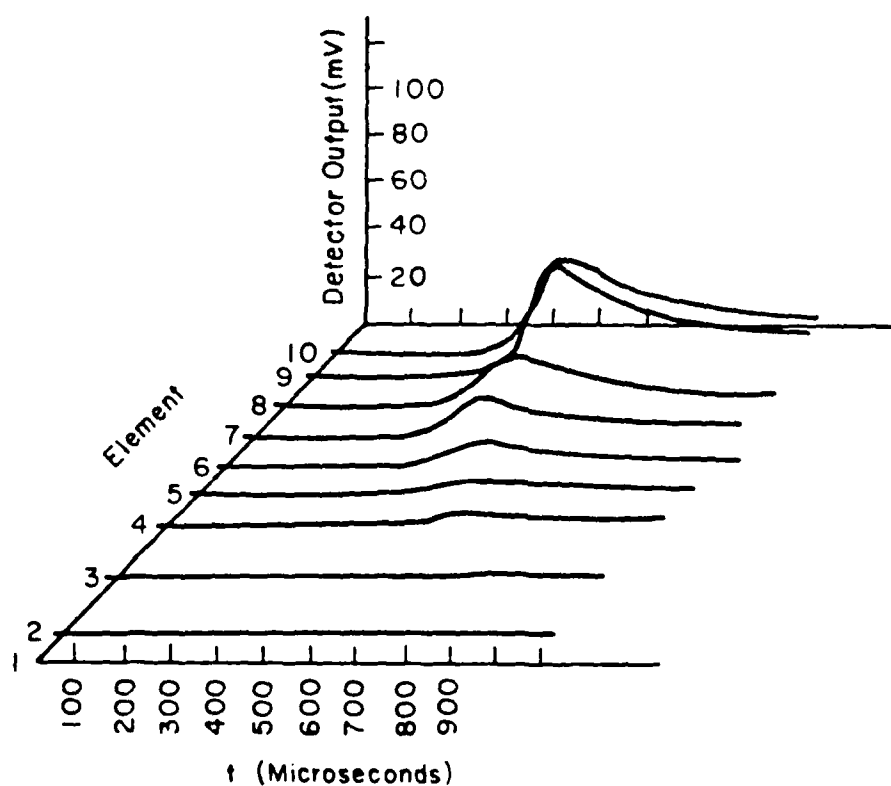


Figure 7: Spatial Profile of I-R Detector Output (20 Micron Spot) During Shear Band Formation in 1018 CRS; Specimen 165.

The Effect of MnS Inclusion Morphology on Shear Band Formation and Machinability

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

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S. Terranova, Undergraduate Student, Division of Engineering

Sources of Support: MRL

Objectives and Approaches:

This research was conducted in collaboration with Dr. H. Yaguchi, Senior Research Engineer, Inland Steel Company Research Laboratories. Dr. Yaguchi supplied bars of 1215 cold drawn steel having MnS inclusions of three different morphologies reflecting a range of sulfide sizes and aspect ratios. Inland Steel adds the MnS inclusions to the 1215 steel matrix to improve its machinability and Dr. Yaguchi has already conducted machinability studies of these steels. Since it has been suggested that shear band formation may be related to machinability, our goal was to determine the relative ease with which shear bands could be produced in thin-walled tubular specimens of these steels when subjected to dynamic loading in a torsional Kolsky bar and then relate that feature to the relative machinability of the three steels.

Research Achievements:

It was found that, despite the similar quasi-static and dynamic stress-strain curves of the three steels, multiple shear bands frequently formed across the gage section in the steel that had the highest inclusion aspect ratio and the lowest inclusion hardness as determined by the rolling reduction, Figure 8. This was also the steel with the poorest machinability. SEM photographs of the fracture surface of this steel showed numerous voids where the inclusions had been torn out, Figure 9. Only single shear bands were produced in the other two modified 1215 steels. Furthermore, in our past work, we have seen only single shear bands in testing a variety of steels. This work will continue with the cooperation of Dr. Yaguchi and Inland Steel Company with a more detailed investigation including SEM studies to determine the role of inclusion morphology on shear band formation and machinability and the factors that cause multiple shear bands to occur in some places.

Publications:

Hartley, K. A., Yaguchi, H., Duffy, J. and Hawley, R. H., "Shear Band Formation and Machinability of Three AISI 1215 Steels Having MnS Inclusions of Different Morphologies," Brown University Technical Report MRL E-157, in preparation.

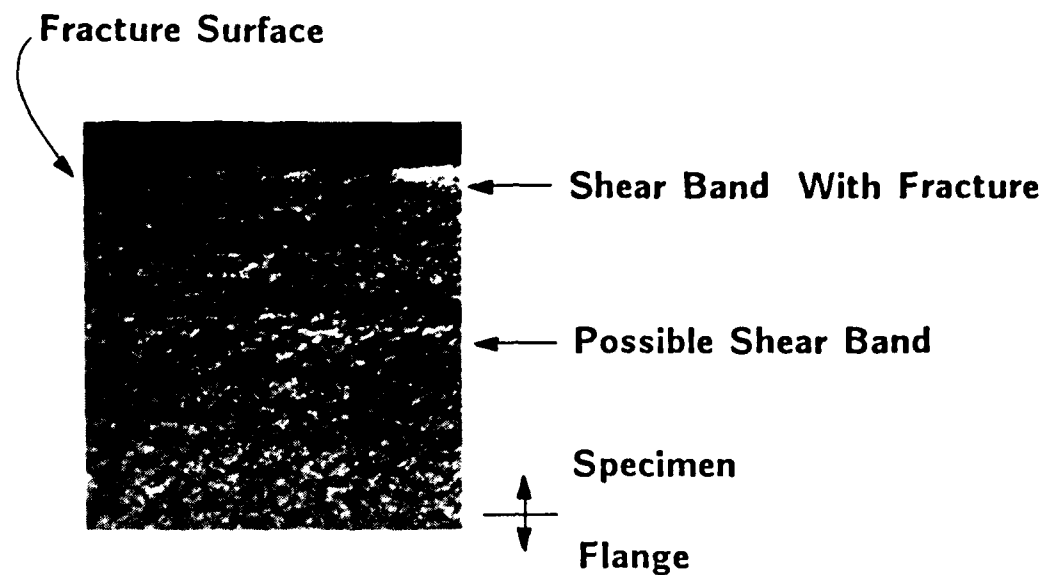


Figure 8: Sectioned Specimen of 1215 Steel 2 Showing Multiple Shear Bands.



Figure 9: SEM Photographs of the Fracture Surface, 1215 Steel 2

Thermal Softening and Shear Band Development

Principal Investigator: A. Needleman, Professor of Engineering

Personnel: J. LeMonds, Graduate Research Assistant, Division of Engineering

Sources of Support: ARO

Objectives and Approaches:

The development of shear bands in the plane strain deformations of viscoplastic solids that exhibit strain hardening, thermal softening and heat conduction has been studied numerically. The specific boundary problem analyzed is a rectangular block with an initial weak spot subject to plane strain compression. The sides of the block are constrained to remain straight, with no lateral force imposed. These boundary conditions model a periodic array of defects subject to remote plane strain compression. We have confined attention to quasi-static deformations and the focus is on the influence of the multi-axial constitutive characterization on shear band development. In particular, the effect of the curvature of the material's flow potential surfaces on shear band development has been analysed. We have carried out analyses using a kinematic type hardening model as well as using a model with isotropically expanding flow potential surfaces. In the isothermal limit, it is well known that the curvature of flow potential surfaces has a major effect on predictions of shear band development. In fact, in that limit, for strain hardening materials with isotropic hardening, shear banding is effectively excluded. When thermal softening is significant, shear bands do occur for the isotropic hardening solid. However, at a given loading rate, shear bands occur sooner and more abruptly in the kinematic hardening solid. Furthermore, the shear bands are narrower.

Mechanics of Multiphase Microstructures

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

Personnel: H. I. Chung, Graduate Student, Division of Engineering
D. Steigmann, Graduate Student, Division of Engineering

Sources of Support: MRL, NSF

Objectives and Approaches:

The basic aim of this research is to provide a predictive understanding of the effect of stress on phase transformations in solids. Presently, we are mainly studying shape-memory materials, quartz, the high temperature A-15 superconductors and the ferroelastic $\text{Nb}(\text{PO}_4)_3$. We are trying to understand the diversity of effects stress can have; in some shape-memory materials, the transformation temperature is increased by both simple tension and simple

compression while in quartz, for example, compression increases while tension decreases the transformation temperature (at different rates). More complex behavior occurs under multiaxial stresses. The objective of this research is to understand these observations as well as some of the diverse microstructures observed.

Research Achievements:

We have developed constitutive equations for materials which can change phase. These equations account for finite deformation, non-uniform change of shape and the appearance of phase boundaries as discontinuities of the deformation gradient. We have analyzed the stability of some simple dead-loaded configurations.

Theory and experiment have been compared quantitatively on two well-studied transformations: thermoelastic martensitic transformations and the α - β transformation in quartz. The analysis predicts correctly the variants observed in shape-memory materials under no loads at the transformation temperature, and the variant which is stable under simple tension of specimens having several different initial orientations relative to the tensile axis (the stable variant is different in each case). In quartz, with latent heat data taken from the measured variation of transformation temperature with pressure ($25.8 \pm 0.3^\circ\text{C/kbar}$), the theory predicts within experimental error the transformation temperature vs. stress relation in uniaxial compression parallel to the optic axis ($5.0 \pm 0.4^\circ\text{C/kbar}$) and perpendicular to the optic axis ($10.6 \pm 0.4^\circ\text{C/kbar}$).

During the course of the investigation we noticed that the theory also predicts a significant loading device effect. That is, whether or not specimens transform at a certain stress level depends on the nature of the loading device, roughly its hardness. Informal thinking about structural transformations in the literature is often concerned with the effect of "stress" on transformation which we think can be misleading because of the loading device effect. Experiments which illustrate the effect are being planned.

Publications:

R. D. James, "Displacive Phase Transformations in Solids," J. Mech. Phys. Solids, to appear.

R. D. James, "The Stability and Metastability of Quartz," Brown University Technical Report, July, 1985.

Plasticity of Crystalline Materials

Principal Investigator: R. J. Asaro, Professor, Division of Engineering
Co-Investigator: A. Needleman, Professor, Division of Engineering

Personnel: S. V. Harren, Graduate Student
H. Mei, Graduate Student

Sources of Support: Metallurgy Section, NSF, MRL and NSF Office of
Advanced Scientific Computing

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 large 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.

For example, 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. During the past two years 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.

Research Achievements:

Development of Texture and Anisotropic Constitutive Behavior

During the past year a comprehensive study of texture development and constitutive behavior following large-strain shear deformations of polycrystals was completed. This work involved collaboration with Dr. T. Lowe of Sandia National Laboratories. In this the effects of material strain rate sensitivity, strain hardening and latent hardening, along with boundary constraints on crystallographic texture have been studied and compared to available experimental data. For example, Fig. 10 shows comparisons of computed and experimentally measured textures for the case of simple shear deformations. This particular calculation began with a simulation of the initial texture of the thin, rolled plate from which the experimental specimen was machined and continued with a calculation of the evolution of texture following large shears. Other calculations, also compared to experiments, have been performed for the case of cyclic shear. The predictions of texture are in close agreement with available measurements and a number of novel correlations have been made. Our calculations have shown that observations of texture rotations can be traced to the influence of boundary constraint on the overall deformation state that develops. In particular, we have shown that when specimens are subjected to an 'unconstrained' shear (i.e., where no normal stresses exit along the axes of shear) the textures undergo a rigid rotation of a fixed amount. This rotation can be linked to reorientations of the principal axes of deformation and to the phenomena of normal strain development during shear. Predictions of full 3-dimensional stress strain response have also been made and compared to experiment. We have also been able to demonstrate that when specimens are sheared with constraints that fix the deformation to be simple shear that normal stresses develop in accordance with experimental measurement. For example, normal stresses on the shearing plane are observed to undergo a transition from compression-to-tension and we have been able to explain in terms of the behavior of 'ideal' texture components.

Localized Plastic Deformation

Computational studies of a unique kind have also demonstrated the importance of anisotropy (texture) along with material rate sensitivity on localized necking in stretched polycrystalline sheets. The computational and constitutive framework we have developed allows us to explore in unprecedented detail the effects of material strain rate sensitivity and anisotropy on ductility limits and the formation of localized necks and shear bands. Our analyses have led to a collaborative project with Dr. O. Richmond of ALCOA on metal forming analyses. The aim of this collaboration is to lay the groundwork for advancing the technology of materials processing as well as to contribute to the fundamental understanding of large strain plastic instability phenomena.

Publications: "Analysis of Large-Strain Shear in Rate-Dependent Polycrystals: Correlation of Micro and Macromechanics," S. Harren, T. Lowe and R. J. Asaro, in press.

Publications:

H. Couque, J. Duffy and R. J. Asaro, "Effects of Prior Austenite and Ferrite Grain Size on Fracture Properties of a Plain Carbon Steel," in press.

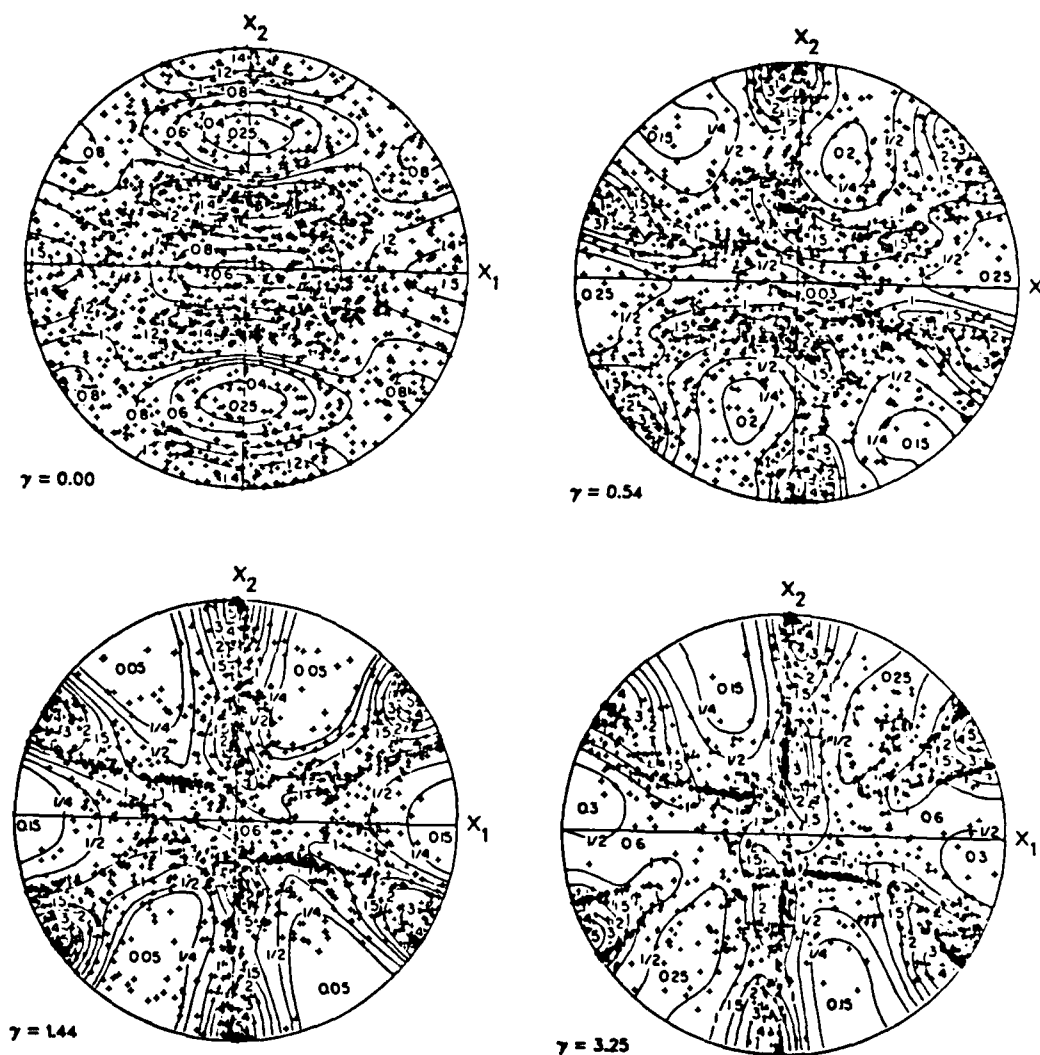


Figure 10 Computed {111} pole figures compared to Williams' experimental data. a) $\gamma = 0$: initial rolled plate stock. b) through d) various shear strain levels. On the figures, the x_1 -direction is the shearing direction and the x_2 -direction is the shear plane normal. The shear strain γ is relative to the rolled plate stock.

Correlation of Microstructure and Dynamic Fracture in Plain Carbon Steels

Principal Investigators: R. J. Asaro, Professor, Division of Engineering
J. Duffy, Professor, Division of Engineering

Personnel: H. Couque, Graduate Student, Division of Engineering
S. Lee, Research Associate, Division of Engineering
R. H. Hawley, Senior Research Engineer, Division of Engineering
P. Rush, Senior Technical Assistant, Division of Engineering

Sources of Support: ARO, MRL

Objectives and Approaches:

It is now generally accepted that under quasi-static loading, cleavage fracture in very low carbon steels originates at carbide plates that form on the ferrite grain boundaries. In contrast, in pearlitic eutectoid steels, fractures originate within the pearlite and the toughness is strongly influenced by the prior austenite grain size. In plain carbon, ferritic-pearlitic steel fractures can initiate in either the pearlite, at isolated carbides, or at other second phase particles and thus correlations must include those with both prior austenite and ferrite grain structure along with pearlite colony structure. Fracture mechanisms are also dependent on strain rate and temperature and thus a full range of loading rates and test temperatures must be included, in particular the ranges that bracket the ductile-to-brittle transition. There have been no prior studies which have been aimed at correlating microstructures and micromechanisms with macroscopic fracture toughness, in particular plane strain fracture toughness, under dynamic conditions.

Research Achievements:

Our studies involved subjecting a 1020 steel to a number of different heat treatments, each consisting of transformations occurring during controlled cooling that were designed to produce variations in both prior austenite and ferrite grain sizes. A range of microstructures was thus produced in which either austenite, or ferrite, or both grain sizes were altered. Dynamic loading is accomplished by tensile stress waves produced by explosive loading at the end of a long rod specimen that contains a circumferential pre-crack. Stress intensity rates in Mode I loading on the order $K_I \sim 2 \times 10^6 \text{ MPa} \cdot \sqrt{\text{m}} \cdot \text{s}^{-1}$ are achieved this way as compared to $K_I \sim 1.0 \text{ MPa} \cdot \sqrt{\text{m}} \cdot \text{s}^{-1}$ for the quasi-static loading. The test temperature range -150°C to 150°C was covered which allowed us to explore fractures in the fully cleavage to fully fibrous range, as well as to study transitions from cleavage-to-ductile.

Fig. 11 shows fracture toughness data for three microstructures containing two different prior austenite and two different ferrite grain sizes. The morphology of these microstructures, as well as local chemistry (e.g. carbon contents in the ferrite), also varies and has been quantified by analytic TEM and STEM microscopy. Under dynamic loading the transition from ductile-to-cleavage fracture occurs over a rather narrow temperature range. Microstructure has a strong influence on the transition temperature as can be seen by the shift toward higher temperatures with increases in microstructural coarseness. Fracture initiation behavior under quasi-static loading displays a

somewhat more complex behavior, especially through the fracture transition temperature range.

The fracture testing has included micromechanical studies of void and microcrack initiation in all three of the microstructures represented in Figure 11. We have identified void and microcrack initiation sites and the manner in which damage accumulates. These data has been used to formulate quantitative models for crack initiation which have successfully explained the general trends and which are currently being used in dynamic finite element studies of quasi-static and dynamic fracture in this test specimen. In addition analytic transmission electron microscopy and micro diffraction has been used to identify crystallographic regions over which cleavage occurs and to relate this to the heat treatment, microstructural evolution and fracture toughness.

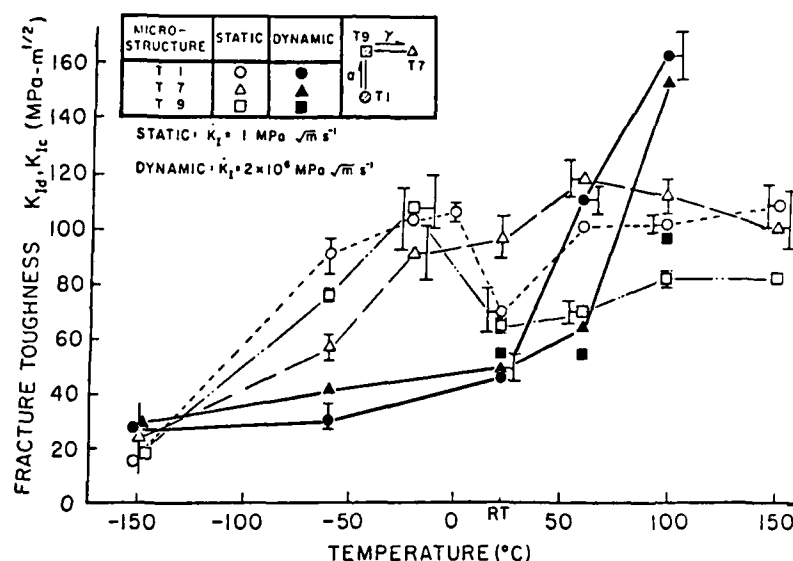


Figure 11: Dynamic and quasi-static fracture toughness in a 1020 steel. Three microstructures designated T1, T7 and T9 are represented; T1 and T9 had a common, fine prior austenite grain structure but different ferrite grain sizes. Microstructures T9 and T7 had a coarse ferrite grain size and different prior austenite grain sizes.

Analyses of Branched Cracks

Principal Investigator: S. Suresh, Assistant Professor, Division of Engineering
C. F. Shih, Associate Professor, Division of Engineering

Sources of Support: MRL, NSF

Objectives and Approaches

Tensile cracks in engineering solids can deviate markedly from the nominal Mode I crack plane due to a variety of mechanical, microstructural and environmental effects. Changes in crack path are generally induced by such factors as multiaxial far-field stresses, interaction of the crack-tip with microstructural inhomogeneities, abrupt load excursions or the embrittling effect of an aggressive environment. In cyclic loading, the phenomenon of crack deflection can lead to lower crack growth rates by reducing the "crack driving force" and by enhancing crack closure loads. To date, quantitative descriptions of possible improvements in fatigue crack growth rates arising from periodic deflections in crack path are not available.

Numerous elastic solutions for crack tip stress intensity factors have been proposed for kinked and forked cracks but there have been considerable disagreements. In recent years consensus solutions appear to have been reached. However, in most practical situations where the crack tip plasticity can develop over a substantial fraction of the kink or fork length, the relevance of such elastic solutions for characterizing the near-tip fields for branched cracks become questionable. For example, the presence of crack-tip plasticity can limit the usefulness of elastic analyses for rationalizing toughening induced by crack deflection in ceramics and composites at elevated temperatures which are typical of service conditions. A topic of particular current interest is the effects of crack-tip plasticity on the near-tip fields for branched cracks. In our recent work, we have attempted to model the effects of crack geometry and crack-tip plasticity in quasi-static and cyclic fracture.

Research Achievements:

We have developed a simple linear-elastic model for estimating the improvements in fatigue crack growth rates arising solely from the geometrical consequences of periodic deflections in crack path and the concomitant changes in crack closure characteristics. Controlled experiments in several high purity aluminum alloys, ferritic-martensitic dual-phase steels and metal matrix composites reveal that the predictions of the model provide realistic (parametric) estimates of possible improvements in cyclic crack growth rates induced solely by periodic deviations from the nominal Mode I crack growth direction. We have also developed a procedure for the determination of plastic near-tip stress and deformation fields under plane strain and small scale yielding conditions for kinked and forked cracks. This method utilizes the known elastic stress intensity factor solutions for kinked and forked cracks and the universal mixed-mode plastic near-tip fields to determine the stress and deformation states in the immediate vicinity of the tip of the kinked or forked crack. The near-tip fields are characterized by an amplitude and a mixity parameter. The procedure allows us to examine the influence of kink (or fork) angle, kink (or fork) length, plasticity and strain hardening characteristics on the local stress

and deformation state. The results indicate that tensile hoop stress and triaxiality decrease with increasing branch angle. This decrease is more pronounced for an elastic-perfectly plastic material than for an ideal linear elastic case. The analyses appear to indicate a general pattern of beneficial effects of crack-tip plasticity on fracture toughness and crack growth resistance for branched cracks irrespective of whether the criterion for fracture is the attainment of a critical stress or strain over a microstructurally-significant distance ahead of the crack-tip. Recent experimental studies of the effects of crack geometry on the apparent improvement in fracture toughness of high purity Al-Li-Cu-Zr alloys are in agreement with the implications of the analyses.

Publications:

S. Suresh, "Fatigue Crack Deflection and Fracture Surface Contact: Micromechanical Models," Metallurgical Transactions, 16A, p. 249 (1985).

S. Suresh and C. F. Shih, "Plastic Near-Tip Fields for Branched Cracks," International Journal of Fracture (1986) in press.

Micromechanics of Failure in Lithium-Containing Aluminum Alloys

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

Personnel: J. Petit, Visiting Research Associate, Division of Engineering
A. K. Vasudevan, ALCOA Research Laboratories

Sources of Support: MRL, NSF, ALCOA

Objectives and Approaches:

Lithium-containing aluminum alloys have been the subject of extensive research investigations over the past few years in view of their potential for immediate applications in aircraft structures. The addition of 1 weight percent lithium to an aluminum alloy increases the elastic modulus by about 6 percent while reducing the density by about 3 percent for lithium additions of up to about 3.5 weight percent. As a result of such beneficial properties stemming from lithium additions to aluminum alloys, many studies are now being carried out on various mechanical and metallurgical characteristics of these alloys. However, the fundamental mechanisms underlying the influence of microstructure on fracture initiation and crack growth resistance, which are properties of practical importance, have not been examined thoroughly in these newer materials. We have undertaken an extensive fundamental study of the micromechanics of fracture under quasi-static, constant amplitude fatigue and variable amplitude fatigue loading conditions in carefully controlled microstructures several high purity aluminum alloys containing Li as well as Cu and Mg. This work is being performed in collaboration with the ALCOA Research Laboratories.

Research Achievements:

The effects of alloy composition and aging treatment on plane strain fracture initiation toughness (K_{IC} , J_{IC}) and crack growth resistance (characterized by the tearing modulus T_R) were investigated in high purity alloys belonging to the Al-Li-Cu-Zr system. The Li/Cu ratio (expressed in terms of atomic fractions) was varied from 2.2 to 25.2 and in each of these alloys, microstructures spanning the very underaged to the severely overaged conditions were studied. In peak-aged and over-aged alloys of higher lithium content, intergranular fracture arising from voids initiated around grain boundary particles dictates fracture initiation toughness and crack growth resistance. In such cases, both K_{IC} and T_R are insensitive to aging beyond the peak strength. When the amount of grain boundary precipitates is limited, the existence of ordered δ' (Al_3Li) particles in the matrix promotes intense slip planarity. While there are reports of experimental evidence indicating a detrimental effect of planar slip on fracture toughness upon artificial aging, there is also a concomitant beneficial (geometrical) effect on crack growth due to severe bifurcation of the crack during quasi-static fracture (e.g., Fig. 1). We have demonstrated with the aid of branched crack models that such bifurcation can account for a part of the microstructural effects on K_{IC} and T_R in some underaged alloys. The magnitude of microstructurally-influenced crack deflection has been systematically correlated with the volume fraction of the precipitates using quantitative transmission electron microscopy. It has been shown that microstructural characteristics, which are generally considered undesirable for fracture initiation toughness, can in fact lead to marked improvements in the tearing modulus. Such results are rationalized based on the observed variations in crack path. In order to separate out the individual effects of Li and Cu and to address some key issues pertinent to the micromechanisms of failure, fracture experiments have also been performed in a high purity Al-Li alloy containing only small amounts of Mn or Zr (used for grain size control). Furthermore, results of heat treatment designed to produce microstructural reversion have been carried out to identify the individual contributions to fracture from matrix deformation and grain boundary failure.

In cyclic crack growth studies, an increase in Li/Cu ratio is observed to provide a monotonic increase in the fatigue crack growth threshold stress intensity factor range. A primary source of this beneficial effect has been identified as the periodic deflections in crack path induced by crack-tip/grain boundary interactions in high Li alloys containing large volume fractions of matrix δ' and a small amount of grain boundary precipitates. Such improved near-threshold crack growth characteristics of higher lithium alloys are also reflected in their better retardation characteristics following single or periodic overloads. We are currently extending our investigation to a study of the ductile fracture mechanisms involving void growth in Al-Li-Cu-Mg alloys which are candidate materials for the next generation of lithium-containing aluminum alloys intended for aircraft structural applications.

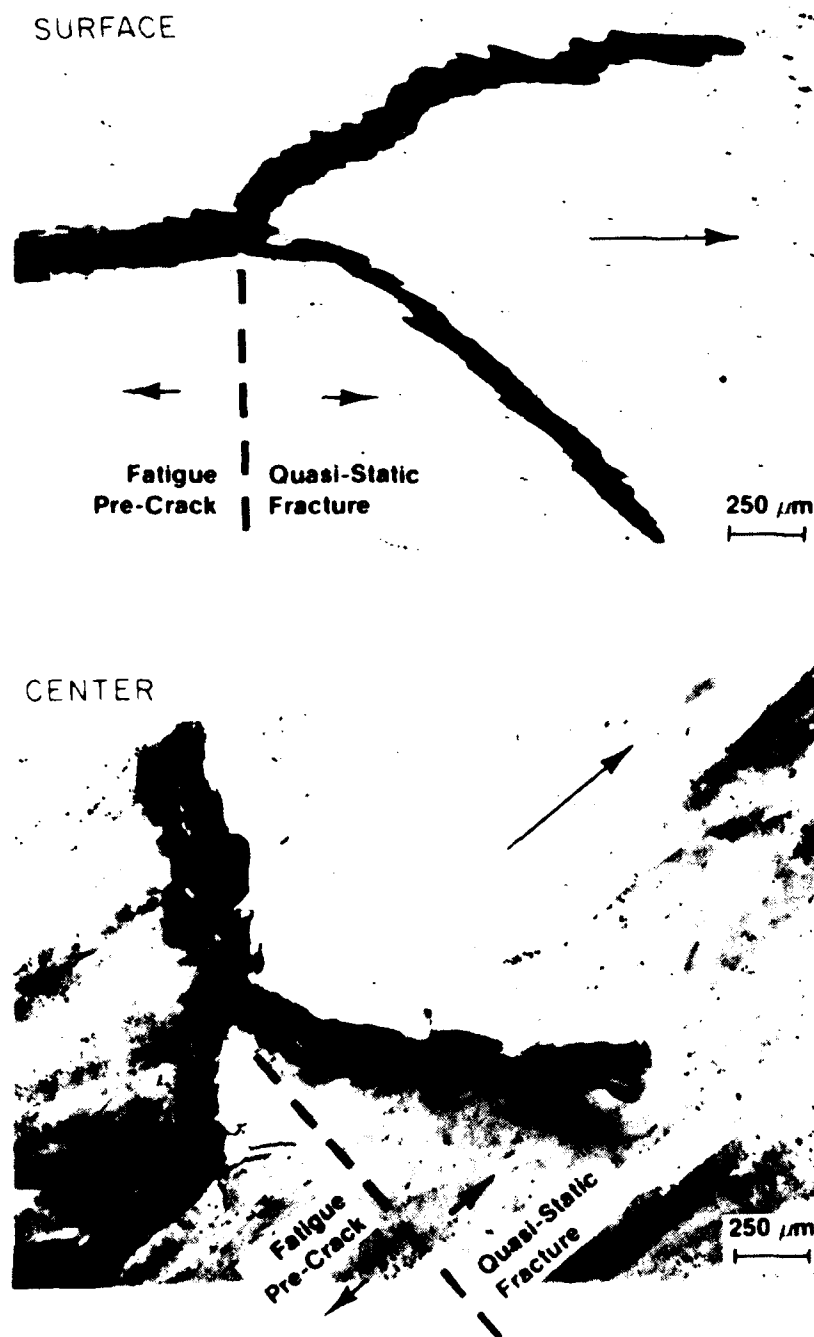


Figure 12: Crack branching during quasi-static fracture as observed on the surface and mid-thickness sections of a 12.74 mm thick compact specimen of an underaged Al-2.9 Cu-2.1 Li-0.12 Zr alloy. Larger arrows indicate nominal Mode I crack growth direction.

Publications:

A. K. Vasudevan and S. Suresh, "Microstructural Effect on Quasi-Static Fracture Mechanisms in Al-Li Alloys: The Role of Crack Geometry," Materials Science and Engineering, 22, p. 37 (1985).

J. Petit, S. Suresh, A. K. Vasudevan and R. C. Malcolm, "Constant Amplitude and Variable Amplitude Fatigue Crack Propagation in Lithium-Containing Aluminum Alloys," in Proc. Third Intl. Conference on Al-Li Alloys, Oxford, July, 1985, edited by C. Baker, The Institute of Metals, London, 1985.

A. K. Vasudevan and S. Suresh, "Lithium-Containing Aluminum Alloys: Cyclic Fracture," Metallurgical Transactions, 16A, p. 443 (1985).

S. Suresh and A. K. Vasudevan, "On the Relationship Between Crack Initiation Toughness and Crack Growth Toughness," Materials Science and Engineering (1986) in press.

S. Suresh, A. K. Vasudevan, M. Tosten and P. R. Howell, "Microscopic and Macroscopic Aspects of Fracture in Lithium-Containing Aluminum Alloys," MRL Report E-156, October, 1985.

Numerical and Experimental Investigation of Crack Growth Under Far-Field Cyclic Compression

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

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

Sources of Support: DOE

Objectives and Approaches:

The application of cyclic compressive loads can result in the propagation of fatigue cracks from stress concentrations. Such cracks, initiated under the influence of residual tensile stresses in the vicinity of the stress concentration, generally grow at a progressively decreasing rate before arresting completely. Although the occurrence of this phenomenon has long been recognized, very little is known about the mechanics and mechanisms of crack advance under imposed cyclic compressive loads. Indeed, the initiation and growth of fatigue cracks under the influence of imposed compressive stresses is a problem of practical importance in a wide variety of engineering situations. Examples of such applications include landing gears and wing-root sections of aircraft, near-surface regions of shot-peened materials, fillet joining the web and head of rails, coil springs of "shellings" in railroad applications, weldments containing residual stresses and components of deep-diving submersibles.

