

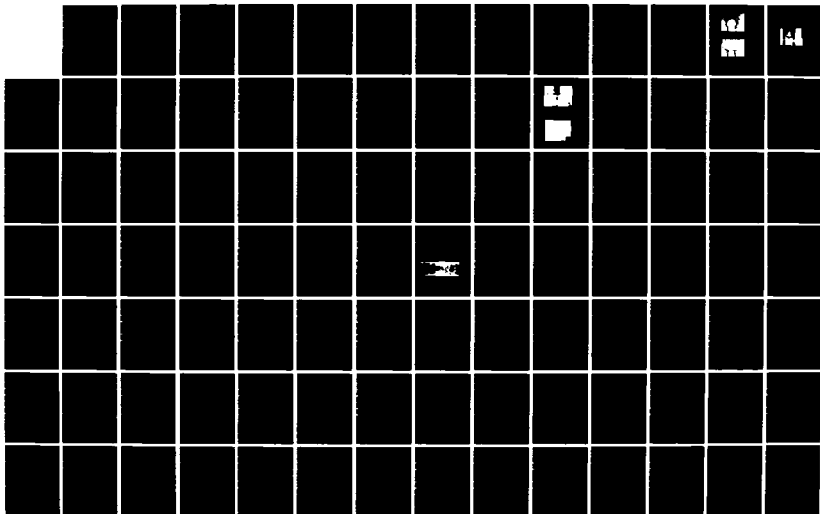
AD-A156 214

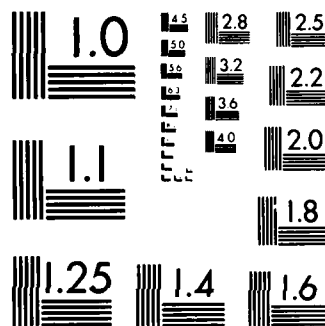
ANNUAL TECHNICAL REPORT MATERIALS RESEARCH LABORATORY 1 1/2
JULY 1983 - 30 JUNE 1984(U) BROWN UNIV PROVIDENCE RI
MATERIALS RESEARCH LAB 30 JUN 84 NSF-DMR82-16726

UNCLASSIFIED

F/G 11/7

NL





MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963-A

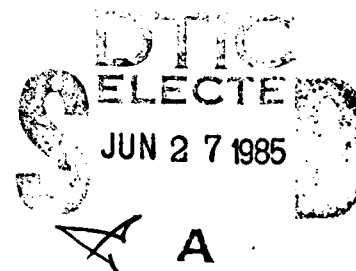
AD-A156 214

ANNUAL TECHNICAL REPORT
MATERIALS RESEARCH LABORATORY
July 1, 1983-June 30, 1984



DTIC FILE COPY

Brown University
Providence, Rhode Island 02912



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

85 06 14 019

1

ANNUAL TECHNICAL REPORT
MATERIALS RESEARCH LABORATORY

BROWN UNIVERSITY
PROVIDENCE, RI 02912

A Report on Grant No. DMR-8216726
from the
National Science Foundation
Washington, DC 20550

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

Distribution of this document is unlimited.

JUN 27 1985

A

A-36

Gas Research Institute

General Telephone Laboratories

National Bureau of Standards

National Institute of Health

National Science Foundation

Office of Naval Research

Petroleum Research Fund

A. P. Sloan Foundation

United States Army Research Office

U.S.-Israel Binational Foundation

United States Department of Energy

University of Rhode Island, Department of Chemical Engineering

University of Wisconsin

CONTENTS

Preface	1
Section 1	
Plasticity and Fracture	
Introduction	2
Research Results	4
Section 2	
Inorganic Glasses	
Introduction	75
Research Results	76
Section 3	
Surfaces	
Introduction	105
Research Results	106
Section 4	
New Initiatives	
Introduction	119
Research Results	120
Section 5	
Central Facilities	
Introduction	129
Research Results	130
Lectures in the Materials Research Laboratory Program, 1983-84 ...	142
List of Staff in the Materials Research Laboratory Program	150
Index of Principal Investigators	151

PREFACE

In 1983/84 the Materials Research Laboratory at Brown University was engaged in interdisciplinary research concentrated in three thrust areas which involved participation of investigators from the Department of Chemistry, Division of Engineering, Department of Applied Mathematics and Department of Physics. A coordinator was responsible for organizing each thrust area, as listed below:

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

In addition, there were three New Initiative programs:

Conformational and Electronic Transitions in Macromolecular Systems	R. Stratt and J. Weiner
New Approaches to Surface Modifications of Organic Polymers	J. W. Suggs
Electronic Properties of Ge-Ge ₃ N ₄ Interfaces	J. Rosenberg

The MRL program was supported by eight Central Facilities which in many cases did not only provide services but were also involved in research, usually on new techniques or new materials.