In this investigation, crack growth from a notch-tip, under the influence of fully compressive far-field cyclic loads, is investigated both numerically and experimentally in notched specimens of a wide variety of metallic materials. This study examines the influence of stress state, crack-tip plasticity, stress range and microstructure on the initial rate of crack growth and the total distance of crack growth under remote compression. We have proposed and experimentally demonstrated some important applications of the phenomenon of crack initiation from a notch under far-field compression to the study of "long" and "short" (tensile) fatigue cracks.

Research Accomplishments:

We have investigated the cyclic crack growth and closure characteristics of flaws emanating from stress concentrations under far-field compression for different stress levels, stress states and specimen configurations. The numerical model utilizes a finite element code (LUCAS) developed in Sweden and modified to simulate simple fatigue loading conditions. This part of the work was performed in collaboration with D. K. Holm and A. F. Blom of the Royal Institute of Technology, Stockholm. The numerical procedure consists of elastic-plastic finite element calculations where the geometrical aspects of crack growth are modelled by releasing the crack-tip node, changing the boundary conditions and solving the contact problem at the crack faces. This enables numerical simulations of crack propagation and calculation of crack closure loads for different combinations of stress ratio, stress state and material properties. Experimentally, the crack growth is monitored using travelling microscopes and closure and opening loads are measured in real time using compliance techniques and a video camera. Figure 13, for example, shows the numerically predicted variation of crack closure under plane strain for 7075-T7351 aluminum alloy tested in the center-notched geometry at three different compressive load range levels at a (minimum to maximum) stress ratio of 10. Experimental results of crack closure show reasonable concurrence with the numerical predictions. Predictions of the total distance of crack growth under far-field compression, based on the fact that complete crack arrest occurs when the computed $P_{cl} = P_{max}$, are also in agreement with experimental observations. These results represent the first detailed analyses of cyclic crack growth under imposed compression, a phenomenon which, in addition to its practical importance, also offers some unique possibilities for significantly improving current test methods for fracture toughness and fatigue crack growth threshold measurements.

In this work, we have experimentally demonstrated that the phenomenon of crack initiation from notches subject to far-field cyclic compression offers a useful tool for quickly obtaining estimates of fatigue crack growth thresholds while minimizing some of the uncertainties inherent in the conventional (load-shedding) procedures. Currently practiced threshold test methods often suffer from the criticism that the measured value of the threshold stress intensity factor range can be strongly influenced by the test method. Furthermore, current procedures lead to an artificial interpretation of the threshold in the sense that they measure the threshold at which cracks *arrest* whereas it is the threshold for the *beginning* of crack growth which is of significance in reality. In this work, a novel test technique is proposed whereby nominally "closure-free" cracks are grown (until complete arrest) from notches under cyclic compressive loads and are subsequently loaded in tension fatigue to

measure the threshold stress intensity range at which crack growth begins. The conditions under which this technique leads to an "error-free" (test method-independent) threshold value have been thoroughly evaluated. The proposed technique leads to considerable savings in testing time and cost and completely eliminates the need for an artificial crack arrest traditionally achieved by means of reductions in stress intensity factor range. We have also shown that the initiation of cracks from notches under far-field compression offers some valuable insights into the growth and closure characteristics of physically-small tensile cracks. Furthermore, the extension of this work to ceramics and composites has revealed that the compression technique provides a unique procedure for introducing controlled, non-catastrophic flaws for fracture tests. The details of the applicability of the compression method to the study of fracture and fatigue behavior of non-metallic materials are currently under investigation.

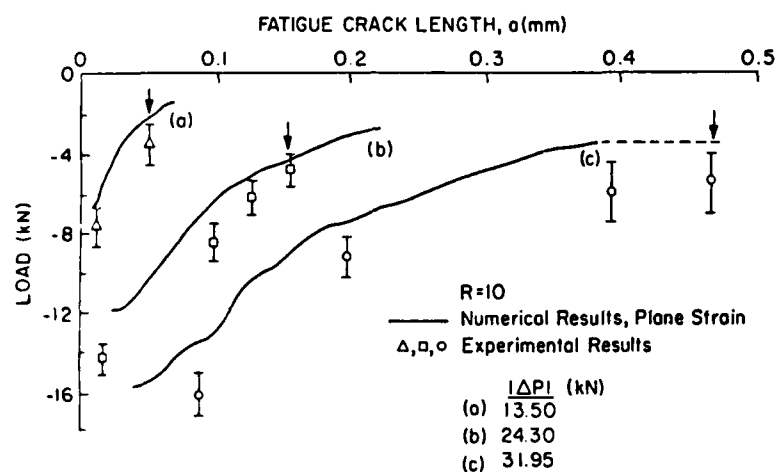


Figure 13: Numerical estimates (for plane strain) and experimental measurements of closure loads for CCT geometry of 7074-T7351 alloy during crack growth in compression.

Publications:

S. Suresh, "Crack Initiation in Cyclic Compression and Its Applications," *Engineering Fracture Mechanics*, 21, p. 453 (1985).

T. Christman and S. Suresh, "Crack Initiation Under Far-Field Cyclic Compression and the Study of Short Fatigue Cracks," *Engineering Fracture Mechanics*, 23, p. 953 (1986).

D. K. Holm, A. F. Blom and S. Suresh, "Growth of Cracks Under Far-Field Cyclic Compressive Loads: Numerical and Experimental Results," Engineering Fracture Mechanics, 23 (1986), in press.

Deformation and Fracture of Two-Phase Alloys

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

Personnel: Y. L. Su, Graduate Student, Division of Engineering
K. M. Cho, Graduate Student, Division of Engineering
H. J. Stanton, Technical Assistant, Division of Engineering

Sources of Support: DOE, MRL Central Facilities

Objectives and Approaches:

The purpose of this part of the research program is to explore the strengthening and failure mechanisms of representative two-phase alloys in order to formulate the deformation characteristics generally applicable to this class of engineering materials. This report includes our results on spheroidized steels, which are particle strengthened alloys consisting of cementite and ferrite, and dual-phase steels, which are phase mixtures consisting of martensite and ferrite.

An appreciable amount of work has already been published on the deformation and fracture behavior, and continuum mechanical and micromechanistic models have contributed to an understanding of specific alloy systems. There are, however, several problems of a fundamental nature which remain to be satisfactorily solved; among which the following will be here considered: 1) the correct criteria of local failure, i.e., crack or void initiation, 2) evaluation of the stress and strain partitioned to each phase during plastic deformation, which accounts for strain hardening, and 3) the criteria or conditions of global failure, i.e., necking and fracture at the end of a tensile test.

Research Achievements:

A comprehensive experimental program has been completed on the deformation and fracture of a dual-phase steel with composition 0.12% C, 1.6% Mn and several different microstructures and volume fractions of ferrite/martensite. The latter were produced by varying the heat treatment conditions, namely, intercritically annealed (IC), step quenched (SQ) and intercritically annealed and tempered (ICT). The different heat treatments produce microstructures which range from martensite islands surrounded by a continuous ferrite matrix (SQ, low martensite) to continuous martensite with embedded ferrite (IC, high martensite). Stress-strain data in tension were obtained on 25 specimens varying in martensite content from 20 vol % to 100 vol %. A microscopic study of the fracture processes was carried out by means of optical and scanning-electron microscopy. An attempt was made to

determine the strain partition in the ferrite and martensite constituents, by means of a 30 μm grid lithographically applied to the surface of tensile specimens before deformation. Typical results are shown in Figure 14. The martensite strain is appreciably less than the alloy strain, as is to be expected, but, unexpectedly, the martensite strain saturates at heavy specimen deformation in the neck. This is probably due to the fact that specimen deformation occurs here mainly by localized shear in matrix ligaments, with little additional load transfer from matrix to particle.

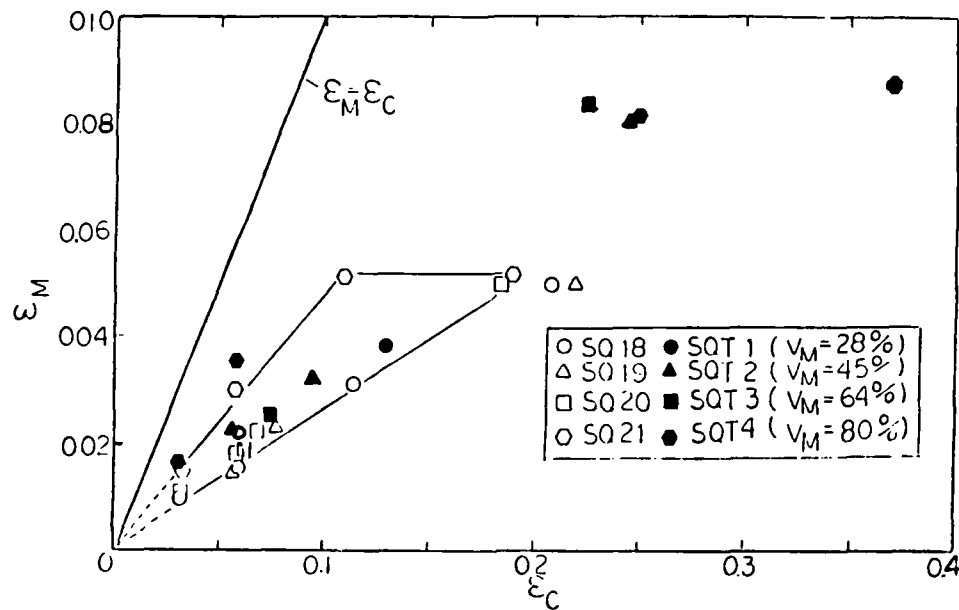


Figure 14: Martensite strain ϵ_M as a function of alloy strain ϵ_C .

Generally, the observation of fracture in the dual-phase steels appears to be in excellent agreement with the experimental and theoretical trends found by Fisher and Gurland in their work on spheroidized steels. In dual-phase steels, void formation is due to the decohesion of the interface between martensite and ferrite and not by martensite particle cracking. Here also, it was observed that void initiation occurs most frequently between closely spaced martensite particles along grain boundaries.

Publications:

Y. L. Su, "Uniaxial Tensile Deformation and Fracture of Dual-Phase Steels," Ph.D. Thesis, Brown University, July, 1985.

J. Gurland and R. J. Asaro, Ductility Improvement, Encyclopedia of Materials Science and Engineering, M. B. Bever, editor, MIT Press, Cambridge, MA (also Pergamon Press) 1985, Article No. 120/00830.

Fracture Toughness of Cemented Carbides

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

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

Sources of Support: MRL

Objectives and Approaches:

The long-range aim of this work is a formulation of a fracture theory for heterogeneous aggregates, although the experimental work is based on cemented carbides only. The overall plan consists of the following major steps: 1) selection and development of a suitable fracture toughness testing procedure, 2) experimental determination of fracture toughness of cemented carbides over a wide range of alloy systems, compositions and microstructural variables, 3) fractography by SEM and analytical electron microscopy, and 4) application of fracture mechanics to the microscale fracture processes in order to develop a descriptive and, perhaps, predictive fracture theory.

Research Achievements:

The first step was completed by evaluation and selection of the "bridge indentation" technique for pre-cracking of single-edge-notched beams (SENB) for fracture toughness testing. As part of the evaluation process, the techniques used for the fracture toughness testing of cemented carbides were reviewed. Experimental results were obtained on SENB specimens pre-cracked by spark machining and bridge indentation, also by indentation cracking. The "bridge indentation" technique was selected as the most reliable method for pre-cracking. The method consists of crack initiation by indentation, followed by crack extension under bridge compression loading and, eventually, fracture by bending under three-point loading.

The SENB method will now be used on selected cemented carbide alloys of widely differing compositions and microstructures, such as WC-Co, TiC-Mo-Ni, TiC-steel and others to be obtained from industrial suppliers. The purpose is to ascertain the relative contributions of carbide, binder and interfaces to the fracture propagation energy. The fracture process in each type of alloy will be studied by a) SEM fractography of fracture surfaces, b) SEM examination of deformed and damaged material on sections near the crack tip and c) "in-situ" observation of crack propagation in electron microscope by use of wedge-loaded miniature notched specimen on microscope loading stage.

Talks on our work on cemented carbides were presented at the International Conference on the Science of Hard Materials, Rhodes, Greece, September 1984; GTE Research Laboratories, Waltham, MA, January, 1985; and TMS-AIME Fall Meeting, Toronto, October, 1985.

Publications:

R. Godse, "Precracking Techniques for Fracture Toughness Testing of Cemented Carbides," Sc.M. Thesis, Brown University, May, 1985.

R. Deshmukh and J. Gurland, "A Study of Microstructural Development and Contiguity During the Liquid Phase Sintering of WC-Co Alloys," in Second International Conference on Science of Hard Materials, A. Hilger, Ltd., Bristol, U.K., (in press).

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

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

Personnel: P. S. Lam, Research Associate, Division of Engineering
W. Yang, Research Assistant, Division of Engineering

Sources of Support: ONR, MRL and 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 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 - 10^5 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 (solid curves in the attached figure). 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 original analysis of the model was based on certain approximations. In subsequent work, the same model was analyzed by detailed numerical calculation. It was found that the results (discrete points in the attached figure) were consistent with the approximate analytical results, at least over the temperature range at which cleavage cracks are observed in polycrystalline iron.

In a related study, the problem of steady growth of an antiplane shear crack in a strain rate sensitive elastic-plastic material was considered. It was assumed that the material is elastic-perfectly plastic under slow loading conditions, but that the inelastic strain rate is proportional to the difference between the stress and the yield stress raised to some power. In earlier work on this problem reported by others in which the possibility of an elastic region in stress space was not considered, it was concluded that the asymptotic crack tip field is completely autonomous, but the local field could not be shown to reduce to a generally accepted rate independent limit as the rate sensitivity of the material vanished. It has been shown that if the possibility of elastic unloading is admitted in the formulation then the asymptotic crack tip solution does indeed approach the correct rate independent limit as the rate sensitivity of the material vanishes. Furthermore, the crack tip field loses the feature of complete

autonomy under these conditions. That is, the crack tip field involves an undertermined parameter that can be determined only from the remote fields.

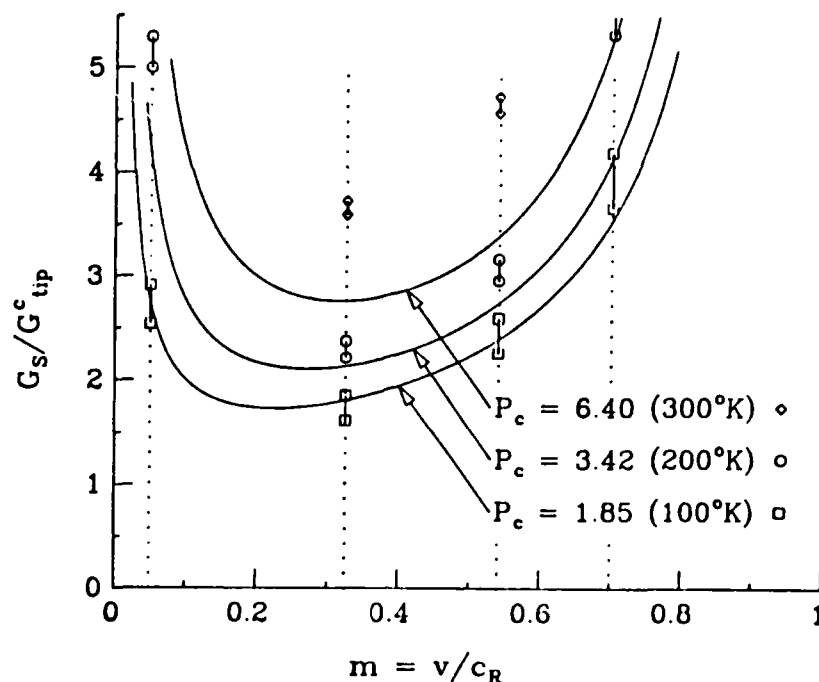


Figure 15: Ratio of the remote crack driving force to the crack tip energy release rate versus the crack tip speed normalized by the Rayleigh wave speed of the material, for material parameters corresponding to three temperatures.

Publications:

L. B. Freund and J. W. Hutchinson, "High Strain Rate Crack Growth in rate-Dependent Plastic Solids," *Journal of the Mechanics and Physics of Solids*, **33**, 169-191, (1985).

L. B. Freund, J. W. Hutchinson and P. S. Lam, "Analysis of High Strain Rate Elastic-Plastic Crack Growth," *Engineering Fracture Mechanics*, to appear.

W. Yang and L. B. Freund, "An Analysis of Antiplane Shear Crack Growth in a Rate Sensitive Elastic-Plastic Material," *International Journal of Fracture*, to appear.

Observations on the Optical Shadow Spot Experimental Method in Dynamic Fracture of Materials

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

Personnel: C. C. Ma, Research Assistant, Division of Engineering
W. Yang, Research Assistant, Division of Engineering

Sources of Support: MRL, NSF

Objectives and Approaches:

The use of the optical shadow spot method, which is also known as the method of caustics, for measuring the intensity of crack tip stress fields is now quite common in experimental work in the fracture of brittle materials. When a plate specimen containing a long through-crack is loaded so that the crack opening occurs in the opening mode, the stress and deformation fields near the crack tip assume the familiar universal spatial distribution. The magnitude of the near tip field, which varies with the load and geometry, is the elastic stress intensity factor. The method is based on the fact that the value of the stress intensity factor can be related to features of the optical field obtained by directing parallel light through a transparent specimen in the crack tip region, or by reflecting light from the surface of an opaque specimen in the crack tip region. The features of this optical field are determined by the nonuniform lateral contraction of the specimen in the crack tip region and, for transparent materials, by the strain dependence of the refractive index. Data are normally interpreted on the basis of the assumption that the crack tip deformation field is a two dimensional plane stress field. Thus, for a given set of system parameters, the magnitude of the crack tip stress intensity factor can be related to some particular dimension in the optical field.

Two aspects of the interpretation scheme have been examined in greater detail than before. For one thing, the optical field used to infer values of the stress intensity factor is determined by conditions over a region of finite extent around the crack tip, typically five or six millimeters in size. Furthermore, it is tacitly assumed in applying the method that the stress intensity factor field is fully established at all times over this finite region. For dynamic fracture events dominated by stress wave effects, the validity of this underlying assumption is not evident, and a study was undertaken to quantify the limits of the assumption. The second issue addressed concerns the assumption of a two dimensional field at points near the crack tip. The theory of plane stress is based on the assumption that transverse shear effects in the specimen are unimportant. However, if the plane stress theory is applied for the case of a through crack in a plate, then very large transverse shear strains are predicted for points close to the crack edge, giving rise to an inconsistency. Because the shadow spot method depends on the interpretation of the data on the basis of plane stress deformations, a study was undertaken to identify the minimum distance from the crack tip required in order to avoid the complication of three dimensional effects.

Research Achievements:

The question of the extent of the stress intensity factor field during crack growth under stress wave loading conditions has been studied by analyzing fracture initiation and crack growth in a plate due to dynamic pressure loading on the faces of a pre-existing crack. The problem was formulated within the framework of two dimensional elastodynamics. At a certain time, a spatially uniform pressure begins to act on the crack faces. The pressure magnitude increases linearly in time for a certain period, and it is constant thereafter. The crack begins to extend at a constant speed at some time after the pressure begins to act, and this time may be less than or greater than the rise time of the loading pulse. The ratio of the normal stress on the fracture plane to the value due to the stress intensity factor field alone is computed for some point at a small fixed distance ahead of the crack tip. A graph of this ratio versus normalized time is shown in Figure 16, for a crack speed of 20% of the dilational wave speed of the material and for three values of the initiation delay time. It is found that for rise times and initiation delay times representative for fracture initiation studies in brittle materials, the time required to establish the stress intensity factor field over a region of the size of interest in the shadow spot method can be a significant fraction of the total observation in an experiment.

To examine the influence of transverse shear on the crack tip stress and deformations in plate fracture specimens, the state of stress in an elastic plate that contains a crack was studied from the boundary layer point of view based on the assumption that the extensional strain in the thickness direction is uniform. As anticipated, the generalized plane stress solution prevails everywhere in the plane of the plate except near boundaries. Near points on any smooth boundary, including the crack faces away from the crack edges, the plane stress solution is only slightly perturbed. Near crack tips, however, a complicated boundary layer is developed. A standard separation of variables approach fails, but an exact solution of nonseparable form has been found. The solution shows a finite lateral contraction of the specimen along the crack edge, in contrast to the plane stress solution, and the inner solution near the crack edge merges smoothly with the plane stress solution at distances from the crack edge of about one-half the plate thickness, as shown in the attached figure. Thus, for shadow spot experiments, the optical fields produced by deformations at points further from the crack edge than one-half the plate thickness should be used if data are to be interpreted on the basis of plane stress theory. The results are consistent with experiments intended to address the same issue carried out by a former student Professor A. J. Rosakis and his co-workers at CalTech, as shown in Figure 17.

Publications:

C. C. Ma and L. B. Freund, "The Extent of the Stress Intensity Factor Field During Crack Growth Under Dynamic Loading Conditions," *Journal of Applied Mechanics*, 53, (1986), to appear.

W. Yang and L. B. Freund, "Transverse Shear Effects for Through-Cracks in an Elastic Plate," *International Journal of Solids and Structures*, 21, p. 977-994, (1985).

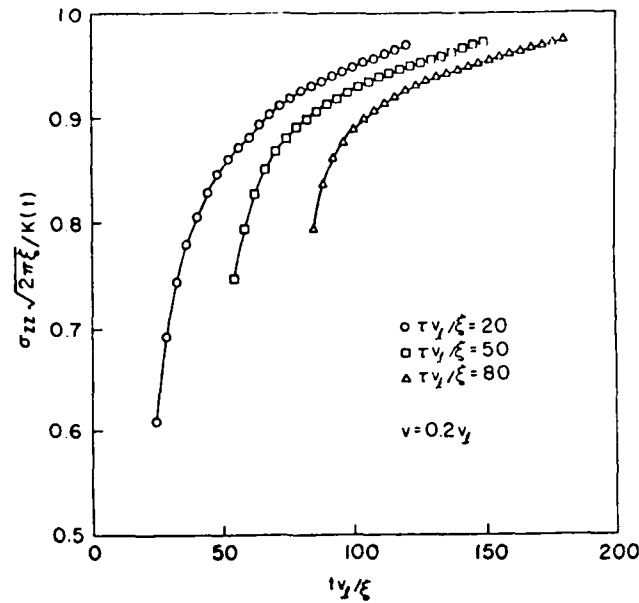


Figure 16: Ratio of the total stress to the stress determined from the stress intensity factor field alone versus nondimensional time, evaluated at a fixed distance ξ ahead of the crack tip. The delay time before onset of crack growth is τ and the longitudinal wave speed is v_L .

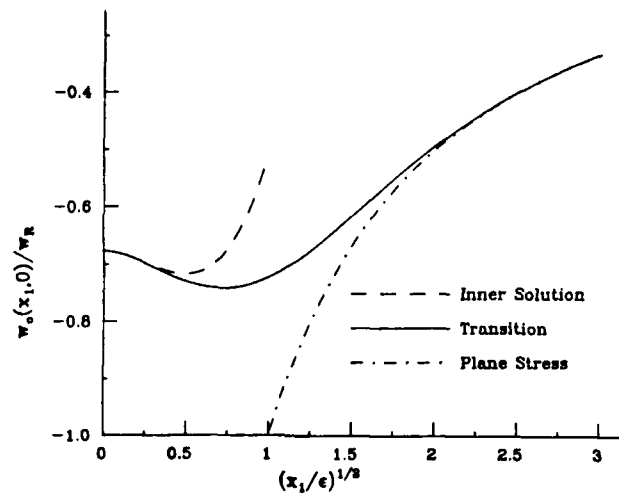


Figure 17: Normalized lateral contraction of the specimen surface versus distance ahead of the crack tip, showing the inner boundary layer solution, transition solution, and the outer plane stress solution. The parameter ϵ is approximately 0.15 times the specimen thickness.

Stress Concentration Near the Edge of a Thin Film Deposited on a Substrate

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

Personnel: W. Yang, Research Assistant, Division of Engineering

Sources of Support: NSF

Objectives and Approaches:

A solid film bonded to a surface of a relatively large sample of a second solid material (the substrate) is a common configuration in a variety of technical fields, including microelectronics, photovoltaics, lubrication and mechanical wear. Any fabrication process in which the film material temperature is different from the substrate material temperature during film formation will result in the presence of internal thermal stresses when the film-substrate structure reaches thermal equilibrium. Even in those cases in which there is no temperature differential between the film and substrate during fabrication, but in which the common fabrication temperature is above ambient temperature, thermal stresses will result upon cooling to ambient temperature unless the thermal expansion coefficients of the film and substrate are identical. Likewise, an operation such as high temperature annealing after fabrication can produce significant thermal stresses. An estimate of the internal residual thermal stress in a uniform thin film layer bonded to a relatively thick substrate can be obtained easily in terms of the thermoelastic properties of the materials involved if it is assumed that the film and substrate are of indefinite extent in the plane of their common interface. However, this standard calculation overlooks the fact that there is no interaction between the film and substrate in this case, and load is transferred from the substrate to the film in some unspecified way at remote points. On the other hand, it is commonly believed that residual stresses provide the mechanical driving force for interface separation in film substrate failures. Therefore, a study was undertaken of the load transfer process between a film and substrate near a film edge, and of some possible failure mechanisms for film-substrate structures.

Research Achievements:

Results have been obtained on several aspects of residual stress development and failure modes that may occur near the edge of a thin film bonded to a deformable substrate. The film is assumed to be thin, and the interface stress is characterized by a shear stress intensity factor. It is shown that if the film is formed by solidification of a melt on a solid surface then the residual stress depends on distance from the film edge mainly through the solidification time, and the stress intensity factor is a decreasing function of solidification time. The influence of adjacent film segments and of nonuniform thickness of the stress intensity factor has also been investigated. For films of polymeric materials, the role of stress relaxation during cooling on the final residual stress distribution has been studied. It has been shown that the final residual stresses may be smaller than for stress states experienced earlier during the process. Film failure through plastic flow at interior points in the film or at the film-substrate interface has also been investigated.

Publications:

W. Yang and L. B. Freund, "Shear Stress Concentration Near the Edge of a Thin Film Deposited on a Substrate," in Mechanics Today, edited by S. Nemat-Nasser, Pergamon Press, (1986) to appear.

Crack Tip Integrals and Associated Domain Forms

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

Personnel: B. Moran, Research Assistant, Division of Engineering

Sources of Support: MRL

Objectives and Approaches:

A series of studies by Shih, Freund, Needleman and coworkers has led to a unified approach to the derivation of crack tip integrals and their associated domain forms. Using this approach, a crack tip mechanical energy flux integral has been derived for general material response and arbitrary crack tip motion; similarly a crack tip mechanical power flux integral has been derived. By invoking appropriate restrictions on the material response and on crack tip motion various forms of crack tip integrals can be obtained, including the J-integral and the C-integral, for rate-independent and rate-dependent elastic-plastic materials. In the context of the adopted approach such crack tip mechanical energy (or power) flux integrals are viewed as direct consequences of momentum balance. Additional crack tip integrals which can be viewed as consequences of total energy balance (first law of thermodynamics) and momentum balance have been obtained. By imposing certain forms of the near-tip temperature field, specialized integrals can be obtained which are suitable for thermo-mechanical loading problems. Dual (or complementary) integrals have been derived by invoking incremental (or rate) momentum balance.

In general, crack tip energy (or power) flux integrals are only defined by the limiting contour, shrunk onto the crack tip. This presents obvious difficulties in numerical evaluation of the crack tip integrals. We recast these integrals in domain forms through the application of domain weighting functions and the divergence theorem over some part of the fracturing solid. These latter integral forms are naturally compatible with the finite element discretization of the domain and are easily incorporated into numerical codes. We find the domain representation of the crack tip flux to be especially suitable for computational studies of crack tip fields, and in particular for the calculation of pointwise flux (or energy release rate) along a three-dimensional crack front.

Research Achievements:

The domain integral approach of quantifying crack tip fields in computational studies have been successfully applied to three types of problems. Shih, Freund and coworkers have carried out full-field three-dimensional finite element analysis of a dynamically loaded three-point-bend ductile fracture specimen and have obtained detailed information on the variation of the J-integral along the crack front from the arrival of the first wave at the crack front to the attainment of quasi-static conditions. Such results are required to develop an experimental method for measuring the dynamic fracture toughness of ductile steels. Shih and coworkers have also obtained the variation of J along a three-dimensional crack front in a body which is thermally stressed into the nonelastic range. The analysis method and the results can have potential applications to delamination or peeling problems in microchips. Numerical studies by Ortiz and coworkers are also in progress where the domain integral approach is being employed to calculate the magnitude of the crack tip fields in a material undergoing microfracture.

Publications:

B. Moran and C. F. Shih, "Crack Tip Integrals from Momentum and Energy Balance," Brown University Report (in preparation).

B. Moran and C. F. Shih, "Crack Tip Integrals in Thermoelasticity and Creep," Brown University Report (in preparation).

Three Dimensional Transient Analysis of Crack Problems

Principal Investigator: C. F. Shih, Associate Professor, Division of Engineering
L. B. Freund, Professor, Division of Engineering

Personnel: T. Nakamura, Graduate Research Assistant, Division of Engineering

Sources of Support: ONR

Objectives and Approaches:

The three-point-bend bar is a common specimen configuration employed for fracture toughness evaluation under quasi-static loading. In recent years, the configuration has been proposed for use in the investigation of fracture resistance of ductile materials under dynamic loading conditions. Shih, Freund and coworkers have carried out computational studies to elucidate the conditions under which interpretable fracture toughness data can be obtained and to assess the accuracy and the consistency of fracture toughness measurement based on measurable fields (if any).

Research Achievements:

Our three-dimensional full-field finite element analysis of a dynamically loaded three-point-bend ductile fracture specimen and simple model studies have shown that the response of the specimen can be conveniently characterized by a short-time response dominated by discrete waves, an intermediate-time response dominated by the structural inertial and kinetic energy, and a long-time response dominated by the deformation energy (or stress work). These three regimes can be distinguished by a transition time, t_T , defined as the time beyond which the total deformation energy exceeds the total kinetic energy of the specimen. Thus the first regime corresponds to times smaller than t_T , the second regime to time about equal to t_T , and the last regime to times greater than t_T . By dimensional analysis, it can be shown that the transition time depends on a dimensionless motion parameter and a dimensionless geometric shape factor, and on the ratio of the characteristic dimension of the specimen to the wave (sound) speed. The transition time and the full form of the equation governing the transition time have been verified by full-field numerical studies.

The transition time has another important role in a J-based fracture methodology. It is not feasible to evaluate the fracture toughness of many important engineering materials by procedures based on linear fracture mechanics. If the material is ductile and fracture initiation takes place after extensive yielding of the ligament, the J-integral may be adopted as the characterizing parameter for fracture toughness. However during the early stages of a dynamic loading process when discrete waves form an important part of the total mechanical field, a significant time may be required for a J-controlled nonlinear crack tip field to become established. Furthermore J cannot be determined by any direct means from a remote load and deformation history until a sufficient time has elapsed and the crack tip field has stabilized. Our full-field numerical studies showed that the transition time provides an estimate of the necessary duration to achieve these conditions. Specifically, meaningful fracture toughness data can be obtained with a ductile three-point-bend specimen if fracture occurs beyond the transition time. Nevertheless certain features of the development of the full-fields must be brought to attention. When the amount of yielding is well-contained, i.e. limited to the vicinity of the crack front, the through-thickness variation of J and of the stresses and strains is relatively small. However as plastic deformation progresses, the through-thickness variation of the fields becomes very substantial. Since experimental measurement can at best provide thickness-average values of the fields, the strong through-thickness variation of the fields along the crack front of a test specimen can only be taken into account with the help of the full-field results.

Publications:

T. Nakamura, C. F. Shih and L. B. Freund, "Analysis of a Dynamically Loaded Three-Point-Bend Ductile Fracture Specimen," Brown University Report ONR 0365/1 (1985), in print, Engineering Fracture Mechanics.

T. Nakamura, C. F. Shih and L. B. Freund, "Three-Dimensional Elastic-Plastic Analysis of a Dynamically Loaded Three-Point-Bend Fracture Specimen," work in progress.

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

Sources of Support: NSF, ALCOA

Objectives and Approaches:

We have carried out analyses of ductile failure processes using a constitutive relation that incorporates a physically based model of micro-void nucleation at second phase particles and the subsequent growth of neighboring micro-voids to coalescence. The micro-voids are represented in terms of a single parameter, the void volume fraction. The material description describes the complete loss of stress carrying capacity due to void coalescence; no separate failure criterion is imposed. In recent work, we have focussed on implications of material strain rate sensitivity for ductile fracture processes.

Research Achievements:

We have analyzed the effect of loading rate in the ordinary round bar tensile test, for a range of loading rates where material strain rate sensitivity is the primary time effect. Our results show that loading rate has a strong influence on neck development and failure when the nucleation of micro-voids is stress controlled but not when nucleation is strain controlled. Due to material strain rate hardening, increased strain rates raise the stress level. For BCC metals the increased stress level can lead to failure by cleavage rather than by ductile void growth. We have extended the material model to allow for loss of stress carrying capacity due to cleavage and, using this framework, have carried out the first analysis of the competition between cleavage and ductile void growth in the Charpy V-notch test. The results show that in the transition region, the details of the development of porosity in the notch tip region play a significant role in the fracture process even when failure occurs by cleavage. When void nucleation is strain controlled, the region of high void volume fraction is confined to the tip of the notch while the peak stress occurs away from the notch where the void volume fraction is negligible. This high porosity lowers stress levels and causes a stress redistribution that raises the stress level away from the notch in the region where cleavage initiates. With stress controlled nucleation, void nucleation occurs over a relatively extensive region and results in lower stress levels in the peak stress region, which delays cleavage.

Publications:

A. Needleman and V. Tvergaard, "Material Strain-Rate Sensitivity in the Round Tensile Bar," Plastic Instability (Proc. Considere Memorial Symposium), pp. 251-262 (1985).

V. Tvergaard and A. Needleman, "Effect of Material Rate Sensitivity on Failure Modes in the Charpy V-Notch Test," J. Mech. Phys. Solids, in press.

R. Becker and A. Needleman, "Effect of Yield Surface Curvature on Necking and Failure in Porous Plastic Solids," Journal of Applied Mechanics, in press.

Determination of the Plastic Strain Concentration Factor in Steels

Principal Investigators: J. Duffy, Professor, Division of Engineering
L. B. Freund, Professor, Division of Engineering

Personnel: A. Marchand, Visiting Research Associate, Division of Engineering
R. H. Hawley, Senior Research Engineer, Division of Engineering
G. J. LaBonte, Technical Assistant, Division of Engineering

Sources of Support: ONR, MRL

Objectives and Approaches:

For a number of years the shadow spot technique, or method of caustics, has been used in fracture research as a means of determining optically the stress intensity factor at the tip of a crack. The method has the advantage of providing a direct measure of the stress intensity factor. Early analyses limited applications to brittle materials in which the material behavior remains essentially elastic throughout loading. A recent analysis by Rosakis, Ma and Freund [J. Applied Mech., 1983, 50, 777] extended the applicability of the method of caustics to materials, such as structural steels, which exhibit a substantial amount of plastic deformation in the vicinity of the crack tip prior to fracture. In this analysis, the plastic strain concentration factor J is related to the transverse diameter D of the shadow spot through a formula which includes the work hardening rate of the specimen material. The goal of the present research was to determine the validity of this analysis in the determination of J by comparing in one experiment results based on the shadow spot technique with those of another independent experimental method for determining J . For this purpose a specially designed double cantilever beam (DCB) specimen that permits application of a load point-displacement method simultaneously with the method of caustics was used. Specimen dimensions are 6" wide and 12" long. A wide opening between the cantilever arms permits mounting of a short hydraulic cylinder that is used to apply an opening force at two opposite, fixed points along the cylinder's axis. The relative displacement of the two load points is measured by a differential transformer and a record of load vs. load point displacement is obtained together with a photographic record of the shadow spots at each load level.

Research Achievements:

The experiments described above were conducted using specimens of 304 stainless steel and an oil hardened tool steel. For each material, both 1/4 inch and 1/2 inch thick specimens were tested. The influence on results of the sharpness of the notch tip was also investigated. The results indicate good

agreement between the two techniques for determining J provided that two size conditions dictated by the underlying analyses are met:

- 1) the initial curve must be deep enough into the plastic zone so that the HRR field can be expected to provide a reasonably accurate description of the prevailing strain distribution and
- 2) the initial curve must be far enough from the crack tip so that conditions of plane stress can be expected to be met along the initial curve. These conditions are assumed to be satisfied if the mean radius of the initial curve is less than one-third of the plastic zone size and greater than one-half the thickness of the specimen.

It was concluded that the optical method of caustics is a powerful experiment for determining fracture toughness under plane stress conditions. It does require that the extent of the plastic zone be known, but it is shown in our work that it is determined through the experiment. A report on this work is in preparation.

Publications:

Marchand, A., Freund, L.B., Duffy, J. and Ma, C.C., "Use of the Shadow Spot Method in Evaluating J for Ductile Steels," presented at meeting of Society of Engineering Science October, 1985.

Hawley, R.H., Duffy, J. and Shih, C.F., "Dynamic Notched Bar Testing," Metals Handbook (Vol. 8), American Society for Metals, pp. 275-283, 1985.

Duffy, J., "Use of the Kolsky Bar in Dynamic Fracture Initiation," Invited lecture presented at 21st Annual Meeting of the Society of Engineering Science, Blacksburg, VA, October 15-17, 1984.

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

SECTION 2 INORGANIC GLASSES

Introduction

Research in the Inorganic Glasses Group at Brown is concerned with gaining an understanding of the properties of glasses at the microscopic level. The approach is to carry out joint and collaborative theoretical and experimental projects to elucidate the structural characteristics of glasses, the dynamic processes they can undergo, and the way the glasses are formed and transformed.

The research accomplishments for this year reflect this approach. For example, Bray, Cole and Risen report extensive studies of the structures of borate, borosilicate, silicate, boroaluminate, borogermanate glasses, of the nature of interionic interactions and ion motion over a wide range of frequency, and of the thermal properties of these glasses, which range from photoconductive to fast ion conductive materials. These NMR, infrared and Raman investigations are coordinated with the group's efforts to improve glass preparative methods and understand thermal history effects. The structural studies are carried out jointly with experimental investigations of the electrical properties of ion conducting glasses by high frequency (time domain reflectometric, TDR) and bridge dielectric methods.

The TDR studies, which have led to the new insights reported here about the relationship between ion mobility and disordering processes, and NMR studies of ion dynamics, constitute experimental aspects of the group's investigation of dynamics in glasses. Theoretical work on polymer dynamics and on phase transitions by Kosterlitz and Pelcovits, as well as theoretical contributions to the understanding of the group's ultrasonic and other relaxation experiments by Houghton and Maris, are described in this report.

Significant results have been obtained by Maris and Tauc using their new method for studying the transport properties of coherent longitudinal phonons in amorphous solids. Of special note is the observation that, under certain conditions, it is possible to measure the ultrasonic velocity and attenuation of thin films of such materials. The method has been shown to have value both for developing ultrasonic transducers at frequencies as high as 450 GHz and for devising diagnostic devices for thin films. Ultrasonic studies by Elbaum have produced new understanding of two level tunneling systems in metallic glasses through investigation of the temperature dependence of their low temperature ultrasonic velocity.

The nature of light-induced defects in a-SiH and of the recombination processes undergone by defects in that glass have been studied by Tauc and coworkers by optical methods including photoinduced absorption and photoluminescence decays. They also have studied the optical modulation spectra of defects in glass, including an amorphous semiconductor (a-SiH), an inorganic glass (a-As₂S₃) and a polymer (trans-(CH)_x). These spectra yield valuable information about the nature of the states in the gap, which often is not well known for amorphous semiconductors.

Results from all of these studies, as well as other important aspects of the program, such as disordered systems theory, theory of spin glasses, and development of new NMR, NQR and TDR methods, are presented briefly in this section.

W. M. Risen, Jr., Coordinator

Study of Structure and Thermal Properties of Different Alkali Borate Glasses by NMR and Thermal Analysis

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

Personnel: J. Zhong, Graduate Student, Physics Department

Sources of Support: MRL

Objectives and Approaches:

Storage batteries using "superionic" conductors as solid electrolytes represent one of the best solutions to the problem of energy storage. Recent investigations on this subject have demonstrated that important advantages are obtained with the utilization of glassy materials as electrolytes. Some of the interesting superionic conducting glasses are ternary borate systems (e.g., $\text{LiF-Li}_2\text{-B}_2\text{O}_3$). In order to understand the conduction mechanism in the superionic conducting glasses, it is necessary as a first step to obtain structural information on the vitreous matrix $\text{B}_2\text{O}_3\text{-M}_2\text{O}$ (where M is the alkali) itself. Nuclear magnetic resonance (NMR) technique are very sensitive to short-range structural changes in glass systems. Therefore, we have studied the B^{11} resonance signal as a function of alkali content in $\text{B}_2\text{O}_3\text{-M}_2\text{O}$ (M = Li, Na, K, Rb, Cs) glasses. Thermal analysis (DSC and DTA) was also used to obtain the glass transition temperature T_g . The results were analyzed in terms of microscopic structural changes due to the introduction of the alkali ions into the glass network, and a direct connection was found between the structural changes and thermal properties of the glass system.

Research Achievements:

N_4 , the fraction of 4-coordinated borons, when plotted as a function of alkali content, shows different forms for different alkali borate glasses: N_4 becomes smaller as the alkali ionic size gets bigger, resulting in a 50% difference for Li and Cs at $R = 0.818$. ($R = \text{mol\% M}_2\text{O/mol\%B}_2\text{O}_3$) T_g values were measured for $R = 0.667$ for alkali borate glass samples with M = Li, Na, K, Rb, Cs, and were found to show a behavior similar to that of N_4 : T_g values are smaller for glasses with larger alkali ions. The observed behavior of the glasses can be explained qualitatively as follows. N_4 and T_g are closely correlated: The increase of T_g as the alkali content increases at low alkali content is due to cross-linking by the 4-coordinated borons, and the fraction of non-bridging oxygens (NBO's) leads to a decrease in T_g and the viscosity. The lower T_g for alkali glasses of larger ionic size compared with that of smaller alkali ionic size means that the former kind of glasses will attain a glass viscosity of 10^{13} dPa's at lower temperatures. This in turn suggests that the alkali oscillation in the alkali glasses of larger alkali ionic size will have a larger amplitude than in the alkali glasses of smaller ionic size at any particular temperature. This simply comes from different degrees of preference in forming borate units for different alkali glasses. As the alkali oxide is first introduced into the borate network, energy differences make the alkali ions become associated first with tetrahedral borate units (since the bonding energy for the 4-coordinated borate unit is larger than that for the 3-coordinated unit). But the bonding energy decreases with the increasing size of the alkali ions. This leads to the

result that larger alkali ions become associated with 3-coordinated borate units with NBO's at smaller alkali contents compared with smaller alkali ions. Agreement is found between this statement and the Raman spectroscopy study done by Lorosch et al. [Ref.] in which they find that the triborate group ($N_3/N_4 = 2$) is predominant with Li^+ , while the tetraborate group ($N_3/N_4 = 3$) is predominant with Cs^+ . N_4 is in turn smaller for alkali borates of larger alkali ionic size.

References:

J. Lorosch et al., J. Non-Cryst. Solids, 69, 1, 1984.

Raman and Infrared Study of Fast Ion-Conducting Alkali Borate Glasses

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

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

Sources of Support: NSF, MRL

Objectives and Approaches:

The nature of fast ion-conducting glasses and the relaxation mechanisms responsible for their conduction and, more generally, dielectric response is not understood. Those based on borate glasses offer the possibility of gaining more understanding because of knowledge about their spectroscopic variations with composition. In this context, the goal of the project is to determine whether alkali halides added to alkali borates modify the glass network and what structural units are formed. This is of particular interest because the structural conclusions are needed to help interpret the high frequency dielectric data obtained in a coordinated project.

Research Achievements:

The laser Raman and mid-infrared spectra of ion-conducting glasses in the $Na_2O \cdot NaF \cdot B_2O_3$; $K_2O \cdot KF \cdot B_2O_3$; $Li_2O \cdot LiF \cdot B_2O_3$ and $Li_2O \cdot LiCl \cdot B_2O_3$ systems were obtained at several values of the MX mole fraction at the level of $0.2M_2O \cdot xMX \cdot B_2O_3$. At this level network modification can be observed by its effect on Raman features due to boroxol rings remaining in the B_2O_3 based network. In all cases evidence for incorporation of X and production of charge-delocalized halide-containing sites was educed. The mid-infrared spectra were found to be consistent with this interpretation and to show further an increase in four-coordinate boron sites, including introduction of BO_xF_y moieties, as well as a decrease in the B-O-B linkages in the network. The conclusion from investigating glasses in this part of the composition region is that polyatomic charge-delocalized anionic sites, which interact more weakly with M^+ ions, are formed and provide the basis for interpreting the unusual dielectric behavior observed on analygous samples. Using the

structural model being developed, the glasses contain more mobile ions at these sites, and the new sites can relax by motion relative to the adjoining network when the cations are separated from them.

Publications:

"Structural and Dielectric Studies of $0.2M_2O \cdot xMX \cdot B_2O_3$ Ion Conducting Glasses," D. E. Turcotte, R. H. Cole and W. M. Risen, Jr., J. Chem. Phys., in preparation.

The Environment of Lithium Cations in Lithium Borate Glasses

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

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

Sources of Support: NSF

Objectives and Approaches:

A study of the distance between the lithium cation and the four-coordinated boron atom in lithium borate glasses is in progress. A measure of this distance compared with the measurement in the corresponding crystalline compounds will reveal similarities in the local structure of glasses and crystals. This measurement is done using two glasses of identical composition except that in one glass the lithium is predominantly ^7Li and in another it is mostly ^6Li . Since ^7Li has a magnetic moment about six times as large as ^6Li it will have a larger dipolar interaction with the boron nucleus. The difference of these effects yields a measurement of the internuclear distance. Because a four-coordinated boron has a negative charge, it is expected that the lithium cation will be found in very close proximity to the four-coordinated boron.

Research Achievements:

This study has been done in lithium borate glasses up to a composition of $R = 0.7$ ($R = \text{mol}\% \text{Li}_2\text{O} / \text{mol}\% \text{B}_2\text{O}_3$). It is found that the strength of the dipolar interaction between the four-coordinated boron and the lithium is proportional to R . This indicates that for every four-coordinated boron in the glass only one lithium cation is structurally associated with it. The distance between the four-coordinated boron and the neighboring lithium ion is between 2.24 and 2.38 angstroms. Crystals of similar compositions have been fabricated and are being similarly measured.

Relaxation in Inorganic Glasses by TDR

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

Personnel: D. Turcotte, Graduate Student, Chemistry Department
P. Winsor, IV, Postdoctoral Research Associate,
Chemistry Department
J. Perl, Postdoctoral Research Associate, Chemistry Department

Sources of Support: MRL, NSF, Exxon

Objectives and Approaches:

The principal objectives were to characterize the dielectric relaxation behavior of inorganic glasses with special emphasis on fast ionic conducting (FIC) glasses and in the range 10^7 to 5×10^9 Hz previously accessible only with considerable difficulty and unexplored as a result. Such measurements can help to define the mechanisms of charge displacements and transport which are important for understanding the remarkably high electrical conductivity of FIC glasses, particularly at temperatures above 100°C , which make them of much technological interest for use in electrical energy storage devices. Time domain reflectometry (TDR) techniques developed for these and other measurements at megahertz to gigahertz frequencies are the principal experimental tools and the studies are coordinated with other infrared and Raman spectroscopic studies.

Research Achievements:

The principal results in the period reported here were for the family $0.2 \text{ Li}_2\text{O} \cdot y \text{ LiF} \cdot \text{B}_2\text{O}_3$ with $0 < y < 0.7$ at temperatures from 25 to 375°C and frequencies (by Fourier transformation of the TDR data) from 10^7 to 3×10^9 Hz. Over this range, we found no evidence of what has been referred to as the "primary conductivity relaxation" observed at lower frequencies for temperatures below 200°C , or of the onset of translational or lattice modes of the sort seen at higher-far infrared-frequencies.

The remarkable features of the results are that the plateau values ϵ_∞ of dielectric permittivity show large increases on raising temperature. As shown in Figure 18, this is true for all compositions and is more pronounced for higher LiF content. A thermodynamic implication of this result from the Maxwell relation $(\delta\epsilon_\infty'/\delta T)_{E^2} = 8\pi (\delta S/\delta E^2)_T$ is that the entropy S associated with ionic charge displacements increases with electric field E and hence partial ordering of ions and sites in the glass network for no applied field. We believe that the behavior is important contributory evidence for a better understanding of structure and transport processes in these glasses, and further experiments with other alkali halide substituents and more extended measurements are in progress.

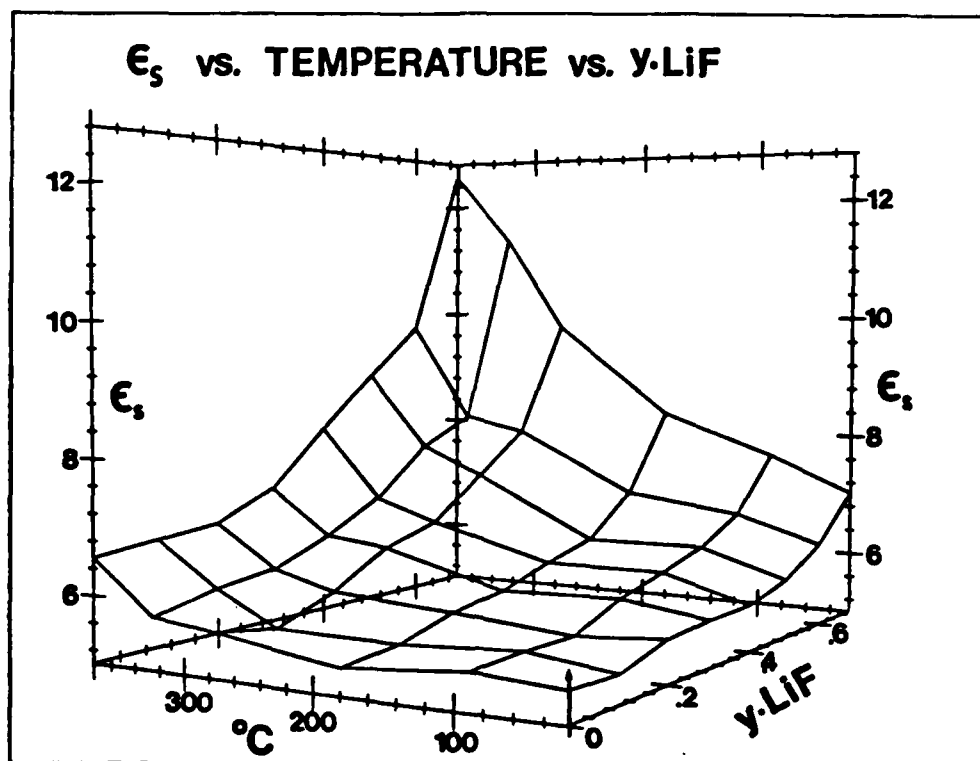


Figure 18

Structural Characterization of the Lithium-Borate Sol-Gel Glass System Utilizing the Method of Nuclear Magnetic Resonance

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

Personnel: E. J. Holupka, Graduate Student, Physics Department

Sources of Support: Sandia National Laboratories

Objectives and Approaches:

The formation of a gel, necessary to the production of sol-gel glasses and glass ceramics, is possible by the hydrolysis and polycondensation of metal alkoxides in alcoholic solution. The resultant general structure of the gel is that of cross-linked polymeric chains. The exact structure of the polymeric chains for binary alkali-borate based gels is not well understood. It is believed that the boron atom is instrumental in the structure and growth of the polymeric backbone.

Nuclear Magnetic Resonance (NMR) studies have been performed on the lithium-borate system prior to hydrolysis and polycondensation. Lithium-borate solutions were obtained from the Sandia National Laboratories characterized by $x\text{Li}_2\text{O}-(1-x)\text{B}_2\text{O}_3$, where x is the molar percent of lithium oxide.

It is known that lithium-borate solutions will not polymerize for $x = 0.0$ and 0.1 . The $x = 0.2$ solution will form a weak gel after a very long aging process. The aging process involves the exposure of the solution to 100% relative humidity. The $x = 0.3$ and 0.4 solutions will form a dense gel. One of the main concerns of this study is to determine why there is no polymerization for solutions containing small amounts of alkali.

Research Achievements:

^1H , ^{13}C , ^7Li , ^{17}O and ^{11}B NMR has been performed on lithium-borate solutions of composition $x = 0.0, 0.1, 0.2, 0.3$, and 0.4 . All experiments indicate the presence of unidentified molecules in the $x = 0.0$ and 0.1 solutions. It has been concluded that these unidentified molecules contain 3-coordinated and 4-coordinated borons. From the ^{17}O and ^{11}B NMR results it has also been determined that these molecules are spatially larger than simple alkyl groups. Since these unidentified molecules have not been observed for $x > 0.1$ it is believed that these molecules are responsible for the breakdown of polymerization for the $x = 0.0$ and 0.1 lithium-borate solutions. Further experiments are in progress to determine the exact structure of these molecules, and a model for the polymeric growth of lithium-borate solutions to form gels is planned for the future. Once the nature of gel formation is fully understood, the gel-to-glass transition will be studied to complete the understanding of the sol-gel production of lithium-borate glasses.

Vibrational Study of Cadmium Borogermanate Glasses

Principal Investigators: W. M. Risen, Jr. and P. J. Bray, Chemistry and Physics Departments

Personnel: G. D. Chryssikos, Graduate Student, Chemistry Department
D. Turcotte, Graduate Student, Chemistry Department
R. V. Mulkern, Graduate Student, Physics Department

Sources of Support: MRL, NSF

Objectives and Approaches:

Cadmium borogermanate glasses and their lead borosilicate analogs have been reported to have interesting electronic and photoconduction properties and a biphasic nature. Understanding cadmium borogermanate and borosilicate glasses in general, and the origin of the photoconductivity in particular, raises challenging questions. Several propositions have been put forward concerning these properties in such vitreous systems, which contain no variable valency ions, ranging from the formation of a "narrow d band" to the presence of interstitial Cd^{+2} or O^{2-} in the glass as in polycrystalline CdO . We have studied the infrared spectra of the cadmium borogermanate glasses throughout the composition region in an effort to provide a structural basis for interpreting the observed properties.

Research Achievements:

The ternary cadmium borogermanate glasses have been studied over the entire glass-forming range by infrared spectroscopy in the $3800\text{-}50\text{ cm}^{-1}$ region. The spectral and structural characteristics of these glasses have been analyzed with respect to the vibrational spectra of binary and ternary glasses of related or analogous composition and of similar structure, and in light of the NMR data we obtained in a companion study of the same glass compositions. It was found that tetracoordination of boron and hexacoordination of germanium both occur, but they do so in a competitive way, as a result of the modification of the network by CdO. The concentrations of three- and four-coordinate boron and a four- and six-coordinate germanium vary with composition in a complex manner, which has been elucidated by analysis of the infrared spectra. This complex variation, which results effectively from competition for oxygen, has been described by a quasi-equilibrium expression for the melt quenched into the glassy state.

Publications:

"An Infrared Study of Cadmium Borogermanate Glasses," G. D. Chryssikos, D. E. Turcotte, R. V. Mulkern, P. J. Bray and W. M. Risen, Jr., J. Noncrystalline Solids, in press, 1986.

An NMR Study of the Photoconducting Glass Systems $\text{CdO-B}_2\text{O}_3\text{-GeO}_2$ and $\text{CdO-B}_2\text{O}_3\text{-SiO}_2$

Principal Investigators: P. J. Bray and W. M. Risen, Jr., Physics and Chemistry Departments

Personnel: R. V. Mulkern, Graduate Student, Physics Department
G. D. Chryssikos, Graduate Student, Chemistry Department
D. E. Turcotte, Graduate Student, Chemistry Department

Sources of Support: MRL, NSF

Objectives and Approaches:

Electronic conduction and near ohmic behavior as well as the diphasic, nature of glasses in the $\text{CdO-B}_2\text{O}_3\text{-GeO}_2$ and $\text{CdO-B}_2\text{O}_3\text{-SiO}_2$ systems have been reported. Several propositions have been put forward concerning the detailed microscopic mechanism for electrical conduction in these systems, which contain no variable valency ions. The objective of this work is to measure and employ ^{11}B and ^{113}Cd NMR data to produce an empirical model of the overall glass structure through the glass-forming region, and to relate it to the results from coordinated infrared studies.

Research Achievements:

The ^{11}B and ^{113}Cd NMR spectra of a large number of glasses through the glass forming regions of cadmium borogermanate and cadmium borosilicate systems were determined. The fraction of four coordinated borons, N_4 , was obtained as a function of molar ratios and analyzed in families of glasses with constant ratios of GeO_2 or SiO_2 to B_2O_3 (K families) and with varying ratios of CdO to B_2O_3 (R). The data for N_4 vs. R fit well to a model analogous to that of Kim and Bray for lead borosilicates. The fraction of the covalently bound cadmium, i.e. network formers, was found to increase linearly with the mole fraction of CdO in the material. This increase was shown to be consistent with both the N_4 data and the ^{113}Cd isotropic chemical shift results.

Publications:

"An NMR Study of the Photoconducting Glass Systems $\text{CdO-B}_2\text{O}_3\text{-GeO}_2$ and $\text{CdO-B}_2\text{O}_3\text{-SiO}_2$," R. V. Mulkern, S. J. Chung, P. J. Bray, G. D. Chryssikos, D. E. Turcotte and W. M. Risen, Jr., J. Noncrystalline Solids, in press, 1986.

Boron and Silicon Coordination in Oxide Glasses: A Statistical Mechanical Model

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

Personnel: R. V. Mulkern, Graduate Student, Physics Department
E. J. Holupka, Graduate Student, Physics Department

Sources of Support: NSF

Objectives and Approaches:

Glass, as a supercooled liquid, has its short range order "frozen" in below T_g (the glass transition temperature) due to the high viscosities in this temperature range. The question as to how, and how much, can this short range order in common multi-component oxide glasses be thermodynamically controlled remains relatively unanswered, both experimentally and theoretically. An extremely simple thermodynamic model is developed to describe the short range bonding arrangement of boron and silicon in alkali-borate and alkali-silicate glasses. The effects of changes in the fictive temperature associated with the final metastable state of the glass on the predictions of the model are investigated.

Research Achievements:

In the alkali-borate glass systems the glass is assumed to consist of five fundamental building blocks. The formation of each particular building block is described by an associated energy of formation, $A_i = E_i/kT$, where i is indicative of the number of bridging oxygens. A classical Boltzman distribution is used for the construction of the glass partition function which describes the glass system. The ratio of the number of tetrahedral borons to the total number of borons (N_4) is calculated as a function of R (the fraction of alkali-oxide to boric-oxide). The agreement of the experimental data from the lithiumborate glass system with the proposed model is acceptable.

As with the alkali-borate glass system, fundamental building blocks for the alkali-silicates are proposed along with their associated energy formation. Again a classical Boltzman equilibrium partition function is constructed and the ratio of the number of silicon tetrahedra with one non-bridging oxygen to the total silicon content (Q_3) is calculated. Excellent agreement between the model's prediction and experimental results were obtained.

The microstructural change of alkali-borate and alkali-silicate glasses subjected to varying quench rates is also calculated. This change in microstructure was concluded to be extremely small for quench rates accessible in the laboratory.

Further studies include the extension of the present model to include glass network formers such as aluminum. The presence of alumina in alkali-borates and alkali-silicates will be investigated, and the question of whether alumina will significantly alter the microstructure of the glass under varying quench rates will be addressed.

Publications:

P. J. Bray, R. V. Mulkern and E. J. Holupka, J. Non-Cryst. Sol., vol. 75, Nos. 1-3, p. 37, October, 1985.

Structural Study of Potassium Borosilicate Glasses

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

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

Sources of Support: NSF

Objectives and Approaches:

Potassium borosilicate glasses have been studied by several investigators in the past few years. They have used various methods, such as Mossbauer spectroscopy, optical absorption spectroscopy, molar volumes and electrical relaxation, to obtain the properties of potassium borosilicate glasses. Up to

now, no useful NMR data has been published. A ^{11}B NMR study of boron coordination in the sodium borosilicate glass system has been performed in the past in this laboratory. It has been shown that, initially, the N_4 value (the fraction of boron atoms in BO_4 units) of the system increases linearly with increasing sodium oxide content in the glass. In this region, the boron coordination in the glass is independent of the SiO_2 content. This behavior continues until the ratio of the sodium oxide content to the boron oxide content is higher than some critical value R_{C1} , which increases linearly with the SiO_2 content of the glass. Between R_{C1} and R_{C2} , N_4 becomes a constant which is equal to R_{C1} . Beyond R_{C2} , N_4 decreases while N_{3A} , the fraction of boron atoms in asymmetric BO_3 units, increases with higher sodium oxide content. A natural extension of the above studies is a ^{11}B NMR investigation of potassium borosilicate glasses.

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 $K = \text{mole}\%\text{SiO}_2/\text{mole}\%\text{B}_2\text{O}_3$, and $R = \text{mole}\%\text{K}_2\text{O}/\text{mole}\%\text{B}_2\text{O}_3$. The slow passage modulation technique was applied to obtain the derivative of the NMR absorption spectrum. The standard area method, obtained by double integration of the derivative spectra, was used to obtain N_4 . The technique of nonadiabatic-super-fast passage was also used to reduce the standard deviations inherent in measurements of N_4 . This technique, which yields the absorption spectrum directly rather than its first derivative, permits faster accumulation of the NMR signals than the slow-passage modulation technique. Finally, computer simulation techniques have been employed to fit the derivative spectra to get N_{3S} and N_{3A} . (N_{3S} is the fraction of boron atoms in symmetric BO_3 units.)

Research Achievements:

The N_4 values of $K = 0, 0.5, 1, 2, 3, 4$ families have been measured, and the N_{3A} and N_{3S} values for $K = 0, 1, 2$, were obtained by computer simulation.

We have found that the values of N_4 , N_{3A} , N_{3S} behave in a qualitatively similar manner to the behavior in the sodium borosilicate system, but the quantitative behavior is different. For the same R and K value, all the N_4 values are lower than the N_4 values for the sodium system, the N_{3A} values are higher than the N_{3A} values for the sodium system, and the N_{3S} values are equal to the N_{3S} values for the sodium system. We have also found that the asymmetric BO_3 units of the potassium system appear earlier (i.e. at lower R values) than the asymmetric BO_3 units of the sodium system. There are four kinds of symmetric BO_3 units in the potassium system. They occur in the boroxol ring unit, tetraborate unit, diborate unit, and di-triborate unit; the latter unit is only found in the potassium borate system. Additional computer simulations will be carried out to gain a full understanding of the microstructure of potassium borosilicate glasses.

Publications:

S. P. Szu and P. J. Bray, " ^{11}B NMR Studies of Glasses in the System Potassium Borosilicate," presented at The American Ceramic Society Glass Division Meeting, Corning, N.Y., November 6-8, 1985.

¹¹B NMR Investigations of Barium Borosilicate Glasses

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

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

Sources of Support: NSF and Polaroid Corporation Grant

Objectives and Approaches:

Using ¹¹B NMR and ideas based upon the Krogh-Moe structural model of alkali borate glasses, the structural environment of the boron atom in the glass system BaO-B₂O₃-SiO₂ is being determined. The fraction (N₄) of boron atoms that are four coordinated to oxygen is being measured by conventional lock-in as well as fast-passage methods. The fractions of borons that exist in the trigonally symmetric and asymmetric environments (N_{3S} and N_{3A}) are being found through computer simulation of the derivative NMR lineshape. The relative abundances of the 4- and 3-coordinated borons are seen to vary with the compositional parameters R and K where the glass composition is R(BaO)-B₂O₃-K(SiO₂). In particular, the behavior of N₄ and N_{3A} is studied and modeled as a function of R and K.

Research Achievements:

It is found that the N₄ versus R data are qualitatively similar to the alkali borosilicate analogues. That is, we find a linear relationship between N₄ and R for small R (0 ≤ R ≤ 0.5). The N₄ behavior breaks near R = 0.5 ending the linearity, and begins to decrease with increasing R. The value of R where the break occurs increases with K. It is expected that the barium borosilicate system will not be entirely analogous to the alkali borosilicate systems, since barium (being an alkaline earth element with ionic charge of +2) may not participate in the glass entirely as a modifier ion. Unlike lithium and sodium, barium may display covalent character (with dependence upon R). The degree of the covalency must be considered when modeling for this system. Therefore, a comparison will be made with systems previously studied containing divalent modifier ions such as the PbO-B₂O₃-SiO₂ and CdO-B₂O₃-GeO₂ systems.

Structural Change at High Sodium Content in Sodium Boroaluminate Glass Elucidated by NMR

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

Personnel: J. Zhong, Graduate Student, Physics Department

Source of Support: MRL

Objectives and Approaches:

Storage batteries using "superionic" conductors as solid electrolytes represent one of the best solutions to the problem of energy storage. Recent investigations on this subject have demonstrated that important advantages are obtained with the utilization of glassy materials as electrolytes. In order to understand the conduction mechanism in superionic conductor glasses, it is necessary as a first step to obtain structural information on the vitreous matrix $B_2O_3-M_2O$ (where M is alkali) itself. In this research we used the characteristics of the NMR technique that are very sensitive to the short-range structural change in the glass system, and studied the B^{11} resonance signal as a function of alkali content. The results were analyzed in terms of microscopic structural changes due to the introduction of the alkali ions into the glass network, and a direct connection was found between the structural changes and an anomaly in the properties of the same glass system observed by different workers.

Research Achievements:

By taking advantage of an exceptionally wide range of glass formation made possible by adding a small amount of Al_2O_3 to the $Na_2O-B_2O_3$ binary system, the NABAL glass system $xNa_2O_3 \cdot (1-x)(0.87B_2O_3 \cdot 0.13Al_2O_3)$ with x up to 0.70 was formed. Conventional Continuous-Wave (CW) NMR techniques were used to observe the B^{11} absorption spectra due to the second-order quadrupolar interaction and dipolar interaction. Spectra under the same measurement conditions were also generated via computer programming and compared with the experimentally obtained spectra. This computer simulation process made all the Hamiltonian parameters characterizing different glassforming units accessible, thus providing us with information concerning microscopic structure. Comparison between the data obtained in this study and the previous studies of the binary sodium-borate glass system shows that the addition of Al_2O_3 in the amount used in this study only "dilutes" the borate network; that is, the number of borate units associated with alkali changes due to the addition of aluminate, but no additional network structural units are introduced. The variation of the Hamiltonian parameters as a function of sodium content found in this study is therefore correlated with the alkali ionic motion and the modification of the glass structure due to the introduction of alkali ions into the different network units. A good explanation was obtained for the anomalous behavior of electrical conductivity observed by Martin and Angell (S. W. Martin and C. A. Angell, J. Am. Ceram. Soc., C-148 (1984)) in terms of the structural change and different activation energies for alkali ions associated with different borate units.

Publications:

J. Zhong and P. J. Bray, "NMR Study of Structure of Sodium Boroaluminate Glass at High Sodium Content," presented at the International Conference on Physics and Chemistry of Glass and Glassmaking, Alfred, NY, July 29-Aug. 2, 1985; accepted for publication in J. Non-Cryst. Solids.

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

Sources of Support: MRL and MRL Optical Facility

Objectives and Approaches:

We are using the picosecond probe and pump technique to study transport properties of coherent longitudinal phonons (strain pulse). Because of the extremely high time resolution (typical pulse duration is 0.1 psec), we can study very thin samples (from a few hundred angstroms to a few micrometers thick) and highly attenuated phonons (up to 10^5 dBcm^{-1}) in disordered materials and at high temperature; there is no other method currently available for these studies. The applications of this technique that we are currently pursuing are in two directions: (i) measurements of the temperature and frequency dependence of the velocity and attenuation of longitudinal phonons in glasses with the aim of obtaining data under conditions that are not accessible to other methods but are of current scientific interest for an understanding of phonon dynamics in glasses, (ii) use of longitudinal phonons for diagnostic studies of thin films, surfaces and interfaces. The wave length of the phonons can be as short as a few tens of angstroms and therefore their propagation is very sensitive to inhomogeneities of this spatial extent.