The largest single source of support for materials research at Brown University was the National Science Foundation, Materials Research Laboratory Section. Sixteen 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 Advisory Committee (R. J. Asaro, R. J. Clifton, L. N. Cooper, P. J. Estrup, G. S. Heller and J. J. Quinn).

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, and 3) 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.

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. 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 high strength steels this past year has led to detailed correlations of microstructures and observed micromechanisms of 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 which have led to a description of localized shearing at crack and notch tips which, in turn, lead to much more detailed and accurate assessments of the role of microstructure and microfracture in macroscopic toughness. 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 numerical methods have been developed which have led to a relatively complete understanding of the process of crack growth in materials which are nearly strain rate insensitive and only weakly strain hardening. These analyses are being used to interpret experiments on dynamic crack propagation in high strength steels.

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 this past year 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. One such model along with applications to path dependent strain hardening and localized necking is discussed in one of the writeups included below.

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

Determination of the Plastic Strain Concentration Factor in Steels

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

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

Sources of Support: ONR, MRL,

Objectives and Approaches:

The shadow-spot technique, or method of caustics, has been used for some time in fracture studies to determine optically the stress intensity factor at the tip of a crack. When this method is applied to metals, the caustic must be observed by reflection from the polished metal surface (1). Until recently the available analyses have limited its application to brittle metals where material behavior is essentially elastic. An analysis is now available that extends the range of applicability to materials, such as structural steels, that exhibit a substantial amount of plastic deformation in the region of the crack tip prior to fracture (2,3). This analysis relates the plastic strain concentration factor J to the transverse diameter D of the shadow spot through a formula that includes the work hardening rate of the metal. It is a more complicated expression than for elastic fracture and requires prior experimental determination of the work hardening exponent for the specimen material. To date no tests have been performed to determine the validity of this formula in providing a value of J by comparing in one test results based on caustics with the results of another independent experimental method. We are currently conducting such a comparison as outlined below.

To fulfill our purpose we must conduct an experiment in which we measure the value of J by an independent means while simultaneously using the method of caustics. For this purpose we are using a specially designed double cantilever beam (DCB) specimen that permits application of a load point-displacement method simultaneously with a record of the caustics. The specimen is 6" wide and 12" long, having a wide-mouth notch at one end; see Figure 1. A short hydraulic cylinder jack is mounted within the wide mouth to force open the notch. The force of this jack is applied at two opposite, fixed points along the jack's axis. The relative displacement of these two load points is measured by a differential transformer and recorded against load on an x-y plotter.

Research Achievements:

Our initial specimen material was a 1020 hot rolled steel. For this material, yielding can occur at the crack tip and within the

cantilever arms. To avoid yield in the arms, the cross-section perpendicular to the symmetry axis was shaped like a stubby H with thicker legs ($5/8$ " thk) on each side of the central thin section ($3/8$ " thk. and 2" wide). The notch was cut along the axis of symmetry, ending with a thin straight cut made with a spark cutter. The thicker outside sections prevented the premature plastic deformation along the outside edges of the specimen as the load was increased.

Initial tests using this material gave poorly defined shadow spots, in spite of extra care taken in polishing the surface of the specimen. It is believed that this blurring of the shadow spot is due to Luder's bands emanating from the plastic zone. Indeed, as loading continues the elastic-plastic boundary on the specimen becomes more and more ragged until plastic zones are seen to shoot out. This non-uniform plastic strain distribution in the metal produces a caustic with a blurred boundary that is, therefore, difficult to interpret.