Research Achievements:

(i) We have observed that under certain conditions the longitudinal phonon propagation can produce sharp features (Fig. 19) which make it possible to measure the ultrasonic velocity and attenuation (Figs. 20 and 21). The sharp features are due to a discontinuity in strain distribution produced by the pump pulse. A detailed theory of this and related effects is being developed. The technique is being applied to other amorphous materials and metals. (ii) A modification of the technique necessary for studying materials in which the strain is not easily detected uses a thin film of an active material as an ultrasonic transducer. Using an extremely thin film of Al on top of the studied film, frequencies as high as 450 GHz have been generated. (iii) As an example of the diagnostic potential of the method, air layers of a thickness of about 100 Å on the surface of As_2Te_3 have been identified from the change of the echo shape.

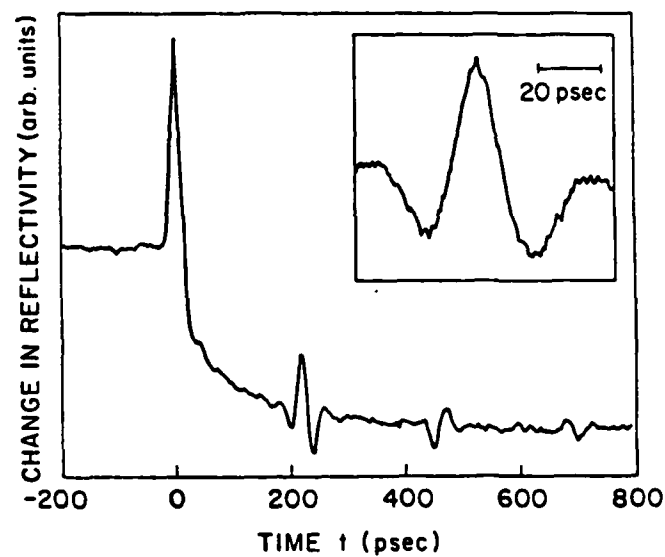


Figure 19: Acoustic echoes in a 2400 Å film of amorphous As_2Te_3 on a sapphire substrate at 300 K. The echoes are detected by observing changes in the reflectivity of the film surface as measured by a probe pulse. The inset shows an expanded view of the first echo.

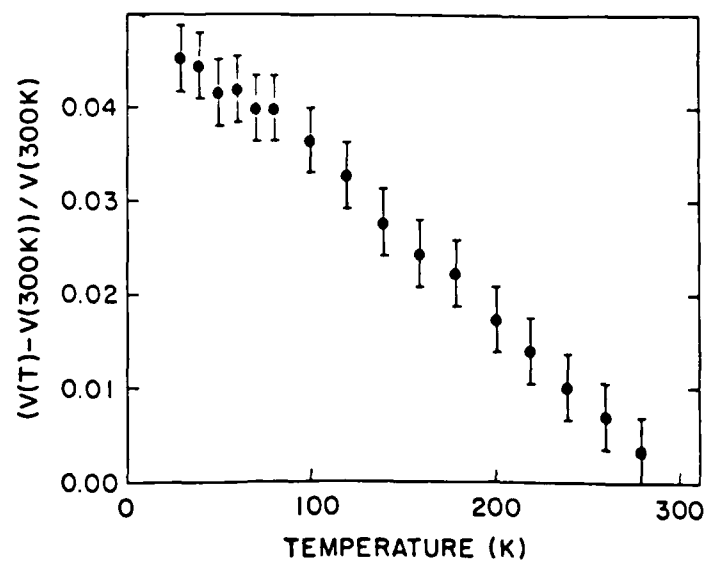


Figure 20: Ultrasonic velocity in amorphous As_2Te_3 as a function of temperature.

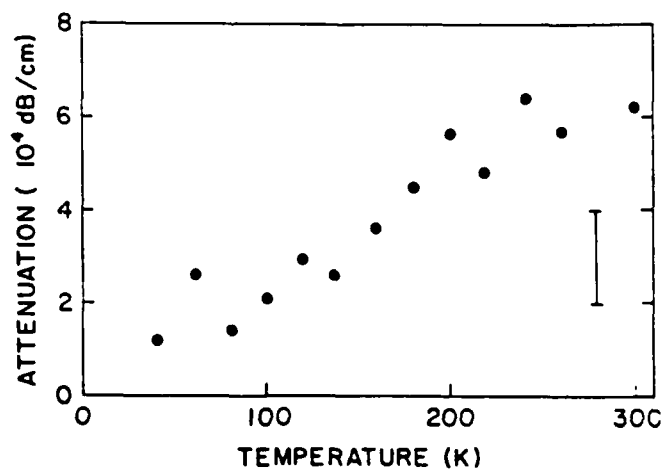


Figure 21: Ultrasonic attenuation at 30 GHz in amorphous As_2Te_3 . The sample was a film of thickness 4150 Å

Publications:

C. Thomsen, H. T. Grahn, H. J. Maris and J. Tauc, "Ultrasonic Experiments with Picosecond Time Resolution," *Journal de Physique*, **46**, C10-765 (1985).

C. Thomsen, H. T. Grahn, H. J. Maris and J. Tauc, "Picosecond Electron and Phonon Phenomena in Amorphous Ge and As_2Te_3 ," *Journal of Non-Crystalline Solids*, **77-78**, 1113 (1985).

Patent Applications:

J. Tauc, H. Maris and C. Thomsen, Optical Generator and Detector of Stress Pulses (pending).

Optical Modulation Spectroscopy of Defects in Glasses

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

Personnel: T. Zhou, Graduate Student, Physics Department

Sources of Support: NSF and MRL Optical Facility

Objectives and Approaches:

Illumination in the main absorption band of a non-metal produces carriers which become trapped in the impurity or defect states in the gap. The carrier trapping produces a change in the optical absorption spectrum. In some spectral regions the absorption coefficient is increased (photoinduced absorption), in other regions it is decreased (photoinduced bleaching). Studies of the spectra produced by optical modulation give information about the states in the gap, in particular about their energies in the charged and neutral states. This is very useful in amorphous semiconductors and glasses in which the nature of these states has often not been convincingly established.

Research Achievements:

We have studied optical modulation spectra in an amorphous semiconductor (irradiated a-Si:H - Fig. 22), inorganic glasses (a- As_2S_3 and a- As_2Se_3) and a polymer (trans-(CH)_x). We have shown that in all three cases the spectra can be explained if one assumes that there are large concentrations of dangling bonds in the materials. The most important parameter one can obtain from these studies is the effective electron correlation energy U_{eff} which can be directly determined from the spectrum when one is able to identify the related absorption and bleaching onsets. The values found for U_{eff} are 0.5 eV in a-Si:H, -1.0 eV in a- As_2S_3 , -0.7 eV in As_2Se_3 and 0.95 eV in trans-(CH)_x.

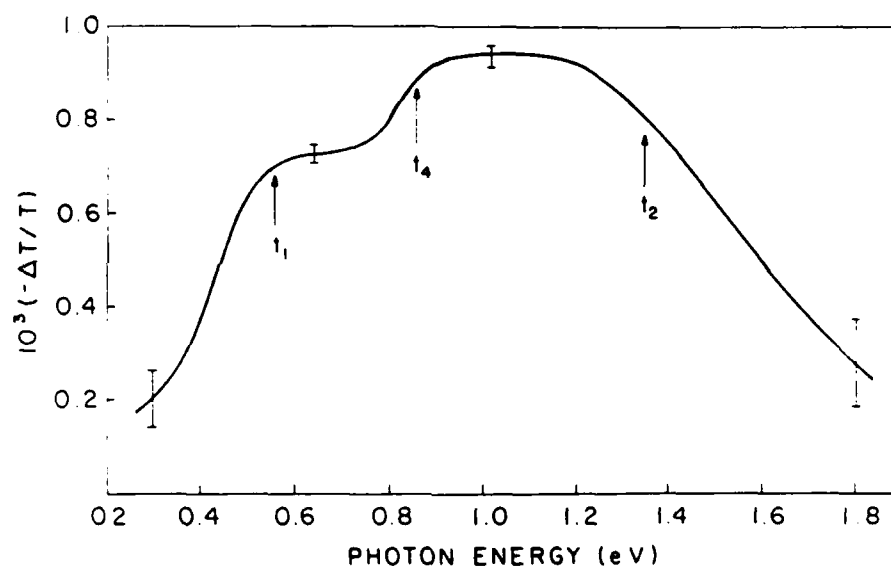


Figure 22: Photoinduced changes ΔT in the optical transmission T in a-Si:H. Transitions t_1 and t_4 are associated with absorption, transition t_2 is bleaching.

Publications:

Z. Vardeny and J. Tauc, "A method for direct determination of the effective correlation energy of defects in semiconductors: Optical modulation spectroscopy," *Phys. Rev. Lett.* **54**, 1844 (1985).

J. Tauc and Z. Vardeny, "Optical modulation spectroscopy of amorphous semiconductors," *Phil. Mag. B* **52**, 313 (1985).

Recombination in a-Si:H Studied by Photoinduced Absorption and Photoluminescence Decays

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

Personnel: D. Pfost, Graduate Student, Physics Department
H. A. Stoddart, Graduate Student, Physics Department

Sources of Support: NSF and MRL Optical Facility

Objectives and Approaches:

In undoped good quality a-Si:H the density of defects deep in the gap is low and the photomodulation spectra consist of absorption regions produced by transitions from the band tails into the adjacent bands and bleaching regions associated with transitions from the opposite band. Photoluminescence spectra are due to transitions from the conduction band tails into the valence band tails. Studies of the decay of the photoinduced absorption band give information about the total recombination and the photoluminescence decay gives information about the radiative recombination. We have been studying these decays as a tool for contributing to an understanding of recombination processes in a-Si:H which are one of the major factors that determine the performance of devices made of this material.

Research Achievements:

We have studied the influence of a bias illumination on the recombination process in a-Si:H by measuring the decay of the photoinduced absorption band. We found that in the time interval of 10 microsecond to 1 millisecond the decay can be represented by a power law $t^{-\alpha}$ where the dispersion parameter α increases with bias illumination. A model describing these experimental data was proposed. A comparison with the experimental data indicates that the band tail states are saturated at high temperatures.

We also studied how the optical biasing influences the decays of photoluminescence. We have observed that at long times the cw photoluminescence is quenched by the pulse illumination (Fig. 23). We have explained this effect as due to the increase of nonradiative recombination produced by transient carriers and found a correlation between the photoluminescence decay and the photoinduced absorption decay.

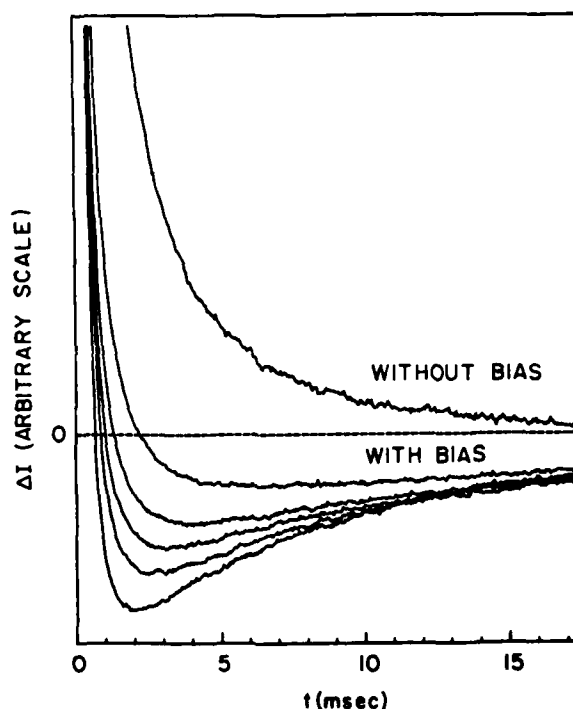


Figure 23: Photoluminescence decay in a-Si:H at 20K. Bias intensities were 64 (highest curve), 127, 191, 254 and 283 mW/cm² (lowest curve). PL intensity ΔI was measured relative to the steady-state PL intensity.

Publications:

J. Tauc, "Time resolved optical modulation spectroscopy of amorphous semiconductors," in Tetrahedrally Bonded Amorphous Semiconductors (edited by D. Adler and H. Fritzsche), Plenum Press, New York, 1985, p. 345.

D. Pfost, Z. Vardeny and J. Tauc, "Optical bias control of dispersive relaxations in a-Si:H," Phys. Rev. Lett. 52, 376 (1984).

D. Pfost, "Studies of spectrally resolved and transient photoinduced absorption in amorphous and microcrystalline tetrahedral semiconductors," Ph.D. Thesis in Physics, Brown University, 1985.

H. A. Stoddart, J. Tauc and Z. Vardeny, "Effect of bias illumination on photoinduced absorption decay in a-Si:H," (Comment) Phys. Rev. Lett. 54, 248 (1985).

D. Pfost, Z. Vardeny and J. Tauc, "Response to the comment by E. Merk, D. J. Dunstan and W. Czaja on the paper Optical bias control of dispersive relaxations in a-Si:H," Phys. Rev. Lett. 54, 251 (1985).

H. A. Stoddart and J. Tauc, "Transient quenching of cw luminescence in a-Si:H," Solid State Communications, 54, 489 (1985).

Light-induced Defects in a-Si:H Observed by Picosecond Photoinduced Absorption

Principal Investigator: J. Tauc, Professor, Division of Engineering and Physics Department

Personnel: J. Strait, Graduate Student, Physics Department

Sources of Support: NSF and MRL Optical Facility

Objectives and Approaches:

We study the thermalization process of photoinduced carriers using picosecond pump and probe technique. The pump pulse of subpicosecond duration produces hot electrons and holes which decay first to the bottoms of the respective bands and then become trapped in increasingly deeper and deeper states in the gap. The probe measures the changes of transmission or reflection produced by these processes as a function of the delay time between the probe and pump pulses. Optical transitions of photoinduced carriers into higher states increase absorption while the occupation of higher states by photoinduced carriers decreases absorption. These two processes determine the photo-induced change in the transmission which is a function of time and can be interpreted in terms of carrier thermalization processes.

Research Achievements:

We have observed that in undoped a-Si:H and irradiated a-Si:H the photoinduced change of transmission, observed with phonons of 2 eV energy for both the pump and the probe, is always negative (photoinduced absorption). However, a-Si:H doped with phosphorus or boron behaves

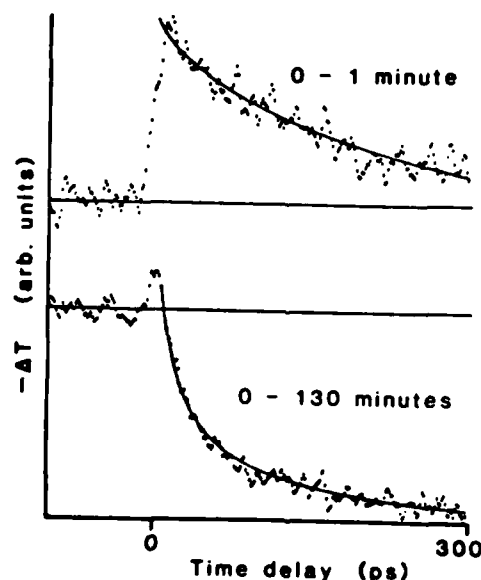


Figure 24: Photoinduced absorption in P-doped a-Si:H measured at 300 K during two different time periods after beginning to illuminate the

differently. At a virgin spot one observes photoinduced absorption onset with subsequent decay. When one continues the measurements for some time, the decays become faster and eventually the signal changes its sign (provided the measurement is done at a high temperature). In this region the photoinduced change in the transmission is positive (a bleaching effect) (Fig. 24). The generation of the bleaching effect is ascribed to photogeneration of dangling bonds in the film. The effect is related to the well known Staebler-Wronski effect (metastable changes in electrical conductivity in a-Si:H produced by light exposure). A model based on the known properties of dangling bonds and dispersive transport of carriers is in good agreement with experimental data on the decay functions including the dependence on temperature and light exposure.

Publications:

J. Strait, "Picosecond photoinduced absorption studies of amorphous silicon," Ph.D. Thesis in Physics, Brown University, 1984.

J. Strait and J. Tauc, "Light-induced defects in a-Si:H observed by picosecond photoinduced absorption," Applied Physics Letters, 47, 489 (1985).

Two-Level Tunneling Systems in Disordered Solids

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

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

Sources of Support: MRL

Objectives and Approaches:

The nearly universal low temperature properties of amorphous solids have been successfully accounted for by the phenomenological two-level tunneling system (TLS) model. This model is based on the existence of localized low energy excitations which are presumed to be intrinsic to the disorder. The actual atomic configuration of these low energy excitations was not specified in the original model; instead it was thought that the TLS could be characterized by a mass m contained in an asymmetric double well potential with separation d . At low temperature ($T \lesssim 1K$), the mass can only occupy the localized ground state of each well, and move between them by quantum mechanical tunneling through the potential barrier of height V , separating the wells. Due to the disordered nature of the amorphous state, there is a distribution of the parameters d , m , and V , and also the energy asymmetry Δ (the offset of the minima of the two wells). For consistency with the results of specific heat and thermal conductivity measurements, the TLS distribution function is usually taken as a constant P .

Notwithstanding the success of the phenomenological TLS model, specific information on what constitutes the tunneling entity or entities has been lacking. The research summarized below was undertaken in an effort to clarify this matter.

Research Achievements:

- (I) We investigated the temperature dependence, at low temperatures, of sound velocity in sintered silicon carbide samples, containing three different sintering additives, boron or beryllium oxide or aluminum nitride. It was found that samples containing AlN or B showed $\ln T$ dependence (T is the temperature) of sound velocity but the one with BeO did not. The slope of the $\ln T$ dependence, which is proportional to the density of states of two level tunneling systems (TLS), is much larger for SiC with AlN than that with B. This sequence and no $\ln T$ dependence in BeO, correlate with the solubility of these additives into SiC, suggesting that the TLS, at least in this case, are created by the additives in solid solutions in the crystals. The samples containing B were heat treated to allow grain growth as well as densification. The density of states of TLS in these samples (measured by the slope of the $\ln T$ dependence of velocity) increased as the grain size increased. This suggests that the TLS do not reside in grain boundaries and that B migrates from the grain boundaries (where it originally segregated) into the bulk, thus creating more TLS inside the grains.

Publications:

A. Hikata, C. Elbaum, Y. Inomata, G. Orange, Y. Takeda, "Ultrasonic Study of Sintered SiC at Low Temperature," *Mat. Res. Bull.* **20**, 823 (1985).

A. Hikata, C. Elbaum, Y. Inomata, G. Orange, Y. Takeda, "Ultrasonic Study of Two-Level Systems in Sintered SiC," *Journal de Physique* **46**, C10-557 (1985).

Research Achievements:

- (II) We have used measurements of the temperature dependence of the low temperature ultrasonic velocity ($d/d\ln T$) ($\Delta v/v$) in metallic glasses to study the effect of structural relaxation on TLS. We have found that annealing at two different temperatures followed by fast cooling produces reversible changes of ($d/d\ln T$) ($\Delta v/v$) similar to those reported previously by Cotts and Anderson for thermal conductivity.

Measurements of many properties of the glass have been found to be reversible (in a metastable state due to nonequilibrium rapid quenching) when the glass is subjected to temperature cycling and rapid quenching. The results of our measurement show that $P\gamma^2$ changes reversibly by about 15% while cycling between 610 and 510°K. Here P is the density of states of TLS and γ is the coupling of TLS to ultrasonic waves. In the same context, Cotts and Anderson found that cycling a sample of PdSi Cu between 520 and 570°K resulted in a 7% change in $P\gamma^2$ as deduced from thermal conductivity measurements. The measurement of the thermal conductivity determines the factor $P\gamma^2$ for the TLS which have energy splittings E on the order of kT , and the resonant contribution to the sound

velocity change depends on TLS with E from $\hbar\omega$ to a few times kT . If we assume that the effect of the annealing is the same for all the TLS in this range of energy splittings, since the temperature range of the two experiments overlapped, the results of the two experiments should be consistent in terms of the amount of reversibility. The difference between the two annealing temperatures for our experiment is twice that of the experiment of Cotts and Anderson, and we find the amount of reversible change of our measurement to be twice that of theirs. Use is made of the excess free volume model to account for these results.

Publications:

G. Cibuzar, A. Hikata and C. Elbaum, "Effect of Thermal Cycling on Ultrasonically Measured TLS Parameters of a Metallic Glass," *Journal de Physique* **46**, C10 (1985).

Disordered Systems Theory

Principal Investigator: A. Houghton, Professor Physics Department

Personnel: F. Seco, Graduate Student, Physics Department
H. Won, Graduate Student, Physics Department

Source of Support: MRL

Objectives and Approaches:

Our research has two main components (1) an ongoing study of the properties of disordered magnets and (2) a recent initiative to study the propagation and attenuation of phonons in very dirty metallic systems both in the bulk and in thin films.

(1) The Ising Model with Quenched Random Fields

The properties of this system, realizable in the laboratory when a uniform magnetic field is applied to a site diluted antiferromagnet, e.g., $\text{Fe}_{0.6}\text{Zn}_{0.4}\text{F}_2$, has provoked intense debate amongst both theorists and experimentalists. We have shown how one can study critical phenomena in this system by means of high temperature series: preliminary results are reported below. Work continues to generate longer series so that we may probe deeper into the asymptotic critical regime.

(2) Ultrasonic Attenuation and Anderson Localization

There is very little detailed work aimed at understanding the effects of strong disorder, $\sigma = \sigma_{\min}$, on phonon propagation and sound attenuation in either bulk metals or thin films. Our starting point has been to study the effect of Anderson Localization and Coulomb interaction on the ultrasonic attenuation in the 'weak localization' limit. Significant corrections to conventional theory are predicted when $\sigma = \sigma_{\min}$ due to anomalous diffusion of the conduction electrons. In the future we propose to study the attenuation on the insulator side of the metal-insulator transition, in the 'electron glass'.

Research Achievements:

We have developed a formalism where by long high temperature series may be used to study the phase boundary of the Random Field Ising Model (RFIM). The series for the RFIM is obtained by partitioning the vertices of the diagrams of the pure Ising series, this procedure can be used in any dimension and for any distribution of random fields. To date we have analyzed series up to eighth order in the high temperature variable. For a bimodal distribution we find that a tricritical point separates a region of the phase boundary for strong disorder at which the ferromagnetic transition is first order from a region at weak disorder where the transition is second order. For a Gaussian distribution the transition is second order along the whole phase boundary for dimension $d > 4$; but for dimension $d < 4$ we again find a tricritical point demonstrating the $D = 4$ is a critical dimension for the RFIM.

We have determined the corrections to the mean field result for the attenuation due to quantum interference. Corrections to the attenuation proportional to $\ln \omega$ and $\sqrt{\omega}$ are found in two and three dimensions respectively. In two dimensions the attenuation is enhanced and if $\omega \tau_{\text{in}} < 1$ the corrections are proportional to $\ln(T\tau)$ increasing as temperature is decreased, here τ_{in} is the electron inelastic scattering time. If we assume that the attenuation at the mobility edge scales then we predict that the attenuation $\alpha = \alpha_0 \omega^{2-\delta}$ where in three dimensions the exponent $\delta = 1/2$.

Publications:

A. Houghton, A. Khurana and F. J. Seco, "Fluctuation-Driven First Order Phase Transition Below Four Dimensions in the Random-Field Ising Model with a Gaussian Random Field Distribution," Phys. Rev. Lett., 55, 856, 1985.

A. Houghton, A. Khurana and F. J. Seco, "High Temperature Series and the Random Field Ising Model," Phys. Rev. B, to be published.

A. Houghton and H. Won, "Sound Attenuation in Metals and Anderson Localization," J. Phys. C. Lett., 18, L507, 1985.

Phase Transitions in Glass, Disordered Magnets and Liquid Crystals

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

Personnel: P. De, Graduate Student, Physics Department
B. J. Minchau, Graduate Student, Physics Department

Sources of Support: MRL, NSF, A. P. Sloan Foundation, U.S.-Israel Binational Science Foundation

Objectives and Approaches:

Our current objective is to study the properties of glass, and glass formation using two approaches: the hydrodynamic theory of glass developed by Das et al., and quasicrystals. The hydrodynamic theory asserts that the nonlinear Navier-Stokes equations for a simple fluid show a tendency towards glass formation. A sharp phase transition to a glassy state does not occur, but the system slows down and experimentally it may be indistinguishable from a glass. We are undertaking a detailed study of this theory to check the validity of perturbation theory used in this approach. We are also examining how more realistic assumptions, such as the asymmetry of the molecules affects the predictions.

We are also interested in quasicrystals as a template for the glassy state. To learn more about the quasicrystalline state we are studying the melting of two-dimensional quasicrystals using a dislocation theory of melting. Quasicrystals display quasi-periodic translational order, and it has been speculated that rapidly quenched liquids approach but do not reach this equilibrium state; instead they form glasses.

Research Achievements:

In the past year we have completed several studies of the smectic C-A transition in thin liquid crystal films, and the low temperature behavior of a particular disordered magnet. For the liquid crystal transition we developed a theory of the critical dynamical behavior with detailed predictions that should be tested experimentally. We also calculated approximately the molecular orientational correlation function which can be measured through light scattering. The techniques developed in this study should be very useful in our present study of two-dimensional quasicrystal melting. In the area of disordered magnets we studied the low-temperature behavior of a two-dimensional XY model with a random field which points up or down along one coordinate axis. We found that this type of disorder induces long-range order (along the direction perpendicular to the field) in a system which in its pure state exhibits only quasi-long-range order. Once again the techniques used to study this two-dimensional system should be invaluable to our quasicrystal study.

Publications:

S. Heinekamp and R. A. Pelcovits, "Spin Correlation Function for the Two Dimensional XY Model," Phys. Rev. B32, 4528 (1985).

S. Heinekamp and R. A. Pelcovits, "Critical Dynamics of the Smectic C-A Transition in Thin Films," Phys. Rev. A32, 2506 (1985).

B. J. Minchau and R. A. Pelcovits, "Two-Dimensional XY Model in a Random Uniaxial Field," Phys. Rev. B32, 3081 (1985).

Polymer Dynamics

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

Personnel: A. Jagannathan, Graduate Student, Physics Department

Sources of Support: MRL

Objectives and Approaches:

The usual method of calculating transport coefficients in polymer solutions is the Kirkwood-Risenman scheme. The objective of this research was to assess the reliability of this method. To do this, one needs the appropriate time dependent correlation functions which yield the transport coefficients. The calculations were limited to calculating these for a single Gaussian polymer chain in a solvent by renormalized perturbation theory.

Research Achievements:

It was shown that the Kirkwood formula for the translational diffusion constant is exact to first order in $\epsilon = 4 - d$ even in a good solvent, but at higher order this is no longer true. For the frequency dependent intrinsic viscosity, the Kirkwood-Risenman method is incorrect.

Publications:

A. Jagannathan, Y. Oono and B. Schaub, "Hydrodynamic Effects on Correlation Function of Gaussian Polymer Chains," Phys. Lett. 113A, p. 341 (1985).

Spin Glasses

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

Personnel: A. Jagannathan, Graduate Student

Sources of Support: MRL

Objectives and Approaches:

This project was on the dynamics of spin glasses using an expansion about an exactly soluble model. The objective behind this was to try to study the freezing process typical of random systems in a special model. The method used was to write down a generating functional which is capable of producing the physical quantities of interest which are the average response and correlation functions. These in turn yield the relaxation times. The essential approximation is to use a $1/N$ expansion about the large N limit where N is the number of spin components.

Research Achievements:

The first topic was fairly successful in that we succeeded in showing that the renormalized relaxation time in the ordered phase of the exactly soluble $N = \infty$ case is driven negative by $1/N$ corrections. This means that the assumed ordered phase is unstable and that the simple phase which appears when $N = \infty$ at low temperatures does not exist in physical systems and a new phase must be sought.

Publications:

A. Jagannathan, B. Schaub and J. M. Kosterlitz, Nucl. Phys. **B256** [FS15], p. 234 (1986).

Approach to Glassy Behavior of Dielectric Relaxation in 3-Bromopentane from 298°K to 108°K

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

Personnel: J. G. Berberian, Visiting Research Professor, Chemistry Department

Sources of Support: NSF, MRL

Objectives and Approaches:

The principal objective was to define the relaxation behavior of a representative glass forming liquid of relatively simple molecules from temperatures well above the melting point nearly to the glass transition temperature over a very wide range of frequencies (10^{10} Hz to 10^{-3} Hz).

There has been a renaissance of theoretical interest in the past two years in the frequency (or time) dependence of relaxation functions in supercooled liquids as the glass transition is approached. The present work was undertaken to define this dependence more completely and over a wider range of temperatures than previously attempted by combining new measurements using Time Domain Reflectometry (TDR) techniques for frequencies from 10 HMz to 5 GHz with previous results (by JGB) for frequencies from 1 MHz to 10^{-3} Hz from bridge and transient methods. With such results, much more definitive determinations of the form of the relaxation function and its changes with temperature make possible more critical comparison with current theoretical predictions. The results can also provide tests of the range of validity of the empirical Williams-Watts, or "stretched exponential" relaxation function and of the "skewed arc" function proposed earlier by D. W. Davidson and one of us (RHC). Similar tests can be made of the range of validity of the empirical Fulcher-Vogel rate law, describing the temperature dependence of the characteristic relaxation time, which has also been widely accepted.

Research Achievements:

Measurements on 3-Bromopentane, selected as a liquid of reasonably simple and symmetrical molecules, have established the following:

- a) The form of the relaxation changes from a simple Debye function (exponential decay in time) at room temperature to a skewed arc function evident below 200°K.
- b) There is increasingly large high frequency asymmetry and deviation from Debye behavior with decreasing temperature to 108°K, as measured by changes of the skewed arc parameter β from 1 to 0.55.
- c) The skewed arc (Cole-Davidson) relaxation function is an excellent fit over the range of relaxation times from 200 ps to 500 seconds, and is significantly better than the best fits possible with the Williams-Watts functions.
- d) Relaxation times τ at temperatures above 200°K have an Arrhenius temperature dependence $\ln \tau \sim \Delta H/RT$ with $\Delta H = 2.75$ kcal/mole and those below 125°K are fitted by the Fulcher-Vogel equation $\ln \tau \sim B/(T - T_0)$ with $B = 742^\circ\text{K}$ and $T_0 = 70^\circ\text{K}$, with the transition between the two regimes on both sides of the melting point at 149°K.

There is reason to believe that such features are characteristic of a considerable number of other glass forming liquids, as they are consistent with less comprehensive results for other simple liquids and for several glycols. On the other hand, distinct differences in relaxation behavior have been found for aliphatic alcohols and for a variety of polymer systems. There is thus no universality in any strict sense of the term, and it remains a task for more detailed molecular theory to understand both the similarities and the differences.

Low-Frequency NQR Studies of Boron and Aluminum

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

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

Sources of Support: NSF

Objectives and Approaches:

Recently, ^{10}B Nuclear Magnetic Resonance (NMR) has been used to determine the various structural groupings found in the sodium borate and lithium borate glassforming systems. The different structural groupings are identified by the effect their different local environments have on the strength and shape of the electric field gradient (EFG) that exists at the nuclear site. The strength and shape of the EFG are characterized by two parameters, Q_{cc} and η respectively. By comparing the various values of Q_{cc} and η found in the glass with the values found in compounds of similar composition, in which the atomic structure is known through x-ray diffraction studies, it is found that at the local atomic level these glasses consist of the same type of atomic groupings that are found in the compounds. Using ^{11}B NMR this type of study has been shown to be extremely useful in many glassforming systems.

^{10}B NMR offers dramatically improved resolution of the quadrupole parameters over ^{11}B NMR. But ^{10}B NMR is more difficult than ^{11}B NMR because of its larger quadrupole interaction and smaller natural abundance. Because of this added difficulty we have been unable to do ^{10}B NMR in the crystalline compounds needed to complete the comparison mentioned above. (NMR is much more difficult in these crystalline compounds than in the glasses due to the increased time needed for the nuclear magnetization to relax to its equilibrium value.)

Another approach to finding the quadrupole parameters of the compounds is to do pure Nuclear Quadrupole Resonance (NQR). NQR is like NMR except that the quadrupole energy splittings are detected without a magnetic field. The resonance frequencies expected are low, and a very sensitive spectrometer is required. Since these samples do not contain hydrogen, double resonance techniques cannot be used. We have been unable to detect ^{10}B or ^{11}B NQR using highly sensitive pulsed NQR spectrometers, presumably because of an extremely short relaxation time. In reviewing the reported boron NQR resonances, they are always found using double resonance or continuous wave (CW) spectrometers. A similar problem also exists in finding ^{27}Al NQR resonances. Thus we are currently building a state-of-the-art Robinson-type CW NQR spectrometer.

Research Achievements:

We have constructed a sensitive state-of-the-art nuclear quadrupole resonance (NQR) spectrometer based on a design by F. N. H. Robinson. Currently, we are working to extend the operating range down to less than 1 MHz, where the boron NQR resonances are expected. This spectrometer design has been shown by Robinson to give a signal to noise ratio at 3 MHz that is limited only by the thermal fluctuations of the sample. Our initial testing has confirmed this observation.

Nonadiabatic Rapid Passage NMR

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

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

Sources of Support: NSF

Objectives and Approaches:

Nonadiabatic Rapid Passage (NARP) NMR has been shown both theoretically and experimentally to give considerable improvement in signal-to-noise ratio over more well known pulsed and continuous wave (CW) lock-in techniques. NARP is done by linearly sweeping either the magnetic field or the frequency through the region of resonance in less than 50 milliseconds. These sweeps are repeated hundreds of times a second, and the detected output is added in a signal averager to give a signal-to-noise ratio that grows with the square root of the number of sweeps. NARP always gives an accurate absorption line shape even if the resonance is slightly saturated. This allows for higher power levels to be used, further improving its advantages in easily saturated samples. NARP is superior to commercially popular pulse and Fourier transform NMR spectrometers for detecting NMR in nuclei with large quadrupole interactions such as ^{11}B .

Research Achievements:

Our CW NMR spectrometers have been operating in the NARP mode for about two years now. Many experiments which were impossible otherwise have been successfully done using NARP. In January, 1986 we will begin operation of a high-field (7 tesla) superconducting magnet and spectrometer purchased from Bruker Instruments. We will be adapting a Robinson-type NQR spectrometer for use as a highly sensitive NARP NMR spectrometer in this magnet. This will give us the ability to study many of the large quadrupole interactions that occur in glasses at this large magnetic field.

SECTION 3 SOLID SURFACES

Introduction

As the ability to characterize static properties of surfaces and interfaces has improved, it has gradually become possible to extend research in this field to studies of surface dynamics. The focus of the MRL thrust at Brown reflects this development; its main objective is to reach a microscopic understanding of processes such as molecular scattering, dissociation and desorption at surfaces. All of these are essential steps in a great many interface phenomena, ranging from surface chemical reactions to epitaxial film growth.

During the period covered by this report, five principal investigators have participated in the thrust, G. J. Diebold, P. J. Estrup, E. F. Green, P. J. Stiles, and S. C. Ying. Through collaborative studies a variety of methods can be brought to bear on a given problem; for example, joint experimental and theoretical work is done on the effects of structure on surface kinetics, and surface analytical techniques are being combined with gas phase laser spectroscopy in studies of surface scattering.

The influence of substrate structural changes on dynamical processes has been investigated experimentally by Estrup and Greene, and theoretically by Ying. Striking effects are observed near reconstructive phase transitions where large changes occur in the phonon spectrum and in the (effective) adatom interactions, and where significant deviations from Arrhenius kinetics are found. Studies of elastic and inelastic scattering are reported by Diebold and by Greene; among the notable results is the demonstration of the versatility of laser fluorescence spectroscopy as a tool in surface dynamics. Progress has also been made by Stiles, Greene, and Estrup in the development of several surface probes, including methods for surface conductance measurements, new atom diffraction techniques and probes of surface vibrations.

P. J. Estrup, Coordinator

Surface Reconstruction of Transition Metals

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

Personnel: J. W. Chung, Graduate Student, Physics Department
M. Altman, Graduate Student, Physics Department

Sources of Support: NSF and MRL (Central Facilities)

Objectives and Approaches:

Structural models are essential to a microscopic understanding of surface properties. Such models are required as the starting point in calculations of electronic and vibrational properties, and provide the basis for the interpretation of adsorption phenomena. In the case of metal substrates, the conventional view of the surface is that of a static arrangement of atoms which in principle can be arrived at by truncation of the bulk crystal, followed by a suitable relaxation to lower the surface free energy. However, recent results suggest that most metal surfaces are much more "active": reconstructions induced by changes in temperature or adsorbate coverage occur frequently and are accompanied by significant modifications of the electron and phonon spectra. These changes in structure are important in all problems involving the surface geometry; furthermore, they can play a crucial role in modifying the adatom-substrate and adatom-adatom interactions that govern the behavior of an adsorbed layer.

In order to study these effects, experiments are carried out on several crystal orientations of bcc transition metals. These are particularly interesting substrates because they exhibit reversible surface reconstructions in readily accessible ranges of temperature and coverage. The principal tool for the structural studies in this work is LEED (low energy electron diffraction). Complementary data are obtained by means of Auger and photoelectron spectroscopy, flash desorption, and work function measurement.

Research Achievements:

New results have been obtained concerning the structural properties of W(100), Mo(100) and Mo(211) surfaces. The available evidence indicates that all of these substrates undergo adsorbate-induced reconstruction; in the case of the (100) orientation, reconstruction is observed even on the clean surfaces at low temperature. On Mo(211) preliminary data suggest that the substrate transformation consists of a lateral shift of the top layer of metal atoms, similar to the phase transition recently discovered for H/W(110).

Striking effects of the substrate structural changes on the effective adatom-adatom interactions are seen in the phase diagrams of H/W(100), (H+O)/W(100), H/W(110), and O/W(100). As an example, the diagram for the last of these is shown in Figure 25, which indicates the surface structures observed in various regions of the coverage-temperature ($T-\theta$) plane. The destabilization of the clean W(100)(2x2) phase caused by small amounts of oxygen can be related to the geometry of the oxygen adsorption site as has been shown theoretically by Ying and co-workers. At higher oxygen coverage, islands of a (2x1) phase are formed in a first-order transition, followed by the

production of a sequence of incommensurate phases. A complete structural analysis of phases such as these is difficult on the basis of LEED data alone; efforts are therefore underway to determine the feasibility of applying surface X-ray diffraction to the problem. This technique is expected to be useful in finding the location of the heavy metal atoms in the reconstructed surfaces. Additional data concerning the vibrational (phonon) properties are needed to elucidate the mechanism of the phase transitions and the nature of the adatom interactions. To this end work has begun to incorporate electron energy loss spectroscopy (HREELS) and infrared spectroscopy in these experimental studies.

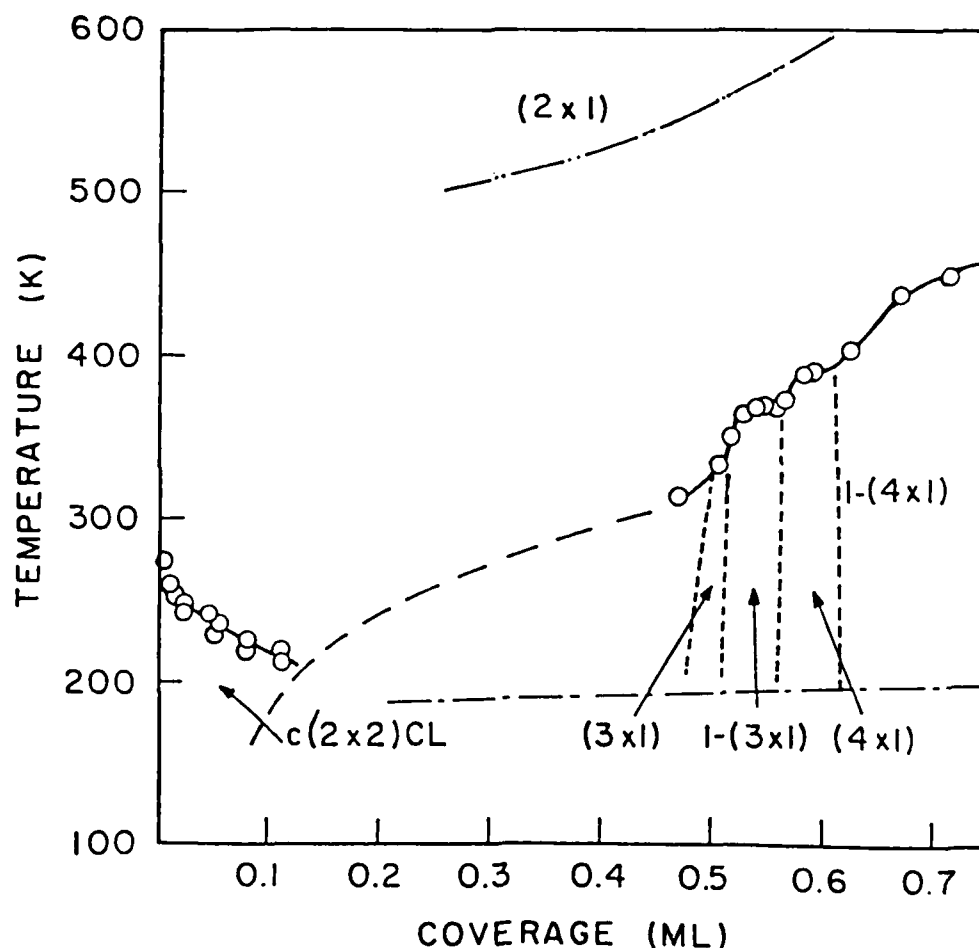


Figure 25: Phase diagram for the reconstructed O/W(100) surface in the temperature-coverage plane.

Publications:

P. R. Estrup, J. W. Chung and S. C. Ying, "Reconstruction of the W(110) Surface Induced by Hydrogen Adsorption," submitted to Physics Review Letters.

P. J. Estrup, "The Effect of Substrate Structural Changes on Adsorption Phenomena," to be published in Accounts Chem. Res.

P. J. Estrup, J. W. Chung and W. Moritz, "The Phase Diagram of O/W(100)," to be published.

Surface Structural Phase Transitions

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

Personnel: S. Tiersten, Graduate Student, Physics Department
L. Roelofs, Assistant Professor, Haverford College

Sources of Support: MRL and ONR

Objectives and Approaches:

In chemisorption systems, a rich variety of surface structures has been found as a function of temperature and adsorbate coverage. The occurrence of different phases can be due to surface electronic structures, adsorbate-adsorbate interaction, or adsorbate substrate interactions. Our objective is to understand which mechanism or mechanisms play the dominant role in a given system and to understand the nature of these phases. The theoretical approach consists of constructing appropriate model Hamiltonians and studying them with numerical simulation methods as well as analytical techniques such as renormalization group methods.

Research Achievements:

In the past years, we have used a deformable lattice gas model to describe the surface structural phase transition on W(100) and Mo(100). We have recently obtained the result that for adsorption on W(100) the initial slope of the T_c (for the 1×1 to $c(2 \times 2)$ transition) v.s. coverage θ is determined mainly by the symmetry of the adsorption site. A bridge site adsorbate such as H enhances the transition, a centered site adsorbate such as O suppresses the transition, whereas an atop site has negligible effects. This theoretical result is confirmed by the experimental data of Chung and Estrup.

A new reconstruction on W(110) has been found by Chung and Estrup. We have proposed a new driving mechanism based on the change in binding energy of the adatoms when the surface is reconstructed. The mechanism is sufficiently general that it may apply to many other chemisorption systems.

We have also proposed a model to explain the reconstruction of Ni(100) surface with a c(2x2) overlayer. This reconstruction comes about because of two degenerate S_1 modes of the Ni(100) surface at the points \underline{X}_1 and \underline{X}_2 are coupled by the adsorbate-substrate interaction. The coupling removes the degeneracy and drives one of the mode soft, leading to the observed reconstruction.

Publications:

S. C. Ying, "Soft Phonons of the Ni(100) Surface," Vibrations on Surfaces IV, England, 1985.

Surface Vibrational Properties and Kinetic Processes

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

Personnel: S. Tiersten, Graduate Student, Physics Department
X. C. Zhang, Visiting Research Associate, Physics Department
T. L. Reinecke, Electronics Division, Naval Research Laboratory

Sources of Support: MRL and ONR

Objectives and Approaches:

Surface kinetic processes such as adsorption, desorption and diffusion form a basis for understanding a number of issues of technological importance including monolayer and interface formation, crystal growth and surface phase transitions and chemical reactions.

Our objective is to understand these processes by studying from first principles the transfer of energy between the adatom and the substrate. In particular, we focus on the vibrational excitations. The approach we use consists of two steps. The first step is to calculate surface vibrational correlation functions which is of interest in its own right. The second step is to use these vibrational correlation functions in a Langevin equation derived from first principle to calculate kinetic properties such as diffusion and desorption.

Research Achievements:

We have calculated various vibrational properties such as spectral densities, surface modes, and correlation functions for both the unreconstructed and reconstructed Si(100) and W(100) surfaces. Surface vibrational modes found on the reconstructed W(100) in our study are in good agreement with recent experimental data. Results for the Si(100) (2x1) surface are shown in Figure 26.

We have derived an analytic expression for the diffusion constant in the limit when the motion of adatom is slow on the time scale of substrate vibration.

For temperatures much lower than the diffusion barrier, we recover the usual Arrhenius behaviour for activated diffusion. For higher temperatures, there are substantial deviations from the simple Arrhenius law.

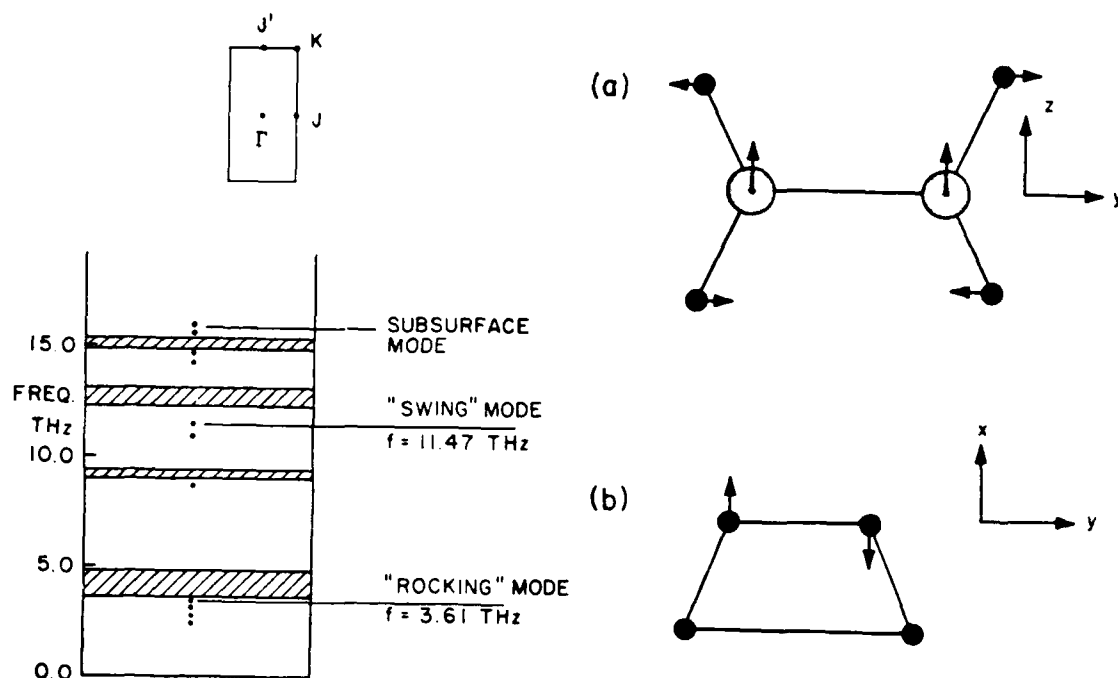


Figure 26: Surface excitations and bulk phonon bands at the corner point of the Brillouin zone. Black dots represent surface phonons.

Publications:

S. Tiersten, S. C. Ying and T. L. Reinecke, "Vibrational Properties of Si(100) 2x1 Surface," Phys. Rev. B, in press.

S. Tiersten, S. C. Ying and T. L. Reinecke, "Dynamics of Semiconductor Surfaces," 12th Annual Conference of Physics and Chemistry of Semiconductor Interfaces, 1985.

T. L. Reinecke and S. C. Ying, "Vibrational Properties of $\sqrt{2} \times \sqrt{2} R45^\circ$ W(100) Surface," Vibrations on Surfaces IV, England, 1985.

S. Tiersten, S. C. Ying and T. L. Reinecke, "Semiconductor surface dynamics and adatom kinetics," International Conference on the Formation of Semiconductor Interfaces, Marseilles, 1985.

Studies of Chemisorption: Desorption and Dissociation Kinetics

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

Personnel: J. Erickson, Graduate Student, Chemistry Department
J. Prybyla, Graduate Student, Chemistry Department

Sources of Support: MRL

Objectives and Approaches:

Processes such as molecular dissociation and desorption are among the fundamental steps which are common to a great variety of surface phenomena. Yet an understanding at the microscopic level of these processes is lacking in most cases. The approach we have chosen to these problems is to obtain detailed experimental data for the kinetics in well-defined systems so that the dependence of the dynamics on the structure and composition of the surface can be explored. For studies of dissociation a method has been developed which monitors the time evolution of the photoelectron spectrum from the surface so that coverage changes for both the adsorbed molecules and the fragments produced by dissociation can be determined. In studies of desorption additional information is obtained by well-established procedures relying on mass-spectrometry. These techniques are combined with LEED and other probes of the static surface properties.

Research Achievements:

By means of isothermal and temperature-ramped photoelectron spectroscopy (UPS and XPS) the rate of dissociation of carbon monoxide, hydrogen disulfide, and ethylene on several molybdenum surfaces have been measured. The results confirm previous findings that structural changes as well as the presence of co-adsorbates, e.g. oxygen, carbon, sulfur or alkali atoms, profoundly influence the kinetics. Qualitatively, the mechanism of these effects can be explained in terms of changes in the local bonding which alter the activation energies and shift the balance between the dissociation step and competing pathways. The quantitative interpretation of the kinetics, however, is made difficult by the apparent failure of the Arrhenius expression $k = A \exp(-E/RT)$ to account for the temperature dependence of the rate coefficients.

Conventional models fail also in the case of our recent results for the kinetics of desorption. Temperature programmed desorption (TPD) of hydrogen from molybdenum(100) gives three peaks which according to the usual interpretation would indicate the existence of three binding states, with the desorption activation energies shown by the step function in Fig. 27a and a constant prefactor (Fig. 27b) of $A = 10^{-2} \text{s}^{-1} \text{cm}^2$. More detailed data -- including adsorption isobars -- show instead that the changes in desorption kinetics are caused not by a multiplicity of states but by a sequence of surface structural changes (Fig. 27). Furthermore, the study shows that at a given hydrogen coverage no single value of E_d can account for the desorption rate, i.e. that the system does not follow Arrhenius kinetics. This result may be true for many other surface systems.

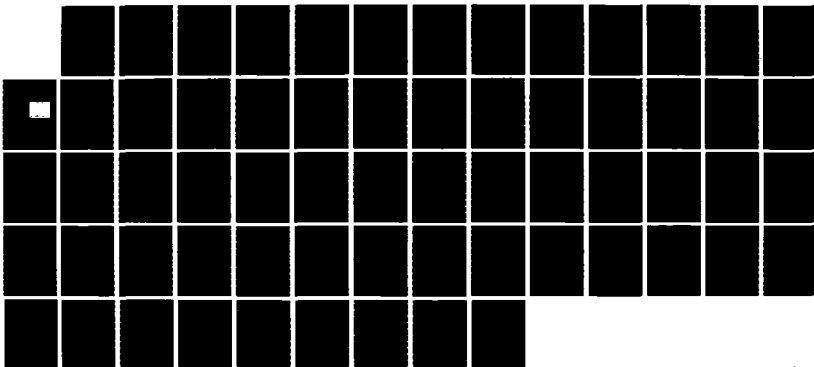
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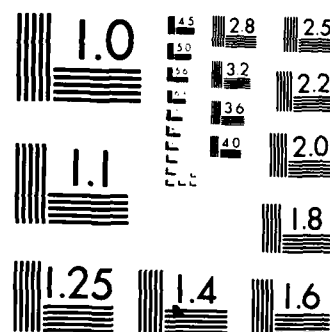
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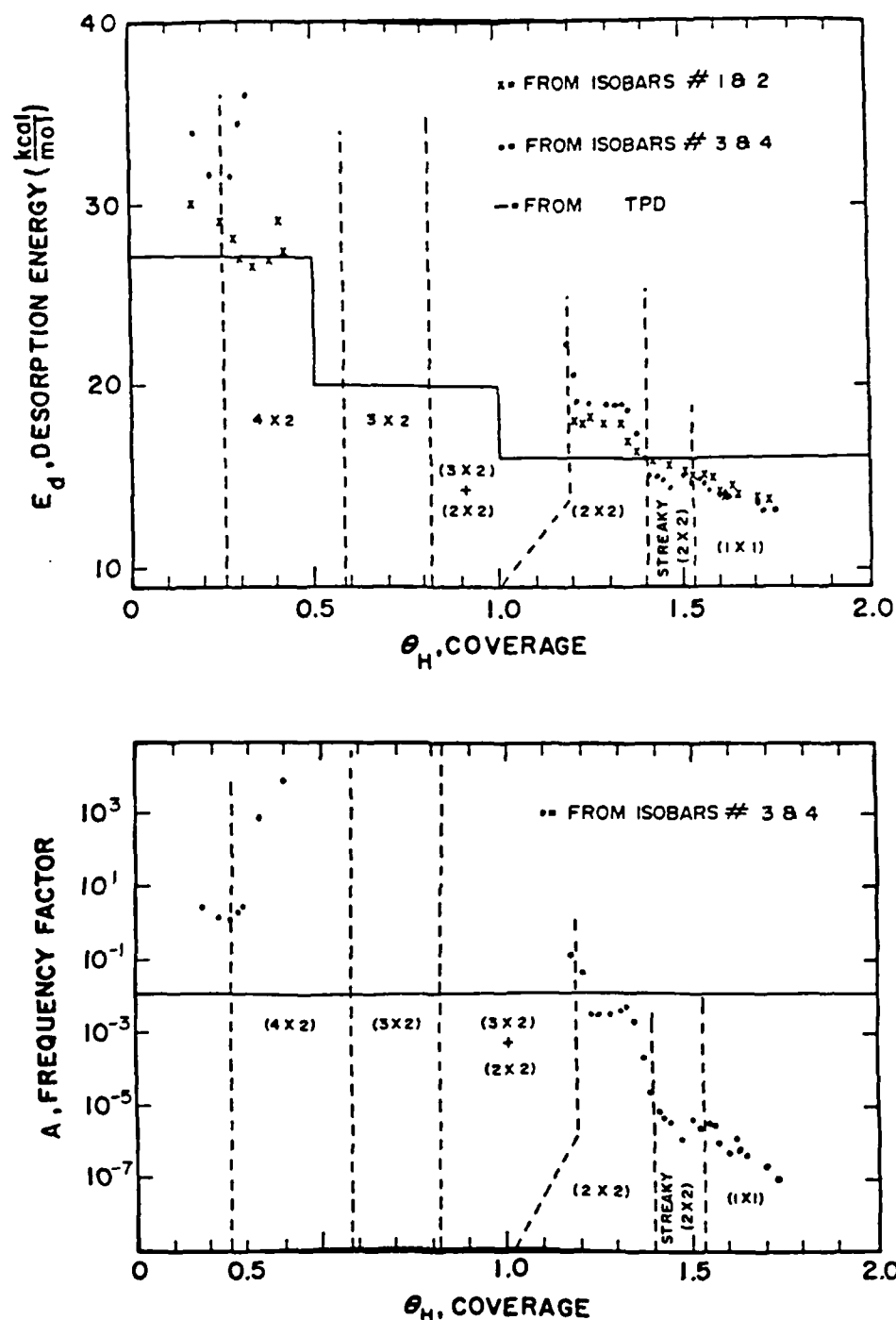


Figure 27: Desorption energy (upper panel) and pre-exponential factor (lower panel) for desorption of hydrogen from Mo(100) as a function of coverage. The straight horizontal lines represent the values obtained by TPD; the points are results from isobars. The vertical lines indicate approximate boundaries between different surface structures.

Publications:

J. W. Erickson and P. J. Estrup, "The Kinetics of CO Dissociation on Mo(110) and Effects of Co-Adsorbates," J. Vac. Sci. Technol. A3, p. 1474 (1985).

J. W. Erickson and P. J. Estrup, "Dissociation of CO on Modified Mo(110) Surfaces," Surface Science (in press).

P. J. Estrup, E. F. Greene, M. J. Cardillo and J. C. Tully, "Influence of Surface Phase Transitions on Desorption Kinetics: The Compensation Effect," J. Phys. Chem. (in press).

Laser Probe of Atom/Surface Impact

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

Personnel: P. R. Muessig, Graduate Student, Chemistry Department

Sources of Support: MRL

Objectives and Approaches:

This project has centered upon the development of a laser probe of atomic relaxation processes at solid surfaces. The experiment uses a single mode dye laser to produce non-Boltzmann hyperfine ground state population distributions in an effusive Na beam via optical pumping. This produces two distinct disequilibria in the ground state energy levels - one between the hyperfine level populations themselves and one between the magnetic sublevel populations of a given hyperfine level. Scattering of such nonthermal beams of Na and LiF surfaces has shown that relaxation of these two disequilibria upon surface impact occurs with substantially different rates; moreover, their surface temperature dependences are markedly different. The aim of this research has been to provide insights into the nature of these surface relaxations, in particular, and to explore the use of laser spectroscopy as a surface tool, in general.

Research Achievements:

The physical significance of collisional quenching of optically prepared atoms is most apparent when the population distributions and the experimental fluorescence intensities are written in terms of state multipoles. When the $F' = 2$ ground state Zeeman level occupation numbers are written as linear combinations of these multipoles, the pumped to unpumped fluorescence intensity ratio from atoms scattered from a surface can be shown to be

$$\frac{5}{8} (1 - R^{21}) = \frac{5}{\sqrt{5}} [T(2,2)_{00}^{\dagger}] + \frac{7}{\sqrt{14}} [T(2,2)_{20}^{\dagger}]$$

$$\frac{5}{8} (1 - R^{22}) = \frac{5}{\sqrt{5}} [T(2,2)_{00}^{\dagger}] - \frac{7}{\sqrt{14}} [T(2,2)_{20}^{\dagger}]$$

where the $[T(2,2)_{KQ}^{\dagger}]$ are the multipole moments of the $F' = 2$ ground state.

The moment $[T(2,2)_{00}^{\dagger}]$ is referred to as the monopole moment of the $F' = 2$ population distribution and monitors the total population of the $F' = 2$ state. It is thus a measure of the disequilibrium between hyperfine states $F' = 1$ and $F' = 2$. $[T(2,2)_{20}^{\dagger}]$ is proportional to quadrupole moment of the $F' = 2$ state, and describes the disequilibrium between the magnetic sublevels of the $F' = 2$ state produced by optical pumping with linearly polarized light.

Figure 28 is a plot of a quenching parameter Q defined as $(R_i - R_s)/R_i$ for D_1 hyperfine pumping as a function of surface temperature, where i and s refer to the incident a scattered Na beams, respectively. Since the plotted curves represent measurement of a simultaneous relaxation of the $[T(2,2)_{00}^{\dagger}]$ and $[T(2,2)_{20}^{\dagger}]$ multipoles, the equations can be used in conjunction with the experimental data to determine the relative amount of relaxation undergone by the two tensors individually. The results of such a calculation show a strong dependence of the relaxation of $[T(2,2)_{00}^{\dagger}]$ on surface temperature, which ranges from no relaxation at room temperature to complete relaxation at a surface temperature of 400°C. The quenching of $[T(2,2)_{20}^{\dagger}]$ on the other hand, shows no correlation with surface temperature: the relaxation appears equally efficient at all temperatures, with a high degree of the incident $F' = 2$ alignment lost after a single surface collision.

In addition to the above experimental work, we have concentrated on the design and construction of a differentially pumped UHV system which will expand the scope and capabilities of the above experiment. Nearing completion, this system will allow us to determine the incident angular dependence of the surface relaxation of optically produced state multipoles in atoms, as well as to study kinetic energy dependences by the use of velocity selective optical pumping methods.

Also of great interest to us at present is the study of experimental and mathematical approaches to the transformation of fluorescence intensity measurements of scattered atomic beams into values of state multipoles whose relaxation has simple physical significance. At present, the mathematical descriptions and experimental geometries required to produce and detect state multipoles of optically pumped atoms are rather complex.

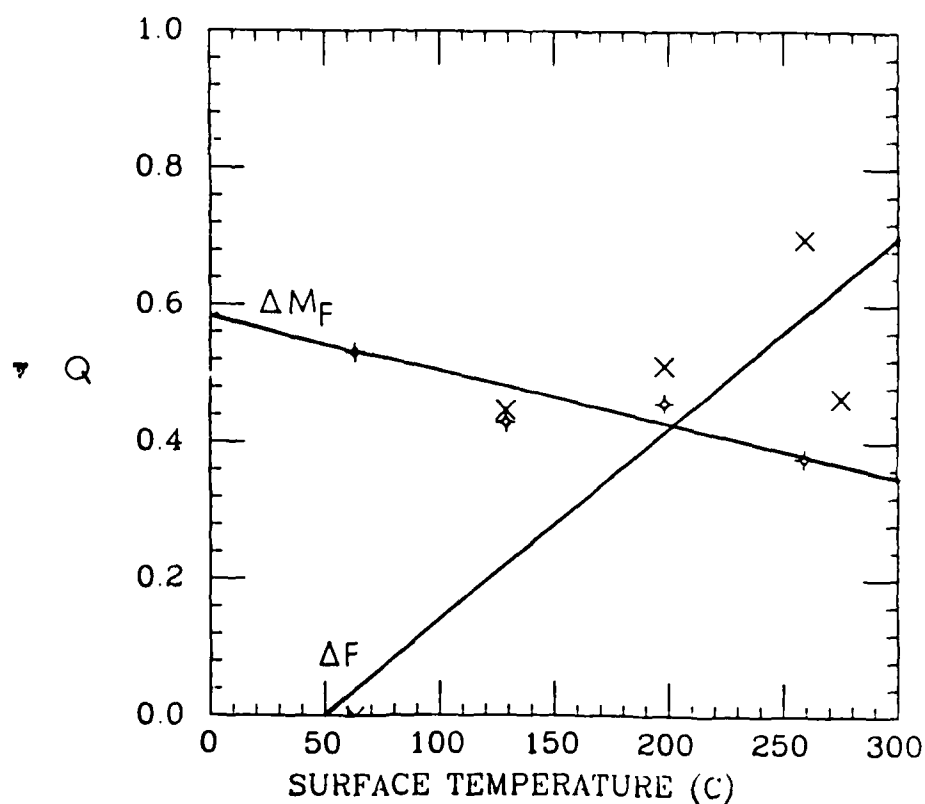


Figure 28: Plot of the quenching parameter, Q , as a function of surface temperature for hyperfine (ΔF) and Zeeman (Δm_F) relaxation of the $F'=2$ ground hyperfine state of Na. Q varies between 0 (no relaxation) and unity (complete spin thermalization). Data were extracted from fluorescence intensity measurements of atoms that had been optically pumped into nonthermal ground state spin distributions by a single mode dye laser, and subsequently scattered from a LiF surface at different temperatures.

Publications:

G. J. Diebold and P. R. Muessig, "Relaxation of Optically Pumped Na on Impact with LIF," Surface Science, in press.

The Scattering and Ionization of Atoms at Surfaces

Principal Investigator: E. F. Greene, Chemistry Department

Personnel: A. D. LeGrand, Graduate Student, Physics Department
D. K. Stewart, Graduate Student, Chemistry Department
T. Tao, Graduate Student, Chemistry Department
J. S. Ha, Graduate Student, Chemistry Department
P. Williams, Undergraduate Student, Physics Department
J. Fechrer, Undergraduate Student, Division of Engineering

Sources of Support: DOE and MRL

Objectives and Approaches:

Thermal beams of noble gases and alkali atoms are used to probe the surfaces of crystals including changes they undergo during surface phase transitions and the efficiencies with which ionization can occur on them. In addition beams having superthermal energies permit studies of the rate of electron transfer between the atoms and the surface as this varies with their distance of separation.

Research Achievements:

The use of a velocity selector to remove all but the nearly elastic scattering of Ne and Ar from the surface of LiF(100) at 300K reveals structure in the differential cross section. Figure 29 shows an example for Ar/LiF(100). Extensive averaging and smoothing is needed, but the structure is clearly visible. A simple theory shows that the structure is sensitive to the potential and may be used to help determine it. Previously such experiments at room temperature have been largely limited to beams of He for which the scattering is mostly elastic.

Superthermal beams of Na (kinetic energy 5-50eV) incident on Si(100) produce ions with nearly unit efficiency in contrast to yields 10-50 times lower for thermal beams. This indicates that the Na is ionized on the surface before it rebounds and that the electron can only return to the ion if the latter is not leaving too rapidly. More extensive studies are expected to show how the probability for the electron transfer varies with the distance over which this takes place.

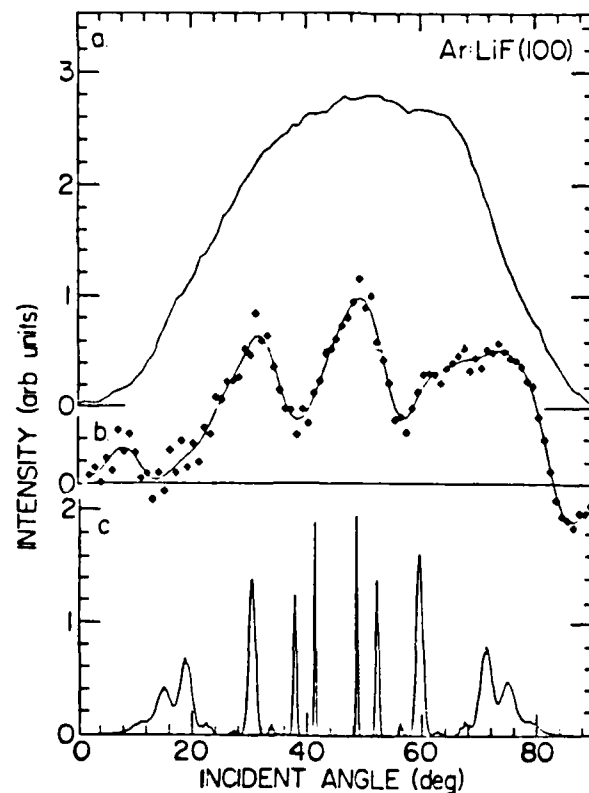


Figure 29: Angular distribution of beam of Ar atoms scattered from LiF(100)<100> with sum of angles of incidence and reflection 90° . Initial Ar energy 63.3meV, surface temperature 294K.

- (a) Measured distribution when detecting atoms of all energies.
- (b) Measured distribution of only nearly elastic scattering.
- (c) Distribution expected according to approximate theory.

Probes of Surface Modification by Surface Conductance Measurements

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

Personnel: D. Popovic, Graduate Student, Physics Department
N. Thantu, Graduate Student, Physics Department

Sources of Support: MRL, NSF, MRL Facilities

Objectives and Approaches

The study of the modification of electronic properties at semiconductor surfaces is in its infancy despite extensive previous work. Traditional surface probes have been utilized in specific cases, but little is known of how it affects electrons at the surface.

We have designed and constructed a simple mechanical configuration and electrical circuits (as illustrated in Figure 30) to study how different treatments of surfaces affects the conducting electrons at semiconducting surfaces. The experimental procedure is to induce surface carriers by the application of a strong electric field perpendicular to the surface. One measures the conductance of these carriers by capacitively coupling to them through the insulator standoffs. By working at sufficiently high frequencies, the impedance of the capacitively coupled sections will be much lower than the resistance of the channel. With the resistance of the gate of this MOSFET-like structure chosen to be much higher than the channel, the total resistance measured by the upper circuit in Figure 30 is that of the channel.