As a result, we next tested specimens made of an oil-hardened tool steel. For this material, plastic deformation is confined to a zone at the tip of the crack. Accordingly, the thicker legs employed with the 1020 HRS are not needed. The strain in the plastic zone is much more uniformly distributed and the elastic plastic boundary is a smooth curve. The observed caustics are better defined than with the 1020 HRS. Two examples are presented in Figures 2a and 2b; the background lines running generally perpendicular to the direction of the crack are slip lines. In Figure 2b the plastic zone ahead of the crack is quite apparent. In each the load and the corresponding load-point displacement have been measured and are recorded. A photograph of the specimen with the hydraulic cylinder in position is presented in Figure 3. We have not yet performed enough tests or interpreted and compared sufficient data points to draw any firm conclusions, however, initial results seem to point towards good agreement once deformation has progressed beyond the elastic limit for the material. This work is continuing.

References:

1. A. J. Rosakis, J. Duffy and L. B. Freund, "The Determination of Dynamic Fracture Toughness of AISI 4340 Steel by the Shadow Spot Method," J. Mechanics and Physics of Solids, Vol. 32, No. 6, 1984, pp. 443-460.
2. A. J. Rosakis, C. C. Ma and L. B. Freund, "Analysis of the Optical Shadow Spot Method for a Tensile Crack in a Power-Law Hardening Material," J. Applied Mechanics, Vol. 50, 1983, pp. 777-782.
3. L. B. Freund, A. J. Rosakis and C. C. Ma, "Optical Determination of the Intensity of Crack Tip Deformation in Power-Law Hardening Materials" in Materials Behavior Under High Stress and Ultrahigh Loading Rates, Ed. J. Mescall and V. Weiss, Plenum, 1983, pp. 265-272.