If the semiconductor being studied is one in which microelectronic processing has been used, one would utilize diffused conducting regions for contacting the surface induced carriers, as the high frequency limitation in the technique described above would not be applicable.

Research Achievements:

We have done some preliminary work with the capacitively coupled scheme outside of a vacuum chamber, and it appears to work. We have designed the necessary masks to do the photolithography for the diffused contacts procedure but do not have any results on that yet.

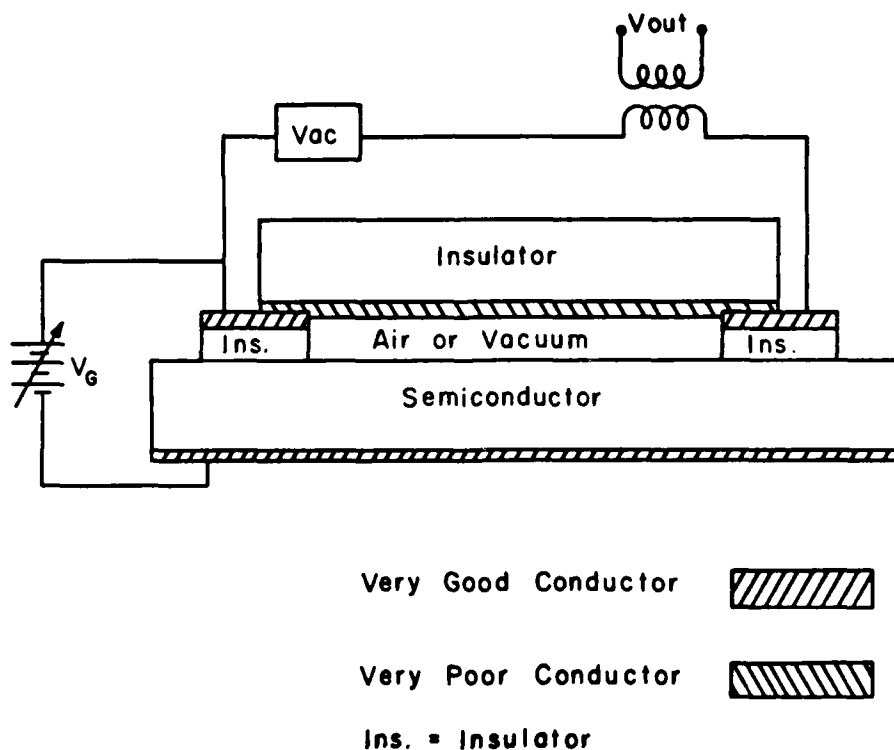


Figure 30: Schematic of circuits for measuring, without resistive contacts, modified surface conductance.

SECTION 4 NEW INITIATIVES

Introduction

During this year three New Initiatives were started in the MRL program at Brown. They initiated programs on electronic materials for semiconductor device applications, surface modification of polymers, and theoretical approaches to treating macromolecules. Significant progress has been made in each of these areas. J. Rosenberg has studied Ge_3N_4 -Ge interfaces and has made the first observation of a p-channel inversion layer in Ge_3N_4 -Ge interfaces and has made the first observation of a p-channel inversion layer in the germanium - germanium (oxy)nitride system. He also reports investigations of pseudomorphic materials for high-speed semiconductor devices, in which the first reported observation of Shubnikov-deHaas oscillations in $\text{In}_x\text{Ga}_{1-x}\text{As}$ grown pseudomorphically on a GaAs substrate was made.

New work on organic polymers includes both chemical treatment of hydrocarbons, by J. W. Suggs, and theoretical macromolecular mechanics by R. M. Stratt and J. Weiner. Suggs reports that the highly oxidizing chromyl trifluoroacetate can be used to functionalize hydrocarbon surfaces without the extensive pitting caused by typical chromic acid treatments. Stratt and Weiner report results from two approaches to incorporating electronic effects in the treatment of macromolecular interactions and transitions.

W. M. Risen, Coordinator

54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100

Electronic Materials for Semiconductor Device Applications

Part I: Physical and Electronic Properties of Ge_3N_4 -Ge Interfaces

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

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

Sources of Support: MRL, Lansdale Transistor & Electronics Corporation

Objectives and Approaches:

Our objective in this project is to study the formation and properties of a high quality insulator on germanium for semiconductor device applications. There are two general areas of application for this work: optoelectronics, and high-speed, low-power digital circuits. The optoelectronics application arises because germanium is one of the most popular materials for photodiodes operating at the 1.3 and 1.5 μm wavelengths used in high-speed optical fiber transmission links. The impact of this study on optoelectronics applications is twofold. Firstly, the development of a passivating insulator on germanium will improve the performance and ease of fabrication of germanium photodiodes. Secondly, the development of a germanium integrated circuit process technology would have significant impact on optical fiber receiver systems. A typical long-wavelength (1.3-1.5 μm) optical fiber receiver currently consists of a discrete photodiode followed by a number of discrete silicon amplifying components. This costly approach could be eliminated if a photodiode were integrated with the amplification circuitry on a single piece of germanium. Germanium field effect transistors (FETs) would also have application to high-speed, low-power digital circuits, because germanium has high mobility for both electrons and holes, which is ideal for complementary FET logic (CMOS). One of the major stumbling blocks in the development of such a technology has been the absence of a germanium-insulator system having sufficient interfacial quality and chemical stability to serve as the basis for germanium FETs.

We are approaching this problem through the study of the germanium-germanium (oxy)nitride system. Native insulating films tend to form better interfaces with semiconductors than deposited films, having a lower density of electrically active localized states at the interface. Germanium (oxy)nitride formed by direct thermal reaction is an attractive choice because it is readily grown and is chemically inert (unlike the oxides), and preliminary studies indicate that it forms a high quality interface with germanium. Our study focusses on the effects of wafer preparation and growth conditions on resulting film properties, and the development of a growth technique which is applicable to germanium FET devices.

Research Achievements:

Preliminary work by Rosenberg had indicated that germanium oxynitride forms a sufficiently good interface with germanium that an n-channel inversion layer can be obtained at the interface of the film with p-type germanium. Functional n-channel FETs were fabricated using a germanium

(oxy)nitride gate insulator. Work during this year has focussed on the properties of films grown on n-type germanium substrates. Metal-insulator-semiconductor (MIS) capacitors were fabricated using germanium (oxy)nitride films on n-type material. Capacitance versus voltage measurements were performed on these structures which show the presence of a p-channel inversion layer under appropriate bias. This is the first observation of a p-channel inversion layer in the germanium-germanium (oxy)nitride system. The presence of a p-channel inversion layer indicates that p-channel FETs are possible (as well as n-channel), which is critical to the goal of germanium complementary FET circuits. Work is continuing on the refinement of the film growth process. Good surface morphologies can now be reproducibly obtained, but a great deal more characterization is needed before the relationship of growth parameters and electrical properties is completely understood.

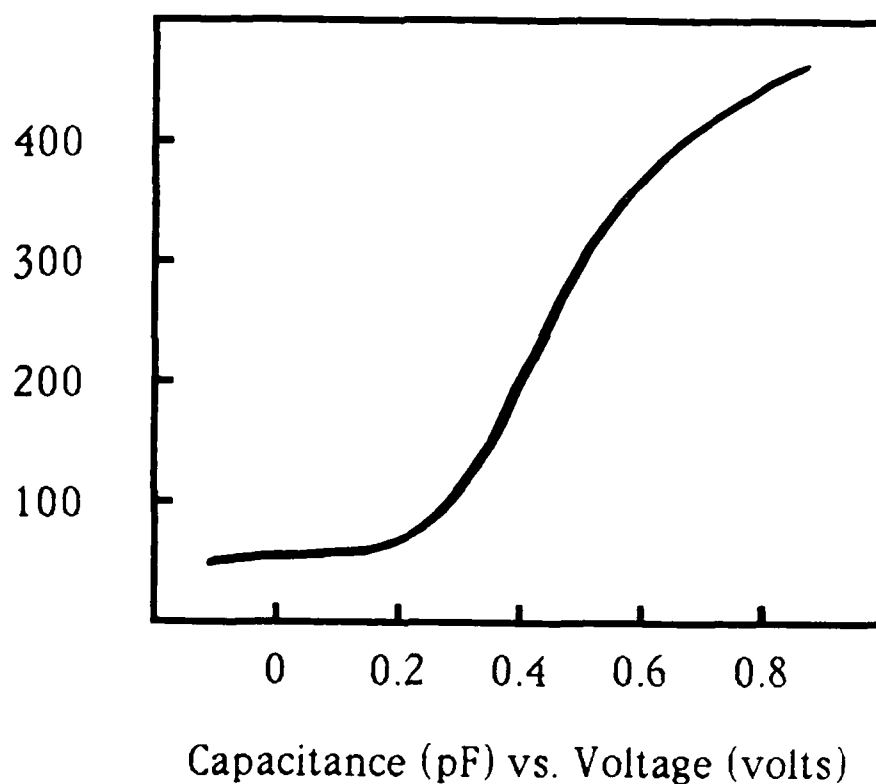


Figure 31: Capacitance-Voltage Plot of Ge MIS Capacitor

Part II. Pseudomorphic Materials for High-Speed Semiconductor Devices
(MRL Central Facility interaction only)

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

Personnel: M. Benlamri, Graduate Student, Division of Engineering
P. D. Kirchner, Research Staff Member, IBM T. J. Watson Research Center
G. D. Pettit, Research Staff Member, IBM T. J. Watson Research Center
J. M. Woodall, Research Staff Member, IBM T. J. Watson Research Center

Sources of Support: IBM Corporation

Objectives and Approaches:

The objective of this project is to study materials and structures which circumvent the requirement of lattice matching in heterojunction pairs. The importance of heterojunctions in optoelectronic devices has long been recognized, and interest in heterojunction devices among the high-speed circuit community is increasing rapidly. One of the restrictions which has traditionally been imposed on the designers of heterojunction devices is that the two materials which make up the heterojunction must have the same lattice spacing so that the crystal planes are continuous and no misfit dislocations are formed. This greatly limits the flexibility of the device designer, since the number of lattice matched semiconductor pairs is not very large.

Our approach to this problem has been to investigate structures in which a lattice mismatched layer of semiconductor is grown which is sufficiently thin so that all of the lattice mismatch can be accommodated as elastic strain, and essentially no dislocations are formed. Such materials are called pseudomorphic. This technique not only eliminates the need for lattice matching if only a thin layer (typically a few hundred angstroms for a lattice mismatch of ~1%) of one semiconductor component is needed, but also creates a new class of very highly strained materials whose electronic properties differ from their unstrained bulk counterparts.

Research Achievements:

Modulation doped heterostructures of GaAs (wider bandgap material) and $\text{In}_{.15}\text{Ga}_{.85}\text{As}$ (narrower bandgap material) were grown by our colleagues at IBM using molecular beam epitaxy. Transistors and other test structures were then fabricated on these layers in the MRL microelectronics facility. This particular material system was chosen because it eliminates the need for heavily doped $\text{Al}_x\text{Ga}_{1-x}\text{As}$ (which is typically used in these structures because it is lattice matched to GaAs). $\text{Al}_x\text{Ga}_{1-x}\text{As}$ is undesirable because it contains trap states (the DX center) which give rise to undesirable effects in transistors, such as uncontrolled shifts in turn-on voltage and failure to operate without illumination.

Transistors fabricated on these pseudomorphic layers showed good overall performance, and none of the problems associated with $\text{Al}_x\text{Ga}_{1-x}\text{As}$ or DX centers. Additionally, low temperature magneto-transport measurements were performed on test structures in Stiles' superconducting magnet facility. Shubnikov-de Haas oscillations which verified the existence of a two-dimensional electron gas at the $\text{In}_{0.15}\text{Ga}_{0.85}\text{As}/\text{GaAs}$ were observed. This was the first reported observation of Shubnikov-de Haas oscillations in strained $\text{In}_x\text{Ga}_{1-x}\text{As}$ grown pseudomorphically on a GaAs substrate. Moreover, the transport measurements demonstrate that the heterojunction interface is of good quality, having an electron mobility roughly $100,000 \text{ cm}^2/\text{volt-sec}$ at 4.2 K and good uniformity, thus demonstrating that the interface is, indeed, not dominated by misfit dislocations.

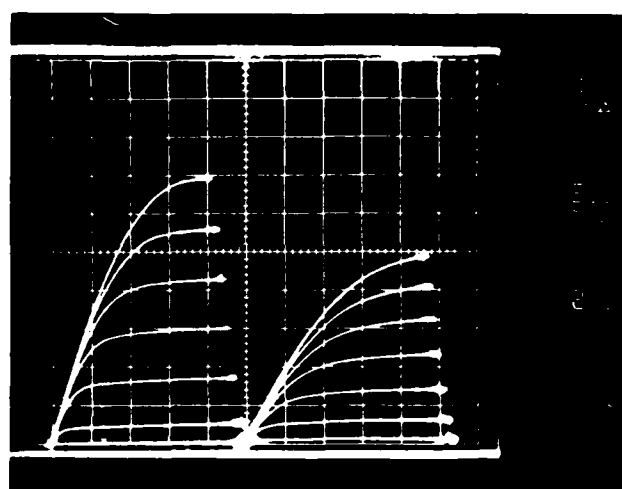
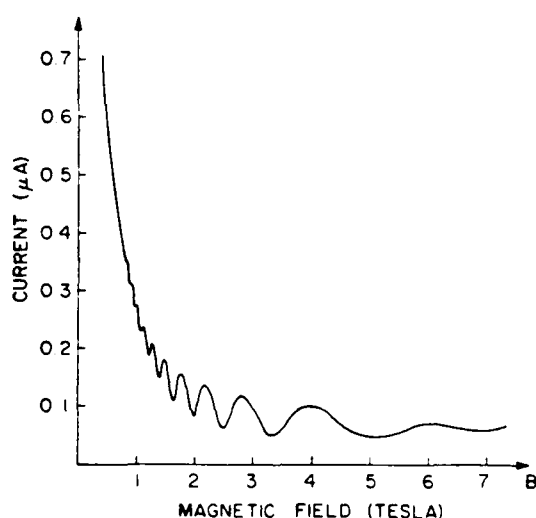


Figure 32:

Magneto-conductance of
Corbino Disc at 4.2 K

2 μm gate length FET characteristics
at 77 K (L) and 300 K (R)

Publications:

J. J. Rosenberg, M. Benlamri, P. D. Kirchner, J. M. Woodall and G. D. Pettit, "Pseudomorphic GaInAs/GaAs Single Quantum Well High Electron Mobility Transistor," Proceedings of the 1985 Device Research Conference (Boulder, CO), VA-5, 1985.

P. D. Kirchner, J. M. Woodall, G. D. Pettit and J. J. Rosenberg, "Pseudomorphic GaInAs/GaAs Single Quantum Well Structures with High Electron Mobility," Proceedings of the 1985 Electronic Materials Conference (Boulder, CO), p. 136, 1985.

Surface Modification of Polymers

Principal Investigator: J. Suggs, Assistant Professor, Chemistry Department

Personnel: L. Ytuarte, Graduate Student, Chemistry Department

Sources of Support: MRL and PRF

Objectives and Approaches:

The aim of this work is to prepare organic polymer surfaces with specific types and densities of surface functional groups. Phenomena such as wear, adhesion and wetting involve processes occurring at or near the polymer's surface. By manipulating the surface chemistry (without making major changes in the surface roughness) one can relate macroscopic behavior (such as adhesion) to a surface's microscopic characteristics.

The use of high energy chemical oxidants, in particular chromyl trifluoroacetate, has allowed us to introduce surface functional groups onto polyethylene in organic solvents, which wet the polymer surface. This leads to a more uniform distribution of surface functional groups, and less surface pitting. Two different causes have been advanced for the poor adhesive properties of polyolefin surfaces, and the improvement caused by oxidative treatments. Either pretreatment eliminates weak boundary layers or oxidation introduces polar surface groups which increase wetting and permit interactions stronger than dispersion forces. By using our chemistry to introduce different types of surface functional groups (ketones, alcohols, amines, carboxylic acids) and the central mechanical testing facilities of the MRL, we are attempting to determine the importance of chemical vs. mechanical effects on the adhesion of polyethylene to aluminum.

Research Achievements:

Our experiments have shown that chromyl trifluoroacetate ($\text{CrO}_2(\text{O}_2\text{CCF}_3)_2$) is able to react with secondary and tertiary C-H bonds of model hydrocarbons at temperatures as low as -50°C . Hexane, for example, gives only 2-hexanone and 3-hexanone with no chain scission. Using high density polyethylene, chromyl trifluoroacetate introduces surface ketone and alcohol functional groups, without the extensive pitting caused by traditional aqueous chromic acid treatments. Attenuated total reflectance infrared spectroscopy is not sensitive enough to detect the chemical changes on polyethylene films caused by $\text{CrO}_2(\text{O}_2\text{CCF}_3)_2$. However, by oxidizing polyethylene powder, pressing this into films and then using transmission infrared spectroscopy, the presence of alcohol and ketone groups is easily seen, as the figure illustrates.

Chemical treatments can further modify the surface functional groups, as followed by infrared spectroscopy. Sodium borohydride gives predominately surface alcohol groups and reductive amination with NH_3 -formic acid gives surface amine groups. An investigation of these modified surface's adhesion properties is now underway.

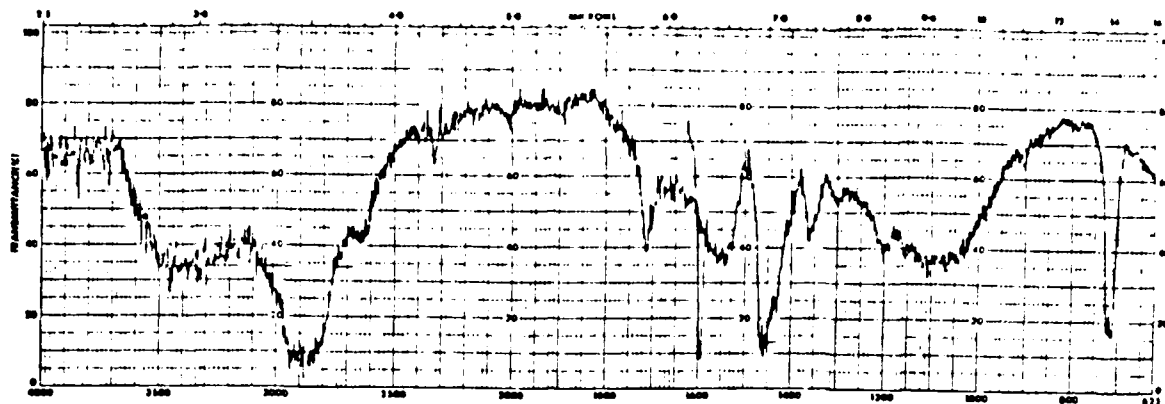


Figure 33

Publications:

J. W. Suggs and L. Ytuarte, "Hydrocarbon Oxidations with Chromyl Trifluoroacetate," *Tetrahedron Letters*, in press.

Conformational and Electronic Transitions in Macromolecular Systems

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

Personnel: V. Dobrosavljevic, Graduate Student, Physics Department

Sources of Support: MRL and NSF

Objectives and Approaches:

The physics and chemistry of conjugated polymers has always been perceived as an interesting case study in the electronic structure of low-dimensional materials. Polymers such as substituted polydiacetylenes, however, have the additional feature of a variable conformation capable of influencing the electronic structure. Hence the traditional polymer science study of conformational behavior takes on a new depth with conjugated polymers. Urethane substituted polydiacetylenes, for example, undergo an abrupt color change as the temperature is varied, a change almost certainly caused by a conformational transition. Light scattering, visible absorption, infrared absorption, and Raman spectra all point, in one way or another, to there being a conformational origin to the transition. The theoretical question we therefore need to answer is what the influence of a variable conformation is on the band gap and density of states of conjugated polymers in condensed phases. By facing this question one confronts the intriguing interplay between the statistical mechanics of conformational equilibria and the electronic structure of particular conformations.

Research Achievements:

There had been little unanimity in the literature about the detailed nature of the polydiacetylene transition, but one set of experimental observations seems incontrovertible - the finding that there were multiple peaks corresponding to what were presumably single spectral features. What had always been assumed was that these peaks were the signatures of several discrete conformational structures, probably structures with fairly well defined effective conjugation lengths. However there was no specific notion of what these structures might be, much less why they were there at all.

We decided to approach the problem from a rather different perspective. Instead of postulating fixed conformational structures, we assumed that the main role of conformational variability was to create *disorder*. Effectively, the polydiacetylene problem was reduced to a one-dimensional amorphous semiconductor with a novel kind of disorder -- conformational disorder. In these terms we were quite naturally able to treat the electronic structure by standard Greens functions techniques. Using a renormalized version of one of these techniques, we were able to show that the electronic density of states had numerous peaks even without explicit conformational structure. The peaks in the spectra therefore were seen to represent conformational disorder present at different length scales. We hope that this encouraging finding will eventually allow us to broaden our understanding of the relationship between conformation and electronic structure in conjugated polymers in general.

Publications:

T. DeSimone, R. M. Stratt, "Some Developments in the Theory of Modulated Order. I. The Role of Fluctuations in the ANNNI Model and the Relevance of the TAP Equation," Phys. Rev. B 32, 1537 (1985).

T. DeSimone, R. M. Stratt and J. Tobochnik, "Some Developments in the Theory of Modulated Order. II. Deformable Lattice Models and the ANNNI Model as a Random Magnet," Phys. Rev. B. 32, 1549 (1985).

Forces in Long-Chain Molecules

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

Personnel: D. Berman, Graduate Student, Division of Engineering
J. Gao, Graduate Student, Physics Department

Sources of Support: MRL and Gas Research Institute

Objectives and Approaches:

The term "rubber elasticity" refers to the mechanical behavior of an amorphous, cross-linked network of long-chain molecules at temperatures above

the glass transition, that is in the regime in which the molecules undergo large amplitude thermal motion with large changes in chain conformation. As such, the subject has far wider areas of application than its name may suggest and it has been referred to by Flory as "central to polymer science".

From the beginnings of the theory just over fifty years ago, a key element has been the force-length-temperature relation, $f(r,T)$, for a long-chain molecule, where f is the axial force required to maintain the ends of the molecule at a distance r when it is at temperature T . This relation has been derived over the years by many different investigators using various formulations and models. All have led to purely tensile relations, that is $f \geq 0$ for all r with $f = 0$. This result has awkward consequences for the theory of rubber elasticity, since it suggests that a network of such chains would collapse to a point.

Research Achievements:

We have analyzed this problem on the basis of a model which contains excluded volume interactions which prevent atoms from occupying the same place in space and is based, from the viewpoint of statistical mechanics, on an ensemble in which the end-to-end distance r is fixed and the force fluctuates. By computer simulation we find that in this case the chain does not have a purely tensile relation, but rather there exists an $r_0 > 0$ such that $f(r_0) = 0$ with $f < 0$ for $r < r_0$.

Previous computations of excluded volume effects have been based on an ensemble in which f is fixed and r fluctuates and these led to a purely tensile relation. In the case of a long-chain molecule, therefore, it appears that these two ensembles do not lead to the same $f(r,T)$ relation in contrast to the case for the corresponding volume and pressure ensembles for a gas.

We have also found a second important difference between the $f(r,T)$ relation for a long-chain molecule and the $p(v,T)$ relation for a gas to which it is often compared. We have examined the fluctuations Δf in the axial force by means of statistical mechanics and computer simulation and find that the relative fluctuation, $\Delta f/f$, remains large even when N , the number of atoms in the chain becomes arbitrarily large.

Publications:

J. H. Weiner and D. H. Berman, "Bond Forces in Long-Chain Molecules," J. Chem. Phys. 82, 548-551 (1985).

J. H. Weiner and D. H. Berman, "Compressive Axial Forces in Long-Chain Molecules Due to Excluded-Volume Effects," J. Chem. Phys. 83, 1311-1315 (1985).

J. H. Weiner and D. H. Berman, "Axial Force Fluctuations in Long-Chain Molecules," J. Polymer Science, Polymer Physics Edition (in press).

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 $3d$ 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 catalysts. 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 changes in resistivity as a function of temperature and this unusual property can be correlated with corresponding changes in crystal structure.

Physics and Chemistry of Semimagnetic Semiconductors
(Cooperative Program with the National Magnet Laboratory at M.I.T.)

Principal Investigator: A. Wold, V. K. Krieble Professor, Chemistry Department

Personnel: D. H. Ridgley, Research Associate, Chemistry Department
Y. Shimony, Research Associate, Chemistry Department
R. J. Kershaw, Senior Research Engineer, Division of Engineering
K. Dwight, Professor (Research), Chemistry Department
D. Heiman, Research Staff Member, M.I.T./Francis Bitter National Magnet Lab
R. L. Aggarwal, Senior Research Scientist, M.I.T./Francis Bitter National Magnet Lab
Y. Shapira, Senior Research Scientist, M.I.T./Francis Bitter National Magnet Lab
P. A. Wolff, Director, M.I.T./Francis Bitter National Magnet Lab

Sources of Support: MRL (Brown University and M.I.T.) and ONR

Objectives and Approaches:

During the past year the effort with M.I.T. has concentrated on the study of the magnetoresistance of members of the system $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ near the Mott transition. At $0.5 < T < 4.2\text{K}$ and for field of order 10kOe , a large positive magnetoresistance is observed in $\text{Cd}_{0.95}\text{Mn}_{0.05}\text{Se}$ and $\text{Cd}_{0.99}\text{Mn}_{0.01}\text{Se}$ samples which are near the Mott transition. The effect is attributed to an increase in the screening radius, caused by the splitting of the conduction band. At higher fields, but below $\sim 80\text{kOe}$, samples with 5% Mn show negative magnetoresistance which is attributed to a decrease in the separation between the Fermi level and mobility edge.

In addition, low temperature photoluminescence studies of $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ samples were carried out for $x = 0.10$ and $x = 0.20$. These studies indicate that for these compositions, the development of the magnetic polaron is accompanied by large changes in the exciton binding energy and radiative lifetime. The formation of the magnetic polaron is quicker in the $x = 0.20$ sample than in the 0.10 sample. In both these samples, the formation time for the magnetic polaron is seen to decrease with decreasing temperature. For the $x = 0.10$ sample there is a temperature range where the magnetic polaron formation time is greater than the exciton lifetime, and the equilibrium state of the system cannot be observed in time-averaged experiments. Finally, the lifetime of the exciton-magnetic polaron complex in the $x = 0.20$ sample is seen to increase with temperature between 4K and 17K .

Research Achievements:

Brown's contribution to the Cooperative Program with the National Magnet Laboratory at M.I.T.: A technique has been developed for the growth of high quality, single grain boules of members of the system $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ with $x = 0.01, 0.05, 0.10$ and 0.20 . All of the boules grown showed uniform manganese distribution. Free carriers were introduced in a controlled fashion by adding gallium to the melt and annealing crystal slices in cadmium vapor. Reproducible carrier concentrations from 2×10^{17} to $2 \times 10^{18}\text{cm}^{-3}$ have been achieved.

In addition, a convenient, non-destructive method for monitoring the Mn uniformity in $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ was shown to be the shift with Mn concentration of an optical absorption edge near 700 nm. The shift is about 4.0 nm for each 1% Mn and the sensitivity is of the order $\pm 0.25\%$ in absolute Mn content.

Publications:

Y. Shapira, D. H. Ridgley, K. Dwight, A. Wold, K. P. Martin and J. S. Brooks, "Magnetoresistance of $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ Near the Mott Transition," J. Appl. Phys. 57, (1), 3210 (1985).

Y. Shapira, D. H. Ridgley, K. Dwight, A. Wold, K. Martin, J. Brooks and P. Lee, "Magnetoresistance Near the Metal-Insulator Transition of $\text{Cd}_{0.99}\text{Mn}_{0.01}\text{Se}$," J. Sol. State Chem. 54, (7), 587 (1985).

J. J. Zayhowski, C. Jagannath, R. Kershaw, D. Ridgley, K. Dwight and A. Wold, "Picosecond Time-Resolved Photoluminescence Studies of Exciton-Magnetic Polaron Complexes in $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$," Solid State Commun. 55, (11), 941 (1985).

J. Warnock, R. Kershaw, D. H. Ridgley, K. Dwight, A. Wold and R. Galazka, "Optical Orientation of Excitons in $(\text{Cd,Mn})\text{Se}$ and $(\text{Cd,Mn})\text{Te}$," Solid State Commun. 59, 215 (1985).

D. Ridgley, R. Kershaw, K. Dwight and A. Wold, "Single Crystal Growth of Several Iron and Rhodium Ternary Oxides in a Reducing Atmosphere," Mat. Res. Bull. 20, 619 (1985).

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

Principal Investigator: A. Wold, V. K. Kriebel Professor, Chemistry Department

Personnel: D. M. D'Ambra, Graduate Student, Chemistry Department
R. Brusasco, Graduate Student, Chemistry Department
R. J. Kershaw, Senior Research Engineer, Division of Engineering
K. Dwight, Professor (Research), Chemistry Department
J. A. Baglio, Research Chemist, GTE Laboratories

Sources of Support: NSF, GTE, MRL and ONR

Objectives and Approaches:

Hydrodesulfurization Catalysts

The results of the past year indicate that from photoresponse measurements, cobalt is present on the surface of MoS_2 and modifies the photoanodic behavior of the dichalcogenide. These findings are consistent with the Hall measurements

which were reported previously (1). Furthermore, the results found in this study support the scanning Auger analysis reported by Chianelli et al. (2) who indicated that cobalt tended to segregate at the surface of MoS_2 .

Cobalt (d^7) or Co(II) found at these edges provides a source of delocalized electrons and hence, recombination centers on the surface of the dichalcogenide. Evidence for this conclusion was found in the decreased photoresponse observed for crystals grown in the presence of cobalt. Recovery of the photoresponse was observed when the surface of the doped crystal was peeled with scotch tape. This process evidently removes a large part of the cobalt.

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R. Brusasco, J. Gnassi, C. Tatian, J. Baglio, K. Dwight and A. Wold, "Preparation and Characterization of Fibrillar Boehmite and Gamma Al_2O_3 ," Mat. Res. Bull. 19, 1489 (1984).

D. M. D'Ambra, J. V. Marzik, R. Kershaw, J. Baglio, K. Dwight and A. Wold, "Preparation and Electronic Properties of MoS_2 and WS_2 Single Crystals Grown in the Presence of Cobalt," J. Sol. State Chem. 57, 351 (1985).

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Crystal Chemistry of V_3O_5 and Related Structures

(Collaborative Program with Army Materials and Mechanics Research Center, Watertown, Massachusetts)

Principal Investigator: A. Wold, V. K. Krieble Professor, Chemistry Department

Personnel: M. L. Gray, Graduate Student, Chemistry Department
R. Kershaw, Senior Research Engineer, Division of Engineering
K. Dwight, Professor (Research), Chemistry Department
W. Croft, Supervisor, Research Chemist, Army Materials and Mechanics Research Center

Sources of Support: MRL, U.S. Army and NSF

Objectives and Approaches:

V_2O_3 single crystals have been grown by chemical vapor transport with HCl and $TeCl_4$ as the transport agents. Oxidized single crystals of V_2O_3 contain V_3O_5 , and the structural similarities which exist between these two compounds allow the V_3O_5 to become an integral part of the corundum structure. The results reported in this study support the crystallographic data of Asbrink (1) concerning the valency distribution of V_3O_5 . V(IV) resides in the corundum-like units of V_3O_5 while the V(III) is situated in the rutile-like units. Upon substitution of V(IV) ($3d^1$) for V(III) ($3d^2$), the temperature and magnitude of the transition for V_2O_3 are lowered.

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1. S. Åsbrink, Acta Cryst. **B36**, 1332 (1980).

Publications:

"Crystal Chemistry of V_2O_3 and Related Structures," accepted for publication in Journal of Solid State Chemistry.

Collaborative Program with Exxon Research and Engineering Company,
Annandale, New Jersey

Principal Investigator: A. Wold, V. K. Kriebel Professor, Chemistry Department

Personnel: R. Kershaw, Senior Research Engineer, Division of Engineering
K. Dwight, Professor (Research), Chemistry Department
J. D. Passaretti, Research Chemist, Exxon Research & Engineering Co.
R. R. Chianelli, Research Chemist, Exxon Research & Engineering Co.

Sources of Support: MRL, NSF and Exxon Research & Engineering Company

Objectives and Approaches:

The transition metal sulfides Co_9S_8 , Ni_3S_2 and Fe_7S_8 have been identified as possible promoters in hydrodesulfurization catalysts. Since the preparation of these compounds is difficult to achieve by direct combination of the elements, a low temperature synthesis involving the treatment of anhydrous sulfates in a controlled $\text{H}_2/\text{H}_2\text{S}$ atmosphere was developed at Brown University. The sulfides prepared were characterized by x-ray diffraction, magnetic susceptibility, and thermogravimetric analysis. The method of preparation was found to yield single phase materials which were free of ferromagnetic impurities. Co_9S_8 and Ni_3S_2 exhibited temperature independent magnetic susceptibility which is consistent with Pauli paramagnetism.

The field dependent magnetic susceptibility measurements for Fe_7S_8 were sensitive to the thermal history of the sample. Annealed samples showed strong field dependent behavior (i.e., large spontaneous magnetization), whereas quenched samples did not. Slow-cooled samples exhibited less field dependent behavior than the annealed samples which indicated less ordering of the vacancies. These observations are consistent with the Bertaut model (1) for vacancy ordering in ferromagnetic Fe_7S_8 .

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R. R. Chianelli, A. F. Ruppert, S. K. Behal, B. H. Dear, A. Wold and R. Kershaw, "The Reactivity of MoS_2 Single Crystal Edge Planes," J. Catal. 92, 56 (1985).