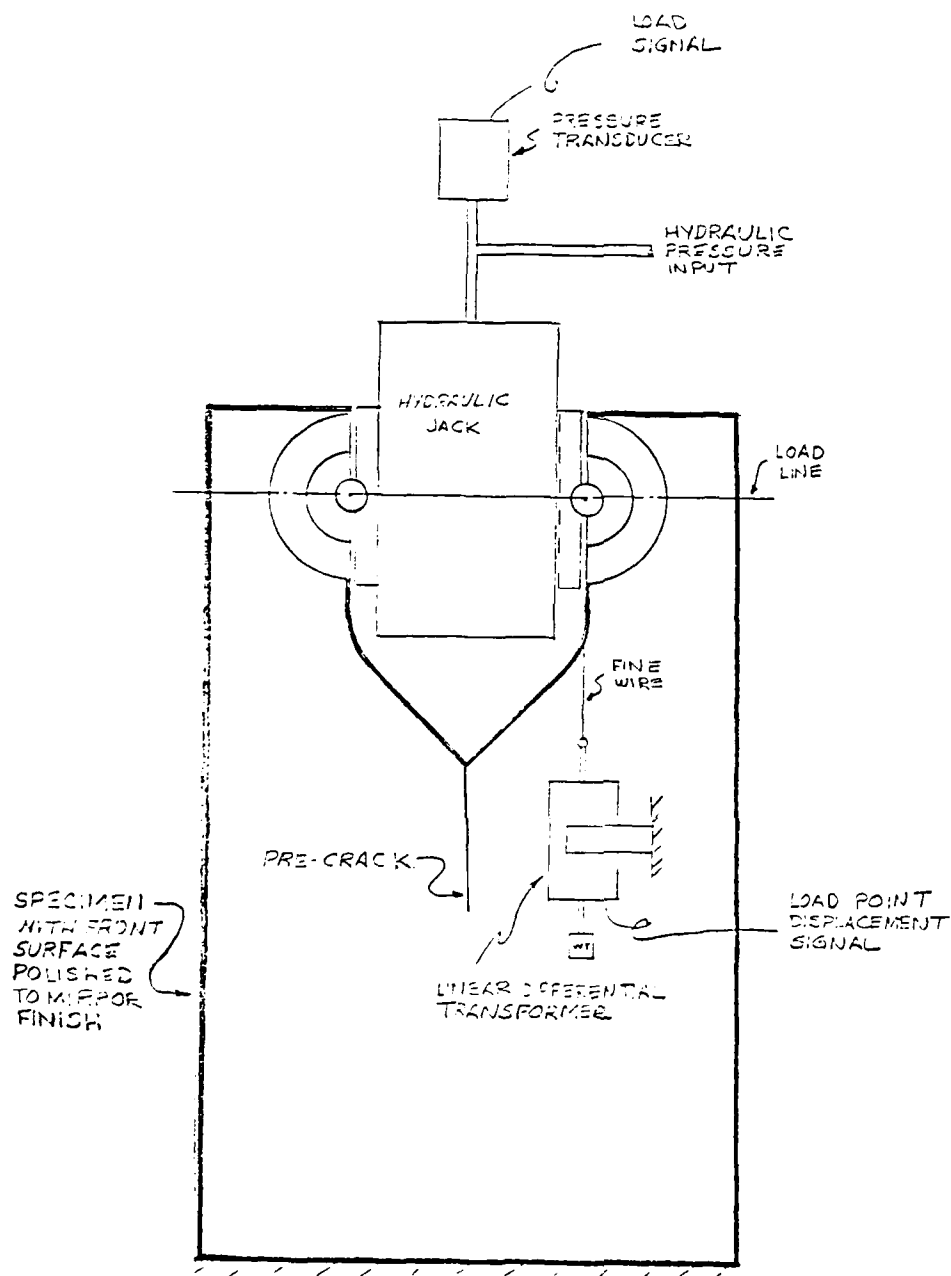


Figure 1: Test Arrangement Showing Modified D.C.B. Specimen for Load Displacement-Caustics Study.



a) Load = 3840 N Displ. = 2.72 mm
Magnification ratio 3.1 : 1



b) Load = 5000 N Displ. = 3.82 mm
Magnification ratio 6.4 : 1

Figure 2: Caustics Formed in Reflection at Tip of Notch in Oil Hardened Steel D.C.B. Specimen at Two Different Loads.

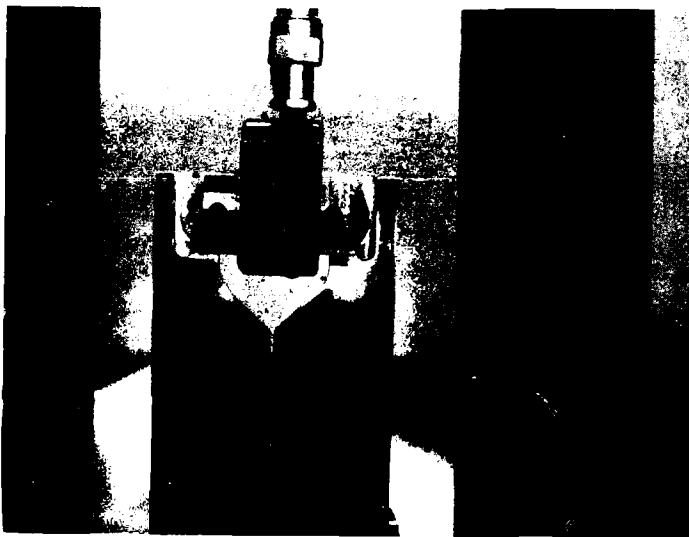


Figure 3: Photograph of DCB Specimen with Hydraulic Cylinder in Place.

Dynamic Crack Growth in Elastic-Plastic Materials

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

Personnel: P. S. Lam, Research Associate, Div. of Engineering
A. S. Douglas, Graduate Student, Div. of Engineering
C. C. Ma, Graduate Student, Div. of Engineering
A. J. Rosakis, Graduate Student, Div. of Engineering

Sources of Support: MRL, ONR, NSF, GE Foundation

Objectives and Approaches:

Understanding of rapid crack growth in materials which can deform plastically is essential in several engineering applications. For example, in a nuclear reactor pressure vessel there is no structural redundancy and, consequently, any fracture that is initiated due to material defects or emergency cooling must be arrested before it penetrates the vessel wall. Similarly, naval ships must be able to sustain some structural damage in the form of crack growth without complete structural failure. In such applications, the structural metals used are selected for their fracture toughness and crack growth can be expected to be accompanied by some plastic flow. The crack growth process is influenced by the nature of the loading, the configuration of the system, the temperature and the microstructure of the material. The objective is to understand the influence of material features and processes on the microscale on the crack growth resistance of materials.