ADDITIONAL PROGRAMS

Photoluminescent and Electroluminescent Properties of Cadmium Doped Manganese Selenide

Preparation and Characterization of Gamma Alumina Particles and Alumina Films

Electrochemical Reduction of Benzene

Preparation and Characterization of Iron Oxide Catalysts

Additional Personnel: S. Davison, Graduate Student, Chemistry Department
Yu-Je, Graduate Student, Chemistry Department
Y-C. Zhang, Graduate Student, Chemistry Department
J. Fournier, Graduate Student, Chemistry Department
Z-D. Zhang, Research Associate, Chemistry Department
H-S. Shen, Research Associate, Chemistry Department
G-Q. Yao, Research Associate, Chemistry Department

Additional Publications:

A. A. Burk, Jr., A. B. Ellis, D. Ridgley and A. Wold, "Photoluminescent and Electroluminescent Properties of $\text{Cd}_{0.95}\text{Mn}_{0.05}\text{Se}$ Electrodes," J. of Luminescence 31 and 32, 969 (1984).

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SECTION 6

SELECTED MATERIALS RESEARCH AT BROWN UNIVERSITY OUTSIDE THE MRL PROGRAM

Introduction

The MRL program at Brown is the center around which much of materials research at Brown is concentrated, including complementary research supported from different sources. In this section we quote some significant results obtained in selected areas outside the current MRL program. In the past, much of this research was started or supported by the MRL. This is the case of research on interfaces which has had a long standing tradition at Brown University; it has recently been extended to research on superlattices. The work on interfaces has been assisted by the MRL Microelectronics Central Facility and part of it (The Conductor-Non-Conductor Interface) has recently been established as an interdisciplinary program partly supported by a grant from IBM. Work on polymers and molecular complexes has always been a part of materials research at Brown University and some projects have been supported as MRL New Initiatives. Another traditional area that is now funded outside the MRL program is the studies of materials properties at low temperatures. Finally, we include the results of a study of the relationship between transport behavior of a membrane and its structure.

INTERFACES AND SUPERLATTICES

Studies of the Fractional Quantum Hall Effect in Silicon MOSFETs

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

Personnel: D. A. Syphers, University of Oregon
J. Furneaux, Naval Research Laboratory

Source of Support: NSF

Objectives and Approaches:

After the discovery of the quantum Hall effect in Si MOSFETs and subsequently in (Ga,Al)As/GaAs heterostructures an entirely new effect was found in the magnetic quantum limit. When just the lowest level was occupied, new quantized states were found. Whereas the earlier discovery involved only characterization by integer values only, this new effect was characterized by odd denominator fractions. The significant difference between the heterostructures and the MOSFETs was that the mobilities of the former were some 10 to 100 times higher. A number of investigators looked for the effect in the MOSFETs available, but no observations were forthcoming. We discovered that we had a mobility $> 3\text{m}^2/\text{Vs}$. In the meantime, reports of Soviet investigators indicated that the effect was observed in samples with mobilities $= 4\text{m}^2/\text{Vs}$. We had available magnetic fields twice what they used and the ability to go to a temperature that was 10 times lower than they did.

Research Achievements:

Our results indicated that one can see results on lower mobility samples, in fact lower than that used in previous investigations that failed. We saw the effect at $4/3$ and $2/3$. We have studied the temperature dependence, the tipped field effect and the magnetic field dependence. While our results did not reproduce those reported by the Soviet investigators earlier, they do agree with the results that they are publishing now.

Temperature Dependence in High Mobility Silicon MOSFETs at Low Temperatures

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

Personnel: R. P. Smith, Graduate Student, Physics Department

Sources of Support: NSF and MRL Facilities

Objectives and Approaches:

The temperature dependence of the conductivity in Si MOSFETs at low temperatures in the range where the conductivity is apparently metallic has long been anomalous. One notes that there is an improvement in the conductivity when one lowers the temperature further. A simple calculation illustrates that there is no improvement expected due to freezing out of the phonons. Recently there have been further theoretical work which suggests that there is a temperature dependence of the screening that might account for the observations. We undertook to study this phenomena for $0.3\text{K} < T < 23\text{K}$ over densities in the range $2 \times 10^{11}/\text{cm}^2 < n_s < 20 \times 10^{11}/\text{cm}^2$.

Research Achievements:

Our measurements nicely illustrate the basic behavior predicted by the theories but deviate in some respects. In particular, a theory by Gold does not predict a saturation at the lowest temperatures which we observe. Although Stern's theory did not include all effects expected to play a role, there is reasonable agreement with the data.

Direct Measurement of the Density of States of a Two-Dimensional Electron Gas

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

Personnel: T. P. Smith, III, Graduate Student, Physics Department
B. B. Goldberg, Graduate Student, Physics Department
M. Heiblum, Research Staff, IBM Corporation

Sources of Support: MRL Facilities, ONR and NSF

Objectives and Approaches:

For the past few years, there has been many efforts to study the magneto-capacitance of two-dimensional electron gases (2DEG). The essence

of the study is that if you increase the voltage across the capacitor-like structure composed of a 2DEG and a metallic counter electrode, you won't increase the charge on the plates if there are no states available with the small energy range corresponding to the change in voltage. It is easy to see that such techniques could reveal the density of states. We and other people have found that the effects are dominated by the increasing resistance that one encounters as one enters the quantum Hall regime. Even so, one was not able to properly correct the data for the resistivity. We secured a sample that had a region where resistive effects were absent and proceeded to measure it.

Research Achievements:

Because one must push charge in and out of our capacitive structure to measure the change in charge due to the change in voltage, the RC time constant limits the frequency that one can use. By working at sufficiently low frequencies, 20 Hz, we were in a frequency regime where there was practically no frequency dependence. We measured the capacitance for the fixed density in our (Ga,Al)As:GaAs heterostructure as a function of magnetic field. Below 0.5T, the oscillations were too small to be usable, and above about 2T, resistance effects were evident.

Our results, when fit to a model density of states, were probably the definitive work on small samples. Other techniques that people have used include the de Haas-van Alphen effect and specific heat measurements. They required much bigger samples, and we feel that their results were dominated by inhomogeneities. The area of disagreement is what the level of state density is between Landau levels. We believe that it is much smaller than other investigators do.

Publications:

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T. P. Smith, III, B. B. Goldberg, P. J. Stiles and M. Heiblum, Phys. Rev. B32 (1985).

CaF₂:Si Metal-Epitaxial Insulator-Semiconductor Field-Effect Transistors

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

Personnel: T. P. Smith, III, Graduate Student, Physics Department
R. People, Research Staff, ATT Bell
J. M. Phillips, Research Staff, ATT Bell
W. M. Augustyniak, Research Staff, ATT Bell
J. M. Gibson, Research Staff, ATT Bell

Sources of Support: ONR, NSF and MRL Facilities

Objectives and Approaches:

The remarkable mobilities obtained in (Ga,Al)As:GaAs heterostructures which are epitaxial structures prompted this program. The limitation in mobilities obtained for Si MOSFETs appears to be the rough interface between the Si and SiO_x and the glassy state of the oxide. The goal of this program was to find an insulator that would grow epitaxially on Si. A systematic study was attempted.

Research Achievements:

CaF₂ was grown epitaxially on Si under many differing growth conditions. Many investigative tools were used to test the material, such as Rutherford backscattering, MOS capacitive studies, IGFET studies and others. The results were promising, but did not produce IGFETs as good as commercial ones. It appears that although the growth is epitaxial, it has a tendency to be leaky. Further, the dislocation density is high enough that the fluctuating potential at the interface is too large.

Publications:

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Floating Gate Measurements of Electrochemical Potential of Silicon MOSFETs in a Magnetic Field

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

Personnel: R. T. Zeller, Graduate Student, Physics Department
B. B. Goldberg, Graduate Student, Physics Department
F. F. Fang, Research Staff, IBM Corporation

Sources of Support: NSF and MRL Facilities

Objectives and Approaches:

Present interest in the magnetoconductivity of quasi-two dimensional electronic systems (2DEG) is very high because of the observation of the quantum Hall effect (which resulted in K. von Klitzing being awarded the 1985 Nobel Prize for Physics). One major unsolved mystery is what is the density of states in this regime. We undertook a few years ago a promising approach and it has recently born fruit. The technique is to separate the 2DEG from a featureless conductor by a thin insulating region. If one now measures the change in the potential between these two conducting regions while varying the magnetic field, one can determine the electrochemical potential variations of the 2DEG. In this circumstance, one keeps the charge on each plate of the capacitor-like structure constant. Therefore one measures the electrochemical potential at fixed density to within an additive constant as a function of magnetic field. It is reasonably straightforward to obtain a fairly unique representation of the density of states theoretically. One of the main difficulties has been a reliable low temperature amplifier.

Research Achievements:

Despite the limitations of the measuring apparatus, we have had startling success so far. We have observed the variations in 2DEGs in Si MOSFETs and (Ga,Al)As:GaAs heterostructures. The behavior in lower fields shows the expected oscillations as a function of magnetic field. However in both systems there was unexpected behavior at high fields. It was observed that in the quantum Hall regime, where the diagonal components of the conductivity are near zero, that the electrochemical potential of the edge of the sample where the lead is attached is hysteretic. This non-equilibrium behavior looks like it has a time constant associated with it that may be hours long. It has been explained as being due to induced eddy currents as one either increases the field or lowers the field. In the latter case the eddy currents will be in the opposite direction of those in the former. Associated with the particular direction of the eddy currents there is a Hall field which results in a particular voltage difference between the inside and the outside of the sample.

Influence of Heterointerfaces on Optical Properties of ZnSe/(Zn,Mn)Se and CdTe/(Cd,Mn)Te Superlattices

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

Personnel: Y. Hefetz, Graduate Student, Physics Department
S.-K. Chang, Graduate Student, Physics Department

Sources of Support: ONR, DOE and NSF

Objectives and Approaches:

The objective of this research (in collaboration with Professor R. L. Gunshor's group at Purdue) has been to develop an understanding of the electronic and magnetic properties of the new group II-VI compound semiconductor superlattice structures, based on the ZnSe/(Zn,Mn)Se and CdTe/(Cd,Mn)Te heterostructures. These strained layer systems have several unique properties, some of which originate from the magnetic character of the Mn-ion. The spin exchange coupling between the localized Mn-ion moments and those of the extended (Bloch-like) states associated with near bandgap optical excitations (excitons) give rise e.g. to anomalously large effective g-factors in the region of wavefunction overlaps in the superlattice structures. We have used this aspect in magneto-optical experiments to determine the character (symmetry) and penetration of the exciton wavefunction in the ZnSe and CdTe quantum 'wells' into the Mn-containing 'barriers'. Picosecond time-resolved experiments have also been used to detail the energy relaxation and localization of excitons through real-time observations of spectral diffusion. Our early work has now shown e.g. how the electronic features of these structures can be dominated by specific microscopic details at the heterointerfaces.

Research Achievements:

We have investigated the influence of interfaces on excitons in (100) oriented ZnSe/(Zn,Mn)Se and in (100) and (111) oriented CdTe/(Cd,Mn)Te strained layer superlattices (Mn-alloy fraction $x \geq .20$) by spectroscopic studies which also include the use of picosecond laser techniques for direct kinetic information of exciton formation and energy relaxation. In these wide gap II-VI systems the valence band offsets are small (on the scale of few tens of meV) and strain dependent which can lead to the situation where the hole states (with degeneracy removed by uniaxial strain) are only weakly confined (1). The exciton states therefore differ considerably from those found e.g. in the GaAs/(Ga,Al)As quantum wells. The use of external magnetic fields to study the exciton states is a powerful spectroscopic tool since the large spin exchange of the hole with the Mn-ion d-electron moments provides a direct measure of the hole's penetration to the alloy 'barrier'. What emerges from our work is a picture in which strain-driven disorder at the heterointerfaces appears to be responsible for producing a substantial density of states for exciton (hole) localization which has a strongly 2-dimensional character. The energy range (ΔE) for localization and its density of states is largest for the (111) CdTe/(Cd,Mn)Te case ($\Delta E \geq 20$ meV), less so for the (100)

CdTe/(Cd,Mn)Te ($\Delta E \leq 10$ meV), and is the smallest for the (100) ZnSe/(Zn,Mn)Se case ($\Delta E \leq 5$ meV); the values are for samples with $x \geq .20$. For the CdTe/(Cd,Mn)Te superlattices, apart from some additional influence by the GaAs substrate, such a decrease in localization follows quantitatively the corresponding decrease in lattice mismatch strain. A further correlation is provided by TEM diffraction data (2) which displays the highest number of superlattice satellite spots for the (100) ZnSe/(Zn,Mn)Se structures (up to 7 orders) and the least number for the (111) CdTe/(Cd,Mn)Te structure (2 or 3 orders) also implying that interface disorder is largest for the latter. On the basis of this and other evidence, we have proposed a model in which alloy compositional fluctuations at the heterointerfaces lead through local strain fluctuations to random quasi-2D potential wells for the heavy-hole (in CdTe) and light-hole (in ZnSe) states.

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"Quasi-Two Dimensional Exciton-Polaron in CdTe/(Cd,Mn)Te Quantum Wells," A. V. Nurmikko, X.-C. Zhang, S.-K. Chang, L. Kolodziejski, R. L. Gunshor and S. Datta, Proc. Conf. on Electronic Properties of 2-Dimensional Systems, Kyoto, Surface Science (in press).

Elementary Excitations in Artificially Structured Materials

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

Personnel: P. Hawrylak, Research Associate, Physics Department
J.-W. Wu, Research Associate, Physics Department
G. Eliasson, Graduate Student, Physics Department

Sources of Support: NSF and U.S. Army Research Office, Durham.

Objectives and Approaches:

With the progress in fabrication of high quality semiconducting superlattice structures by molecular beam epitaxy, interest in artificially structured solids has been greatly stimulated. Normal and superconducting metals, magnetic materials, and insulators have been incorporated as constituents in novel artificially structured solids. In order to understand the transport and optical properties of all of these artificially structured solids, it is necessary to first understand the single particle excitations, more complicated excitations like excitons and excitonic molecules, and the collective excitations like plasmons and phonons. During the past year, we have studied the following topics:

- 1) Impurity states in semiconductor quantum well structures.
- 2) Bulk and surface collective charge density excitations of semiconductor superlattices.
- 3) Plasma modes in periodic metallic heterostructures.
- 4) Magnetic polaron effects in semimagnetic semiconductor quantum well structures.
- 5) Elementary excitations of a two-dimensional electron gas.

Research Achievements:

1. On impurity states in semiconductor quantum well structures, we have used a simple variational wave function to determine how the energy of a donor or acceptor depends on barrier height, well width, and position of the impurity within the well. When free carriers are present, they screen the impurity potential. A number of authors have considered this screening for a single quantum well. We have been able to include multiple quantum well screening effects and the effects caused by the presence of a surface or interface.
- 2) Bulk collective charge density excitations consist of intra- and inter-subband modes. The dispersion of these modes has been investigated as a function of the structural parameters of the superlattice. In addition, new types of surface modes (Giuliani-Quinn and Wu-Hawrylak-Quinn) have been proposed. The dispersion of these surface modes and their coupling to external probes (Raman scattering intensities and inelastic electron energy loss intensities) have been studied.
- 3) Periodic metallic heterostructures consist of periodic arrays of essentially three-dimensional thin films. In these materials, bands of bulk plasmons, which satisfy Bloch's theorem, can propagate at frequencies above the lowest bulk plasma frequency of a constituent film. The dispersion relations for these bulk plasmon bands have been derived.
- 4) In semimagnetic semiconductors like $\text{Mn}_x \text{Cd}_{1-x} \text{Te}$, the exchange interaction between free carriers and the localized spins of Mn ions can lead to a "magnetic polaron" effect. How this effect changes the single particle energies and exciton energy of a quantum well structure (like $\text{Mn}_x \text{Cd}_{1-x} \text{Te}/\text{Cd Te}/\text{Mn}_x \text{Cd}_{1-x} \text{Te}$) has been studied.
- 5) For a strictly two-dimensional electron gas, we have studied how a spatially varying electron density modifies the 2D plasmon dispersion. As in the case of the three-dimensional metallic heterostructures, bands of plasma modes are found. The dispersion of these bands and its dependence on the material parameters have been studied.

In addition, we have investigated the "exciton" energies of systems with integral Landau level filling. The possibility of a ferromagnetic instability and the cyclotron resonance spectrum have been studied.

Finally, we have proposed that the Tao-Thouless picture for the fractional quantum Hall effect is incorrect because it omitted the fundamental elementary excitations, discommensurations between different "parent" states. These excitations, which we named FRACHTONS, when dressed by Coulomb interactions seem very closely related to Laughlin's fractionally charged quasiparticles. Because of the unusual properties of FRACHTONS, standard many body techniques fail (Wick's theorem doesn't hold; FRACHTONS satisfy fractional statistics), and we have made no progress in calculating properties of the system for more than a small number of particles.

Publications:

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"Shallow Impurity States in Semiconductor Quantum Well Structures," (with W. Liu), Phys. Rev. B31, 2348 (1985).

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"Triplet Exciton and Ferromagnetic Instability of a Two Dimensional Electron Gas with a Filling Factor $\nu=2$," (with G. Giuliani), Solid State Comm. 54, 1013 (1985).

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"Polariton Modes in Semiconducting Superlattice Systems," (with W.-M. Liu and G. Eliasson), Solid State Comm. 55, 533 (1985).

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"Intersubband Collective Excitations of the Surface of a Semiconductor Superlattice," (with P. Hawrylak and J.-W. Wu), Phys. Rev. B31, 7855 (1985).

"Inelastic Light Scattering by Collective Charge Density Excitations in Semi-Infinite Semiconductor Superlattices," P. Hawrylak, J.-W. Wu and J. J. Quinn, Phys. Rev. B32, 5169 (1985).

"Inelastic Electron Scattering by Collective Charge Density Excitations at the Surface of a Semiconductor Superlattice," P. Hawrylak, J.-W. Wu and J. J. Quinn, Phys. Rev. B32, 4274 (1985).

"Magnetoplasma Surface Waves on the Lateral Surface of a Semiconductor Superlattice," J.-W. Wu, P. Hawrylak, J. J. Quinn and A. Fetter, submitted to Phys. Rev. B.

"Magnetic Interactions in Quasi-Two Dimensional Systems," J. J. Quinn, Nature 317, 389 (1985).

"Plasmon Bands in Periodic Conducting Heterostructures," G. Eliasson, G. Giuliani, J. J. Quinn and R. F. Wallis, to appear in Phys. Rev. (1985).

"Inelastic Electron Scattering by Collective Charge Density Excitations at the Surface of a Semiconductor Superlattice," P. Hawrylak, J.-W. Wu and J. J. Quinn, Proc. of VI Int. Conf. on Electronic Properties of 2-D Systems, Kyoto, 1985, page 803 (1985); also to appear in Surface Science.

"Lateral Surface Magnetoplasmon in a Semiconductor Superlattice and Edge Magnetoplasmon of a Two-Dimensional Electron Gas," J.-W. Wu, P. Hawrylak, G. Eliasson and J. J. Quinn, Proc. of VI Int. Conf. on Electronic Prop. of 2-D Systems, Kyoto, page 797 (1985); also to appear in Surface Science.

"Surface and Bulk Plasmon-Polariton Bands in Periodic Metallic Heterostructures: Effects of Retardation," R. F. Wallis, G. Giuliani and J. J. Quinn, to appear in Surface Science (1985).

"Magnetic Polaron Effects in $\text{CdTe}/\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ Quantum Well Systems," (with J.-W. Wu and A. Nurmikko), to appear in Solid State Comm. (1986).

"Plasmons in Semiconducting Superlattices with Complex Unit Cell," (with R. A. Mayanovic and G. F. Giuliani), submitted to Phys. Rev. (1986).

"Lateral Surface Magnetoplasma Modes of Type II Superlattices," (with J.-W. Wu and P. Hawrylak), to be submitted to Solid State Comm. (1986).

"Cyclotron Modes of Semiconducting Superlattices," (with J.-W. Wu), to be submitted to Solid State Comm. (1986).

"Theory of Lateral Surface Magnetoplasmon in a Semiconducting Superlattice," (with J.-W. Wu, P. Hawrylak and G. Eliasson), submitted to Phys. Rev. (1986).

"Screened Coulombic Impurity Bound States in Semi-Infinite Multiple Quantum Well Systems," (with P. Hawrylak), submitted to Phys. Rev. (1986).

"Inelastic Light Scattering from Collective Excitations of a Type II Superlattice," (with P. Hawrylak and G. Eliasson), in preparation.

"Plasmon Bands of a Two-Dimensional Electron GAs with Spatially Varying Electron Density," (with G. Eliasson), in preparation.

"On the Existence of Acoustic Plasma Modes of Structured Semiconductor Superlattice Systems," (with G. Eliasson and G. F. Giuliani), in preparation.

Books:

Report on Artificially Structured Materials, National Academy Press (1985) (Chairman of Committee).

IONOMERS AND MOLECULAR COMPLEXES

Glass Transitions in Ionomers

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

Personnel: I. W. Shim, Graduate Student, Chemistry Department

K. Sun, Graduate Student, Chemistry Department

Sources of Support: ONR, MRL

Objectives and Approaches:

Ionic oxide glasses have been shown in our previous work to exhibit vibrations in the far infrared spectrum due to the motions of cations relative to their sites. Evaluations of the cation-anionic site force fields have been made on the basis of this spectral information. In studies of metaphosphate, arsenate, borate, and certain silicate glasses, relationships between these forces and processes leading to glass formation and glass transition have been indicated. To explore these relationships, it is important to be able to focus on particular interactions by investigating systems in which the network forces are quite different from those in oxide glasses. This would permit focussing on the cation-anionic site interactions themselves. Metal ion containing ionomers provide an excellent model system because the polymeric backbone provides both the glass features of connectedness between anionic sites and entanglement through the polymer but it allows formation of cation-anion ionic crosslinks, which may be either random or clustered. The cation and composition-dependences of T_g in ionomers as well as their far infrared spectra are under investigation.

Research Achievements:

In previous work we discovered that the cation-anionic interactions give rise to observable vibrations in ionomers, and that the strength of these interactions usually were greater for M^{+2} than for M^{+} cations. While this is to be expected, it is inconsistent with some reported T_g data on these alkali and alkaline earth, as well as transition metal-containing, ionomers. Three aspects of the systems could be responsible for the lack of simple correlation of the ionic forces and T_g data. One, which we explored in our recent work, is that the ionic clustering and crosslinking serves to form sufficiently strong interactions that the glass transition is that of the polymeric chains between ionic domains and is not connected with the cation-anion binding. This is consistent with the variations observed with anionic concentration and constancy of T_g within series of ionomers with similar cations. The second and third aspects, however, could nullify the conclusions and therefore required study. They concern the state of ligation, in this case solvation, of the cations. We now have investigated the relationship between thermal processes of desolvation and glass transition and find that the apparent T_g

varies with degree of solvation due both to overlap of features in the calorimetric measurement and to the fact that the interionic forces change as the cation can interact directly, rather than through ligands, with the anionic sites. This slowing of the effective modification of the nature of the cations should help to interpret the role of polar network units in ionic oxide glasses as they influence the way cations can connect network segments.

Publications:

V. D. Mattera, Jr. and W. M. Risen, Jr., "Composition Dependence of Glass Transitions in Ionomers," J. Polymer Science (Polym. Phys.), in press, 1986.

W. M. Risen, Jr., "Spectroscopic and Thermal Studies of Ionic Interactions in Ionomers," A.C. S. Symposium Series 302, Chapter 4, 1986, American Chemical Society, Washington, D. C.

K. Sun, I. W. Shim and W. M. Risen, Jr., "Composition and Solvent Dependence of Glass Transitions in Ionomers," J. Polym. Science, in preparation, 1986.

Catalysis by Transition Metal Ionomers: The Catalytic Oxidation of CO Over PFSA (Nafion) - Supported Rh, Ru and Pt.

Principal Investigator: W. M. Risen, Jr., Chemistry Department

Personnel: V. D. Mattera, Jr., Graduate Student, Chemistry Department

Support: ONR, MRL

Objectives and Approaches:

Ionomers are polymers that are functionalized with ionic groups attached at various points along the polymeric backbone but are not extensively crosslinked. They can microphase separate to form ionic domains into which transition metals can be introduced by ion exchange and then treated to reduce, dehydrate, react or, generally, activate them. We have shown that metals in the domains can undergo such reactions, including ones which yield species which are analogous to postulated catalytic intermediates. It thus was clear that they have the potential to function as catalysts. Moreover, since the domain structure can serve to hold reactant gaseous molecules in the region of the metal sites for a relatively long time, they can be thought of as small, isolated chemical reactors embedded in a medium which also has reactant and product separation capacity. The objective of this work was to determine whether metal-containing ionomers would exhibit catalytic properties.

Research Achievements:

The ionomers of Rh, Ru and Pt with perfluorocarbonsulfonate (PFSA or Nafion) were formed by ion exchange, reduced, either by H_2 or by reductive deamination, and used in a reactor-flow system to catalyze the CO oxidation ($CO:O_2::2:1$). Studies were carried out in a single pass differential reactor at various temperatures (25-375°C) and gas flow rates, and the products were determined gas chromatographically. The materials were studied by electron microscopy after reduction to determine the metal particle size distributions which are narrow and peaked around 30Å. Combining the kinetic data and calculated metal dispersions, the turn over frequencies (TOF) and activation parameters were obtained. Each system catalyzed the CO oxidation effectively. The TOF's for the formation of CO_2 over Nafion-supported noble metal catalysts were found to be consistent with those observed over conventional silica supported catalysts; i.e., the activity sequence is $Ru > Rh > Pt$. Comparison of the activation energies with those over conventional supports shows that the slowest reaction (Pt) proceeds at the same rate regardless of support, but the faster ones are diffusion limited in the ionomer case. Overall, the results show that ionic domains in ionomers exert morphological control over metal particle growth and serve as chemical reactors for catalysis.

Publications:

"A Kinetic Study of the Catalytic Oxidation of CO over PFSA (Nafion) Supported Rhodium, Ruthenium and Platinum," V. D. Mattera, Jr., D. M. Barnes, S. N. Chaudhuri, R. D. Gonzalez and W. M. Risen, Jr., J. Phys. Chem., in press (1986).

Optical and Vibrational Properties and Crystal Structures of Molecular Complexes: Biphenyl-TCNQ and p-Terphenyl-TCNQ

Principal Investigator: W. M. Risen, Jr., Chemistry Department

Personnel: V. D. Mattera, Jr., Graduate Student, Chemistry Department
E. I. Kamitsos, Graduate Student, Chemistry Department

Support: ONR, MRL

Objectives and Approaches:

Charge transfer complexes in which there is either substantial transfer of charge or relatively little interaction with nearly zero charge transfer have been studied widely, and a number of types of interaction have been invoked to explain the observations. By combining TCNQ with large conjugated π - electron system - containing molecules with relatively high ionization potentials, it may be possible to achieve significant interaction dominated by one mode of interaction, with

little charge transfer. The systems BP-TCNQ and TP-TCNQ were selected to achieve this result.

Research Achievements:

The complexes of biphenyl and p-terphenyl with TCNQ were prepared in crystalline form, and single crystal x-ray diffraction studies were performed to determine the geometries of the moieties in the complexes. This showed small but systematic variations in bond lengths of the TCNQ and the organic components were caused by complexation. The Raman and infrared spectra of the materials yielded vibrational frequency shifts which cannot be interpreted in the conventional way as reflecting a simple BP to TCNQ or TP to TCNQ electron transfer. In fact, inconsistent signs for this degree of transfer are obtained from the various Raman band shifts. The result is that such an electron transfer postulate does not explain the data and that another mechanism is required. We interpret the crystal structure and vibrational data to show that the dominant mode of coupling involves particular interactions between the π - electron systems, which cause a charge redistribution in each moiety without net charge transfer. This charge redistribution is reflected not only in the bond lengths and vibrational frequencies but also in the stacking geometry of the complexes, which is dominated by the favorable positioning of the wing double bond of the TCNQ symmetrically over one benzenoid ring of the BP or TP moiety. Thus, complexes have been obtained in apparently charge transfer systems in which control is exerted by π - π interactions without charge transfer.

Publications:

"Optical and Vibrational Properties and the Crystal Structures of Molecular Complexes: Biphenyl-TCNQ and p-Terphenyl-TCNQ," E. I. Kamitsos, V. D. Mattera, W. T. Robinson and W. M. Risen, Jr., J. Molecular Structure, 143, 211 (1986).

PROPERTIES OF MATERIALS AT LOW TEMPERATURES

Crystal Growth Kinetics and Solid-Liquid Interface Mobility

Principal Investigator: C. Elbaum, Professor, Physics Department

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

Source of Support: NSF

Objectives and Approaches:

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) Andreev and Parshin proposed that crystal growth proceeds in an entirely different way, that the solid-liquid interface has very high mobility, and that at $T = 0$ K the process is continuous and reversible, i.e., without dissipation. Thus at $T = 0$ the coefficient K is infinite; 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 decreases with increasing temperature. This proposal led to a number of experimental and theoretical investigations on helium crystal growth. It was realized, in particular, that a sound wave propagating from liquid to solid could cause rapid freezing-melting when the interface is highly mobile. Thus, pressure changes would be taken up by the advancing or receding interface, where the pressure would be near or at the equilibrium melting value and sound transmission between the two media would be substantially reduced or even suppressed. This reduction in transmission provides a method of studying growth kinetics.

We have used this approach to investigate the processes that occur at the solid-liquid interface of helium-four and to measure the growth coefficient. For this purpose ultrasonic waves, at a frequency of 10 MHz, were propagated in a direction normal to the interface; the temperature range covered was $0.65\text{K} \leq T \leq 1.4\text{K}$.

Research Achievements:

We have made the first measurements of acoustic reflection, together with acoustic transmission at the solid-liquid interface of ^4He . The results were used to determine the temperature dependence of the interface mobility and of the growth coefficient. We have also determined, using the acoustic reflection and transmission values, the total relative acoustic energy absorbed in the melting-freezing process as a function of temperature. This absorbed energy displays a relaxational character, which leads us to propose a new mechanism for

limiting the interface mobility. Specifically, we find that the experimental results on the melting-freezing process can be accounted for by the need to accommodate thermally generated vacancies at the interface. At low temperatures this process is governed by quantum tunneling and at higher temperatures by classical (thermally activated) diffusion. The transition between the two regimes occurs at about 1K.

Publications:

M. B. Manning, M. J. Moelter and C. Elbaum, "Helium-4 Solid-Liquid Interface Mobility and Ultrasonic Energy Absorption Mechanisms," J. Low Temp. Physics 61, 447 (1985).

Supercooling of Liquid Hydrogen

Principal Investigators: G. M. Seidel and H. J. Maris, Professor, Physics Department

Personnel: J. Cardon, Graduate Student, Physics Department
F. J. B. Williams, Visiting Professor, Physics Department
(from Centre d'Etudes Nucleaire de Saclay)

Sources of Support: NSF

Objectives and Approaches:

The principal aim of this research is the study of the supercooling properties of liquid hydrogen to determine whether H_2 can be maintained in the liquid state at sufficiently low temperatures to permit the observation of Bose condensation in this quantum fluid. While theoretical considerations suggest that it may be possible to supercool liquid H_2 all the way to absolute zero, no experimental studies have been reported on either its supercooling behavior or on the magnitude of the liquid-solid interfacial energy, of critical importance in estimating supercooling. Research has been initiated to study the supercooling of small drops of liquid H_2 by measuring the temperature dependence of the homogeneous nucleation rate from liquid to solid several degrees below the normal freezing point of 14K. From these measurements the surface energy can be deduced and used to predict the likelihood of achieving supercooling at much lower temperatures.

Research Achievements:

Droplets of liquid H_2 from 50μ to 1 mm diameter have been made neutrally bouyant in a gas of 4He at modest pressures from 14 to 18 Bars in the temperature range from 11 to 14K. In such an environment, suspended

freely without contact to a solid container, the nucleation rate for conversion to the solid can be measured in the supercooled region down to 10.6K. From the measured rate the liquid solid surface energy has been deduced to be $0.874 \text{ erg cm}^{-2}$ at 11K. Based on these results it appears that if small drops of liquid H_2 can be cooled rapidly below 8K, then the liquid may be relative stable against solidification (a thermally activated process the probability for which decreases at sufficiently low temperatures).

Publications:

G. M. Seidel, H. J. Maris, F. J. B. Williams and J. G. Cardon, "Supercooling of Liquid Hydrogen," Phys. Rev. Lett. 56, 2380 (1986).

Study of Freezing of Hydrogen in Porous Materials

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

Personnel: R. Torii, Graduate Student, Physics Department

Sources of Support: NSF

Objectives and Approaches:

The only element which remains a liquid at zero temperature is helium. Helium does not freeze because its low mass and weak interatomic forces lead to large quantum-mechanical zero-point vibrations. The next element which comes nearest to being a liquid at $T = 0 \text{ K}$ is hydrogen. This should freeze at 25 K if quantum effects did not occur, but actually freezes at 13.8 K. The difference in energy between liquid and solid phases is small, even at $T = 0 \text{ K}$. In our experiments we are placing liquid hydrogen into small pores. This adds a surface energy term which favors the liquid, and lowers the freezing temperature. The aim of the research is to produce liquid hydrogen at temperatures far below its normal freezing temperature, and to study its properties under these conditions.

Research Requirements:

We have measured the specific heat of molecular hydrogen in several porous materials. The hydrogen was converted to the para state by a catalyst before introduction into the pores. The specific heat was measured by recording the temperature while the sample was cooled by a mass of calibrated thermal link connected to a low temperature reference point. When a small amount of hydrogen was introduced into the pores the specific heat C was found to be approximately proportional to T^2 , and no discontinuity in C associated with freezing was detected. When more hydrogen was introduced a freezing transition was detected. The temperature at which this freezing took place has been studied for different porous materials.

Study of Growth of Solid Helium-4 Crystals

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

Personnel: M. J. Graf, Graduate Student, Physics Department

Sources of Support: NSF

Objectives and Approaches:

The interface between liquid and solid helium is unique in several aspects. It is the only phase boundary between liquid and solid which exists even at zero temperature. Although the transition between liquid and solid is, in principle, a first order transition, the latent heat is extremely small. Consequently, the heat liberated does not limit the rate at which freezing can occur. The aim of this research is to study the growth rate of solid helium crystals under a variety of conditions, and to relate the results to theories of kinetic processes which can occur at the interface.

Research Achievements:

The growth coefficient K of a crystal is defined as

$$K = \frac{\dot{\xi}}{\Delta\mu}$$

where $\dot{\xi}$ is the rate at which the solid grows, and $\Delta\mu$ is the difference in the chemical potentials of the liquid and solid. To study K we direct a sound wave at the interface. The pressure oscillation associated with this wave creates a $\Delta\mu$ at the interface, thereby causing melting or freezing to occur. The amplitude of the wave transmitted across the interface depends on K , and hence a measurement of the transmission can be used to determine the growth coefficient. We have used this approach to determine K under conditions of very rapid growth. We find that when the growth velocity $\dot{\xi}$ reaches a value of $\sim 1000 \text{ cm sec}^{-1}$, K begins to decrease rapidly. We interpret this in terms of a simple model for dissipation at the surface.

TRANSPORT OF MATERIAL THROUGH MEMBRANES

Theory of Membrane Transport

Principal Investigator: E. A. Mason, Newport Rogers Professor, Chemistry Department; Professor, Division of Engineering

Personnel: K. D. Knierim, Research Associate, Chemistry Department
M. Waldman, Research Associate, Chemistry Department
L. F. del Castillo, Visiting Research Associate, Chemistry Department

Sources of Support: NSF

Objectives and Approaches:

Transport of material through membranes has many applications in science and engineering, and is also of great importance in biology and medicine. People have labored for over 100 years to give a mathematical description of the laws of membrane transport (e.g. Fick's law of diffusion dates from 1855). This has not been easy and many formulations have been proposed, covering a wide variety of ideas and approaches, and it has not been clear what their strengths and weaknesses were, what relationships existed among them, or even whether they were mutually consistent.

The first purpose of this theoretical research was to develop the mathematical description of transport across membranes, without restrictions regarding concentrations, ideal behavior, or number of components. The methods used were those of classical statistical mechanics. The second purpose was to use the statistical-mechanical results to clarify the status of and relationships among previous theories. The third purpose was to use the results in more practical ways, such as to probe membrane structure and to describe and explain complicated membrane phenomena.

Research Achievements:

We now have developed what we believe is a general statistical-mechanical theory of membrane transport, and have shown the relations of previous theories (suitably corrected where necessary) to it and hence to each other. A few surprises have emerged, such as the role of viscous flow in relation to semipermeability and Onsager reciprocity. If viscous flow is assumed not to cause separation of the components of a solution, then semipermeable behavior is impossible because the viscous flow provides a permanent leak for all components. If the possibility of separative viscous flow is introduced to remedy this defect, then Onsager reciprocity is lost.

Study of the relationships between transport behavior and membrane structure has also produced some surprises. For example, in some cases it has

been possible to put fairly tight mathematical bounds, of the order of $\pm 10\%$ or so, on various fluxes, regardless of the detailed structure of the membrane. In some other cases we have succeeded in showing how transport measurements can be used to probe membrane structure. Here the surprise is that bounds can be put on the structure, so that one can say exactly what the measurements establish, no more and no less. This is in contrast to the more traditional approach of assuming some model for the structure and adjusting its parameters to fit some measurements; this approach can be grossly misleading because many radically different models may fit the data equally well.

Publications:

"Bounds on Solute Flux and Pore-Size Distributions for Non-Sieving Membranes," K. D. Knierim, M. Waldman and E. A. Mason, J. Membrane Sci., 17, 173 (1984).

"The Role of Viscous Flow in Theories of Membrane Transport," E. A. Mason and L. F. del Castillo, J. Membrane Sci., 23, 199 (1985).

"Generalization of Membrane Reflection Coefficients for Nonideal, Nonisothermal, Multicomponent Systems with External Forces and Viscous Flow," L. F. del Castillo and E. A. Mason, J. Membrane Sci., submitted.

LECTURES IN THE MATERIALS RESEARCH LABORATORY PROGRAM, 1984-85

September 25, 1984

Solid Mechanics Seminar: Professor J. R. Rice, Harvard University, *"CONSERVED INTEGRALS AND ENERGETIC FORCES"*.

September 27, 1984

Solid Mechanics Seminar: Dr. Son Nguyen, Ecole Polytechnique, Paris, France, *"THERMAL EFFECTS IN CRACK PROPAGATION: THEORY AND EXPERIMENT"*.

October 5, 1984

Chemistry Colloquium: G. McClelland, Harvard University, *"THE ROTATIONAL MOTION OF HIGHLY EXCITED MOLECULES"*.

October 10, 1984

Joint Mechanics and Materials Seminar: Dr. Norman Fleck, Division of Applied Sciences, Harvard University, *"FATIGUE CRACK GROWTH DUE TO VARIABLE AMPLITUDE LOADING"*.

October 11, 1984

TEA Session - Physical Chemistry: Alan LeGrand, Brown University, *"SCATTERING OF NOBLE GASES FROM LiF"*.

October 11, 1984

Condensed Matter Seminar: John E. Furneaux, Naval Research Laboratory, *"THE QUANTUM HALL EFFECT IN MOSFET'S WITH VARIABLE INTERFACE CHARGE"*.

October 17, 1984

Combined Materials Science/Plasticity and Fracture Seminar: Dr. Patrick Franciosi, Laboratoire P.M.T.M., C.N.R.S., Universite Paris-Nord, France, *"STRAIN HARDENING AND LATENT HARDENING MECHANISMS IN F.C.C. METALS"*.

October 18, 1984

TEA Session - Physical Chemistry: Professor R. Cotterill, Technical University of Denmark, *"CRYSTAL, GLASS, LIQUID AND GAS: TOWARDS A UNIFIED PICTURE"*.

October 18, 1984

Solid Mechanics Seminar: Dr. Steve Passman, Sandia National Laboratory, Albuquerque, New Mexico, *"A NEW FORMULATION OF MIXTURE THEORY"*.

October 19, 1984

Chemistry Colloquium: Robert Fulton, Florida State University, *"RECENT PROGRESS IN THE THEORY OF NONLINEAR DIELECTRICS"*.

October 22, 1984

Solid Mechanics Seminar: Dr. B. D. Reddy, University of Cape Town, South Africa, *"VARIATIONAL INEQUALITIES ASSOCIATED WITH DEFORMATION THEORIES OF PLASTICITY"*.

November 1, 1984

TEA Session - Physical Chemistry: E. F. Greene, Brown University, *"THE INTERACTION OF FAST MOLECULES WITH SURFACES"*.

November 8, 1984

TEA Session - Physical Chemistry: Professor G. J. Diebold, Brown University, *"QUANTUM BEATS EXCITED BY MOLECULAR PHOTODISSOCIATION"*.

November 9, 1984

Glass Group Seminar: Christian Thomsen, Department of Physics, Brown University, *"PICOSECOND OPTICAL STUDIES OF PHONONS IN AMORPHOUS SEMICONDUCTORS"*.

November 9, 1984

Chemistry Colloquium: Philip Phillips, M.I.T., *"ELECTRON LOCALIZATION IN A HARD SPHERE FLUID"*.

November 12, 1984

Physics Colloquium: Dr. Elihu Abrahams, Rutgers University, *"RELAXATION OF GLASSES"*.

November 12, 1984

Solid Mechanics Seminar: Professor Michael P. Wnuk, Department of Civil Engineering, University of Wisconsin-Milwaukee, *"QUASI-STATIC FRACTURE IN STRAIN-HARDENING MATERIALS"*.

November 15, 1984

Chemistry Colloquium: William H. Miller, University of California-Berkeley, *"RECENT DEVELOPMENT IN THE CHEMICAL DYNAMICS OF POLYATOMIC SYSTEMS"*.

November 19, 1984

Solid Mechanics Seminar: Professor Jan Tullis, Department of Geology, Brown University, *"DEFORMATION OF POLYPHASE AGGREGATES: GEOLOGICAL IMPLICATIONS"*.

November 26, 1984

Combined Materials and Solid Mechanics Seminar: Dr. Stan Lynch, Aeronautical Research Laboratories, Department of Defense, Melbourne, Australia, *"ENVIRONMENTALLY-ASSISTED CRACKING: FRACTOGRAPHIC AND MECHANISTIC ASPECTS"*.

November 27, 1984

Combined Materials and Solid Mechanics Seminar: Professor William W. Gerberich, Chemical Engineering & Materials Science, University of Minnesota, *"STATICS AND DYNAMICS OF SINGLE CRYSTAL CLEAVAGE"*.

November 29, 1984

Inorganic Seminar: Professor Richard Eisenberg, Chemist, Rochester, *"THE JOYS OF IRIIDIUM CHEMISTRY"*.

November 30, 1984

Glass Group Seminar: James Kakalios, University of Chicago, *"AMORPHOUS SEMICONDUCTOR SUPERLATTICES"*.

November 29, 1984

TEA Session - Physical Chemistry: John Erickson, Brown University, *"THE KINETICS OF DISSOCIATION ON Mo(110) AND THE EFFECTS OF Co-ADSORBATES"*.

November 30, 1984

Chemistry Colloquium: Julius Rebek, University of Pittsburgh, *"BINDING FORCES AND CATALYSIS"*.

December 3, 1984

Solid Mechanics Seminar: Profesor W. S. Goyle, University of Cape Town, *"THE ANALYSIS OF COUPLED SHEAR WALLS BY THE FINITE ELEMENT METHOD"*.

December 6, 1984

TEA Session - Physical Chemistry: Dr. Robert G. Cole, Brown University, *"MOLECULAR ROTATIONS IN CONDENSED PHASES"*.

December 13, 1984

TEA Session - Physical Chemistry: Paul R. Muessig, Brown University, *"LASER PROBE OF ATOM/SURFACE IMPACT: HOW MUCH TENSOR CAN IT GET?"*

December 14, 1984

Glass Group Seminar: Professor William Risen, Department of Chemistry, Brown University, *"PRELIMINARY OBSERVATIONS OF GLASS-LIKE BEHAVIOR OF CONJUGATED POLYMER MOLECULES IN SOLUTION"*.

January 31, 1985

Inorganic Seminar: Mr. Yi-Tai Qian, Brown University, *"REDUCIBILITY OF IRON OXIDES AND THEIR BEHAVIOR IN FISHER-TROPSCH PROCESS"*.

January 31, 1985

TEA Session - Physical Chemistry: Diane K. Stewart, Brown University, *"SURFACE IONIZATION OF SODIUM ATOMS ON Si(100)"*.

February 4, 1985

Combined Materials and Solid Mechanics Seminar: Professor William Johnson, Department of Metallurgical Engineering and Materials Science, Carnegie-Mellon University, *"SOME ELASTIC EFFECTS ON TWO-PHASE MICROSTRUCTURES"*.

February 4, 1985

Physics Colloquium: Professor Edward A. Mason, Brown University, *"STUDY OF ION-MOLECULE FORCES BY TRANSPORT MEASUREMENTS"*.

February 6, 1985

Condensed Matter Physics Discussion Group: Hugh Stoddart, Brown University, *"ELECTRON RELAXATION IN AMORPHOUS SEMICONDUCTORS"*.

February 7, 1985

Inorganic Seminar: Georgios Chryssikos, Brown University, *"OXYGEN CHEMISORPTION ON SILVER"*

February 11, 1985

Physics Colloquium: Dr. C. M. Varma, AT&T Bell Labs, *"HEAVY FERMIONS AND THEIR SUPERCONDUCTIVITY"*.

February 12, 1985

Combined Materials and Mechanics Seminar: Dr. David L. Davidson, Institute Scientist, Southwest Research Institute, San Antonio, Texas, *"FATIGUE CRACK GROWTH AND CRACK TIP MECHANICS"*.

February 13, 1985

Condensed Matter Physics Discussion Group: Michael Graf, Brown University, *"TRANSMISSION OF SOUND THROUGH THE LIQUID-SOLID HELIUM INTERFACE"*.

February 15, 1986

Inorganic Glasses Group Seminars: A. Houghton, Brown University, *"SOUND ATTENUATION IN DIRTY METALS"*.

February 20, 1985

Condensed Matter Physics Discussion Group: Professor G. Seidel, Brown University, *"THE MOTION OF SOME SPHERES: SUPERCOOLED HYDROGEN"*.

February 21, 1985

Condensed Matter Seminar: Dr. J. Klafter, Exxon Research, *"TRANSPORT AND REACTION ON FRACTAL LATTICES"*.

February 22, 1985

Inorganic Glasses Group Seminars: Professor R. Pelcovits, Brown University, *"HYDRODYNAMIC THEORY OF GLASS"*.

February 25, 1985

Solid Mechanics Seminar: Professor L. B. Freund, Division of Engineering, Brown University, *"ANALYSIS OF DYNAMIC ELASTIC-PLASTIC CRACK GROWTH"*.

February 27, 1985

Condensed Matter Physics Discussion Group: Professor Brian Minchau, Brown University, *"THE TWO DIMENSIONAL XY MODEL IN A RANDOM UNIAXIAL FIELD"*.

February 28, 1985

Inorganic Seminar: Dr. Frank T. Smith, Kodak Research Laboratories, *"APPLICATION OF METAL-ORGANIC COMPOUNDS FOR THE CHEMICAL VAPOR DEPOSITION OF SEMICONDUCTORS"*.

February 28, 1985

Condensed Matter Seminar: Dr. P. Hawrylak, Brown University, *"STAGING AND STAGE-TRANSFORMATIONS IN INTERCALATION COMPOUNDS"*.

March 1, 1985

Special Condensed Matter Seminar: Dr. Gordon Thomas, AT&T Bell Labs, *"RECENT DEVELOPMENTS IN THE METAL-INSULATOR TRANSITION"*.

March 6, 1985

Condensed Matter Physics Discussion Group: Professor Milton Cole, Penn State University, *"GAS SURFACE INTERACTIONS"*.

March 7, 1985

Solid Mechanics Seminar: Professor David Parks, M.I.T., *"LARGE INELASTIC DEFORMATION OF GLASSY POLYMERS"*.

March 7, 1985

Condensed Matter Seminar: Dr. Susan Coppersmith, Brookhaven Lab, *"COLLECTIVE EFFECTS IN CHARGE DENSITY WAVES"*.

March 7, 1985

Inorganic Seminar: Mary Gray, Brown University, *"PROPERTIES OF VANADIUM IV AND VANADIUM III OXIDES"*.

March 11, 1985

Physics Colloquium: Professor Paul Steinhardt, Institute for Advanced Study and University of Pennsylvania, *"PENROSE TILES, ICOSAHEDRA. QUASI-CRYSTALS: A NEW FORM OF MATTER?"*

March 13, 1985

Condensed Matter Physics Discussion Group: Dr. J. Wu, Brown University, *"COLLECTIVE EXCITATIONS NEAR THE LATERAL SURFACE OF A SUPERLATTICE"*.

March 14, 1985

Condensed Matter Seminar: Professor Robert Westervelt, Harvard University, *"NONLINEAR OSCILLATIONS AND CHAOS IN SEMICONDUCTORS"*.

March 14, 1985

Inorganic Seminar: David D'Ambra, Brown University, *"PREPARATION AND CHARACTERIZATION OF DOPED AND UNDOPED MoS_2 SINGLE CRYSTALS"*.

March 14, 1985

Solid Mechanics Seminar: Dr. Luis Resende, University of Cape Town, *"A DAMAGE CONSTITUTIVE MODEL FOR ROCK"*.

March 20, 1985

Condensed Matter Physics Discussion Group: Professor Xi-Chen Zhang, Brown University, *"EXCITON KINETICS IN SEMI-MAGNETIC SEMICONDUCTOR $\text{Cd}_{1-x}\text{Mn}_x\text{Te}/\text{Cd}_{1-y}\text{Mn}_y\text{Te}$ MULTIQUANTUM WELLS"*.

March 21, 1985

Chemistry Colloquium: Dr. Sylvia Ceyer, M.I.T., *"DYNAMICS OF MOLECULAR CHEMISORPTION"*.

March 21, 1985

Chemistry Colloquium: Dr. Sylvia Ceyer, M.I.T., *"DYNAMICS OF MOLECULAR CHEMISORPTION"*.

March 21, 1985

Solid Mechanics Seminar: Professor Herbert Kolsky, Brown University, *"DYNAMIC RESPONSE OF FIBER REINFORCED BEAMS"*.

March 22, 1985

Joint Inorganic Glass and Condensed Matter Seminar: Professor M. Pollak, Department of Physics, University of California at Riverside, *"ELECTRON GLASS"*.

March 25, 1985

Solid Mechanics Seminar: Professor Frank Moon, Cornell University, *"FRACTAL CONCEPTS IN CHAOTIC VIBRATIONS OF MECHANICAL SYSTEMS"*.

April 3, 1985

Condensed Matter Physics Discussion Group: Professor Ernst Sigmund, *"PHONON SCATTERING AT DEFECTS IN SEMICONDUCTORS"*.

April 4, 1985

Inorganic Seminar: Jay Fournier, Brown University, *"HYDROGENATION OF CO OVER IRON(III) OXIDE FACTORS EFFECTING PRODUCT DISTRIBUTION"*.

April 4, 1985

Condensed Matter Seminar: Professor Wolfgang Moritz, University of Munich, West Germany, *"SURFACE RECONSTRUCTION OF PLATINUM, IRIDIUM AND GOLD"*.

April 4, 1985

TEA Session - Physical Chemistry: Robert Stewart, Brown University, *"REAL AND IMAGINARY QUANTUM INTERFERENCE EFFECTS IN MULTIPHOTON ABSORPTION"*.

April 8, 1985

Physics Colloquium: Professor S. B. Libby, Department of Physics, Brown University, *"THE QUANTUM HALL EFFECT, LOCALIZATION AND THE THETA VACUUM"*.

April 8, 1985

Materials Science Seminar: Dr. Robert D. Field, Department of Metallurgy and Mining Engineering, University of Illinois-Champaign, *"MICROSTRUCTURES IN RAPIDLY SOLIDIFIED ALLOYS"*.

April 10, 1985

Condensed Matter Physics Discussion Group: Fernando Seco, Brown University, *"HIGH TEMPERATURE SERIES AND THE RANDOM FIELD ISING MODEL"*.

April 11, 1985

Inorganic Seminar, David Turcotte, Brown University, *"VIBRATIONAL AND DIELECTRIC STUDIES ON FAST IONIC CONDUCTING BORATE GLASS"*.

April 11, 1985

Condensed Matter Seminar: Dr. Michael Widom, Harvard University, *"ICOSAHEDRAL SYMMETRY IN A POLYTOPE MODEL OF GLASS"*.

April 12, 1985

Materials Science Seminar: Timothy R. Dinger, Department of Materials Science and Mining Engineering, University of California at Berkeley, *"Y-Si-Al-O-N GLASS: FORMATIONS, PROPERTIES AND CRYSTALLINE BEHAVIOR"*.

April 12, 1985

Inorganic Glass Seminar: Robert Mulkern, Physics Department, Brown University, *"STATISTICAL MECHANICAL MODELS OF BORON COORDINATION IN ALKALI BORATES AND ALKALI BOROSILICATES"*.

April 15, 1985

Materials Science Seminar: Dr. Kannan M. Krishnan, National Center for Electron Microscopy, Lawrence Berkeley Laboratory, University of California at Berkeley, *"CHANNELING ENHANCED MICRO ANALYSIS: PRINCIPLES AND APPLICATIONS"*.

April 17, 1985

Condensed Matter Physics Discussion Group: Professor Charles Elbaum, Brown University, *"HELIUM AND TWO LEVEL TUNNELING SYSTEMS IN GLASSES - AN UNUSUAL MIXTURE"*.

April 18, 1985

Condensed Matter Seminar: Dr. Y. Chabal, AT&T Bell Laboratories, *"HIGH RESOLUTION SURFACE IR SPECTROSCOPY: HYDROGEN ON SILICON (100)"*.

April 18, 1985

TEA Session - Physical Chemistry: Professor Eric Suuberg, Chemical Engineering, Brown University, *"THE MACROMOLECULAR AND COLLOIDAL NATURE OF COAL"*.

April 22, 1985

Solid Mechanics Seminar: Professor J. F. McNamara, University College, Galway, Ireland, *"PRACTICAL NUMERICAL MODELLING OF NONLINEAR PROBLEMS IN OFFSHORE MECHANICS"*.

April 24, 1985

Materials Science Seminar: Dr. Robert M. Briber, Jr., Polymer Division, National Bureau of Standards, *"IMAGING OF HARD SEGMENT DOMAINS IN SEGMENTED Co-POLYMERS BY ELECTRON MICROSCOPY"*.

April 24, 1985

Condensed Matter Physics Discussion Group: Dr. G. Forgacs, SACLAY, Brookhaven, *"WETTING OF A DISORDERED SUBSTRATE"*.

April 25, 1985

Inorganic Seminar: Jay Fournier, Brown University, *"REDUCTION OF CARBON MONOXIDE WITH IRON CATALYST"*.

April 25, 1985

Joint Condensed Matter/Inorganic Glass Group Seminar: Dr. John Toner, IBM, Yorktown Heights, NY, *"HYDRODYNAMIC THEORY OF THE GLASS TRANSITION"*.

April 25, 1985

TEA Session - Physical Chemistry: Dr. Aviv Amirav, Tel Aviv University, *"ENERGY TRANSFER AND DISSOCIATION IN COLLISIONS OF I₂ MOLECULES WITH SURFACES: MgO(001), SAPHIRE(0001), AND DIAMOND(111)"*.

April 26, 1985

Inorganic Glass Seminar: Jin Hui Zhong, Physics Department, Brown University, *"NEW EVIDENCE OF PAIRING OF ALKALI IONS IN MIXED ALKALI GLASSES"*.

April 29, 1985

Physics Colloquium: Professor Peder Estrup, Brown University, *"STRUCTURAL TRANSFORMATIONS OF METAL SURFACES"*.

May 1, 1985

Condensed Matter Physics Discussion Group: Professor J. S. Brooks, Boston University, *"TWO-DIMENSIONAL BEHAVIOR IN ORGANIC CONDUCTORS"*.

May 2, 1985

Condensed Matter Seminar: Professor Bruce McCombe, State University of New York, Buffalo, *"PUTTING THE SQUEEZE ON HYDROGENIC IMPURITIES IN SEMICONDUCTORS"*.

May 6, 1985

Department of Computer Science: Professor Benoit B. Mandelbrot, IBM Research Center and Harvard University, *"FRACTALS: HOW TO IMITATE THE MOUNTAINS AND THE CLOUDS, AND TO CREATE WILD AND WONDERFUL NEW SHAPES"*.

May 6, 1985

Solid Mechanics Seminar: Professor Richard Skalak, Director of Bioengineering Institute, Department of Civil Engineering & Engineering Mechanics, Columbia University, *"VISCOELASTIC MODELS OF WHITE BLOOD CELLS"*.

May 8, 1985

Condensed Matter Physics Discussion Group: Dr. N. Read, Brown University, *"HEAVY FERMION SUPERCONDUCTOR AND THE KONDO LATTICE MODEL"*.

May 9, 1985

Inorganic Seminar: Dana Ridgley, Brown University, *"GROWTH AND CHARACTERIZATION OF MAGANESE DOPED CADMIUM SELENIDE SINGLE CRYSTALS"*.

May 10, 1985

Joint Inorganic Glass Seminar/Condensed Matter Seminar: Dr. U. Strom, Naval Research Laboratory, Washington, D.C., *"PHOTOEXCITED PHONON TRANSPORT IN SEMICONDUCTORS"*.

May 13, 1985

Special Condensed Matter Seminar: Professor David Sherrington, Imperial College, *"SPIN GLASS - PAST, PRESENT AND FUTURE"*.

May 17, 1985

Special Condensed Matter/Inorganic Glass Seminar: Professor Manuel Cardona, Max-Planck Institute, Stuttgart, *"PHONONS IN SUPERLATTICES"*.

May 20, 1985

Solid Mechanics Seminar: Professor Bertil Storakers, Department of Strength of Materials and Solid Mechanics, Royal Institute of Technology, Stockholm, *"DISPLACEMENT BOUNDS AT FINITE DEFORMATION APPLIED TO PLANE MEMBERS"*.

May 23, 1985

Solid Mechanics Seminar: Professor P. Perzyna, Polish Academy of Sciences, Warsaw, Poland, *"INTERNAL STATE VARIABLE DESCRIPTION OF DYNAMIC FRACTURE OF DUCTILE SOLIDS"*.

May 28, 1985

Solid Mechanics Seminar: Professor Juan Simo, University of California at Berkeley, *"ON A ONE-DIMENSIONAL FINITE STRAIN MODEL: GEOMETRIC AND COMPUTATIONAL ASPECTS"*.

May 29, 1985

Reserch Seminar in Probability and Pattern Theory: Professor Brian Ripley, University of Strathclyde, *"IMAGE PROCESSING"*.

May 29, 1985

TEA Session - Physical Chemistry: Tanya Didascalou, Brown University, *"THE INVERSE OPTOACOUSTIC PHENOMENON"*.

May 30, 1985

TEA Session - Physical Chemistry: Seung Min Park, Brown University, *"FABRY-PEROT INTERFEROMETER FOR OPTOACOUSTIC DETECTION"*.

June 18, 1985

Materials Science Seminar: Dr. Steven R. Nutt, Center for Solid State Science, Arizona State University, *"NON-EQUILIBRIUM PHASE DISTRIBUTION IN AN ALUMINUM ALLOY - SILICON CARBIDE COMPOSITE"*.

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A. Wold, Professor
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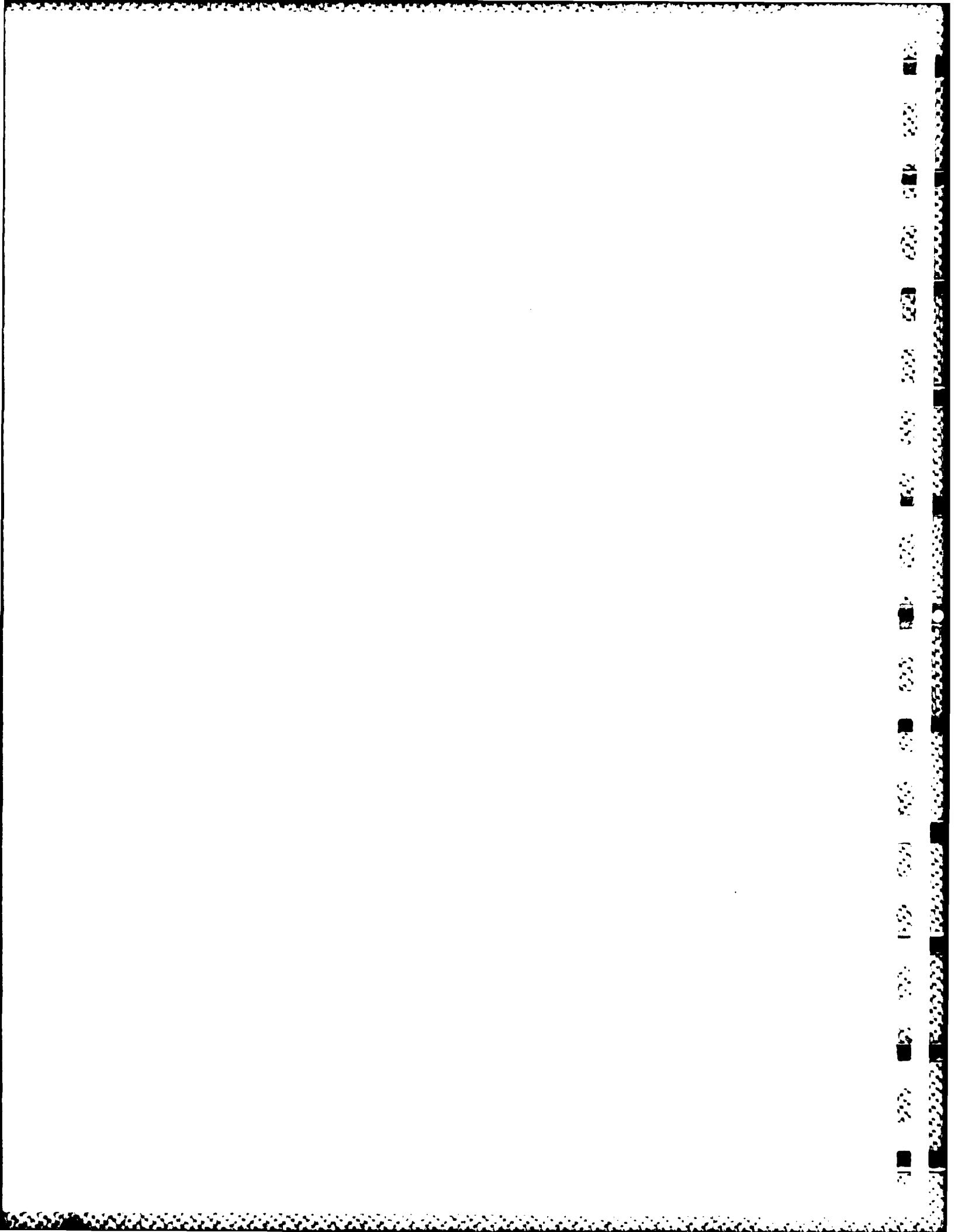
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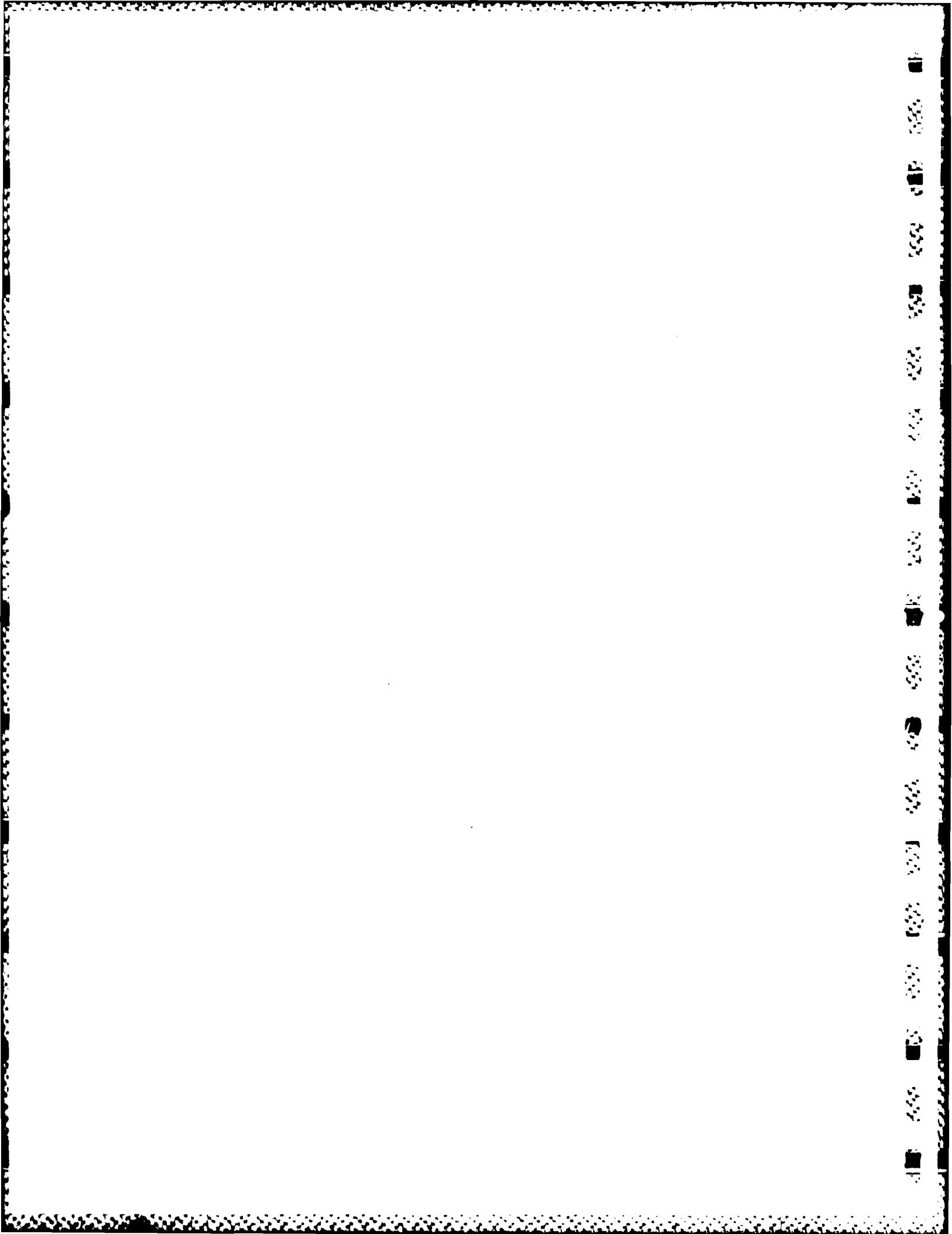
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S. Tiersten, Graduate Student
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D. A. Young, Graduate Student
J. Zhong, Graduate Student



INDEX OF PRINCIPAL INVESTIGATORS

| | |
|------------------|--|
| Asaro, R.J. | 15, 26, 29 |
| Bray, P.J. | 56, 58, 60, 61, 62, 63, 64, 66, 84, 85 |
| Clifton, R.J. | 4, 5, 7 |
| Cole, R.H. | 57, 59, 82 |
| Diebold, G.J. | 94 |
| Duffy, J. | 18, 22, 29, 52 |
| Elbaum, C. | 11, 12, 13, 76, 133 |
| Estrup, P.J. | 87, 92 |
| Freund, L.B. | 41, 44, 47, 49, 52 |
| Greene, E.F. | 97 |
| Gurland, J. | 38, 40 |
| Houghton, A. | 78 |
| James, R.D. | 24 |
| Kosterlitz, J.M. | 81, 82 |
| Maris, H.J. | 68, 134, 135, 136 |
| Mason, E. A. | 137 |
| Needleman, A. | 24, 26, 51 |
| Nurmikko, A. V. | 122 |
| Pelcovits, R.A. | 80 |
| Quinn, J. J. | 124 |
| Risen, Jr., W.M. | 57, 59, 61, 62, 129, 130, 131 |
| Rosenberg, J. | 101, 103 |
| Seidel, G. M. | 134 |
| Shih, C.F. | 31, 48, 49 |
| Stiles, P.J. | 98, 117, 118, 120, 121 |
| Stratt, R.M. | 106 |
| Suggs, J.W. | 105 |
| Suresh, S. | 31, 32, 35 |
| Tauc, J. | 68, 71, 73, 75 |
| Weiner, J.H. | 9, 107 |
| Wold, A. | 110, 111, 113, 114 |
| Ying, S.C. | 89, 90 |



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9-86