Research Achievements:

Through research at Brown over the past few years, we have developed a relatively complete understanding of the process of crack growth in elastic-plastic materials which are strain rate insensitive and which have a low rate of strain hardening, properties typical of high strength structural steels, for example. The project has involved mathematical analysis of crack growth phenomena, large scale numerical simulation studies, and experiments on fast fracture in steel. Through collaboration with Professor D. Parks, a colleague at M.I.T., a numerical scheme was developed for simulating fast crack growth in an elastic-plastic material under the simple anti-plane shear mode of deformation. During the course of this work, we discovered an exact mathematical solution for certain features of the deformation field. This was the first exact result on dynamic elastic-plastic fields in the literature, and its availability provided an extremely important check on the numerical code. The code was then extended to the more realistic case of plane strain crack growth. Of particular interest was the relationship between the remote applied crack driving force and the crack tip speed predicted on the basis of a crack growth criterion imposed on the microstructural level of ductile deformations at the crack tip. This

Publications:

J. Duffy, "Strain Rate History Effects and Dislocation Substructure at High Strain Rates," in Material Behavior Under High Stress and Ultrahigh Loading Rates, Ed. J. Mescall and V. Weiss, Plenum, 1983, pp. 21-37.

J. Duffy, "Temperature Measurements During the Formation of Shear Bands in a Structural Steel," Mechanics of Material Behavior, Ed. G. J. Dvorak and R. T. Shield, Elsevier, 1984, pp. 75-86.

K. A. Hartley and J. Duffy, "Strain Rate Temperature History Effects During Deformation of FCC and BCC Metals," Inst. Phys. Conf. Ser. No. 70, presented at 3rd Conf. Mech. Prop. High Rates of Strain, Oxford, 1984, pp. 21-30.

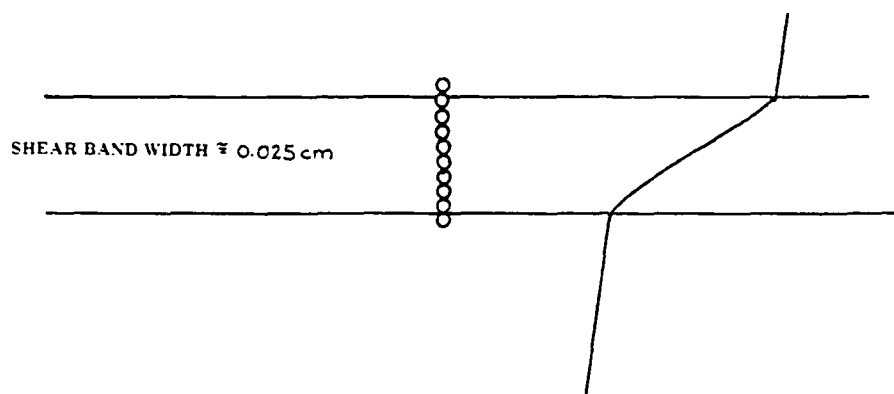
J. Duffy, "The Use of the Kolsky Bar in Dynamic Fracture Initiation," invited lecture for Society of Engineering Science, Blacksburg, Virginia, October, 1984.

R. J. Clifton, J. Duffy, K. A. Hartley and T. G. Shawki, "On Critical Conditions for Shear Band Formation at High Strain Rates," Scripta Metallurgica V18, 1984, pp. 443-448.

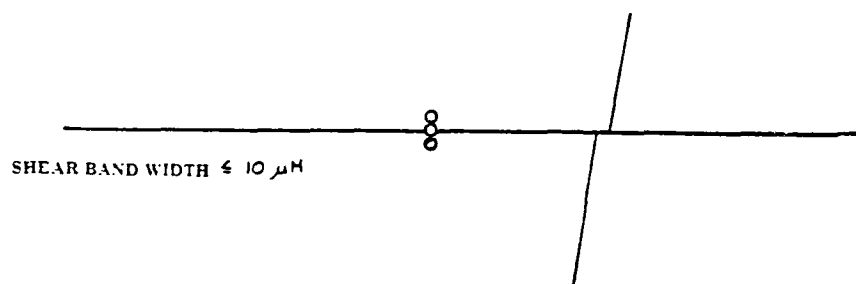
J. Duffy, H. Couque and R. J. Asaro, "Correlation of Microstructure with Dynamic and Quasi-Static Fracture of a Plain Carbon Steel, Brown University Technical Report #DAAG29-81-K-0121/7, 1984.

S. Tanimura and J. Duffy, "Strain Rate Effects and Temperature History Effects for Three Different Tempers of 4340 VAR Steel," Brown University Technical Report #DAAG29-81-K-0121/4, 1984 (submitted for publication).

SPOT SIZE = $20\mu\text{M}$



DEFORMED BAND 1018 COLD ROLLED STEEL



TRANSFORMED BAND 4340 VAR STEEL

Figure 3: Schematic of Detector Spot Size Compared to Shear Band Width.

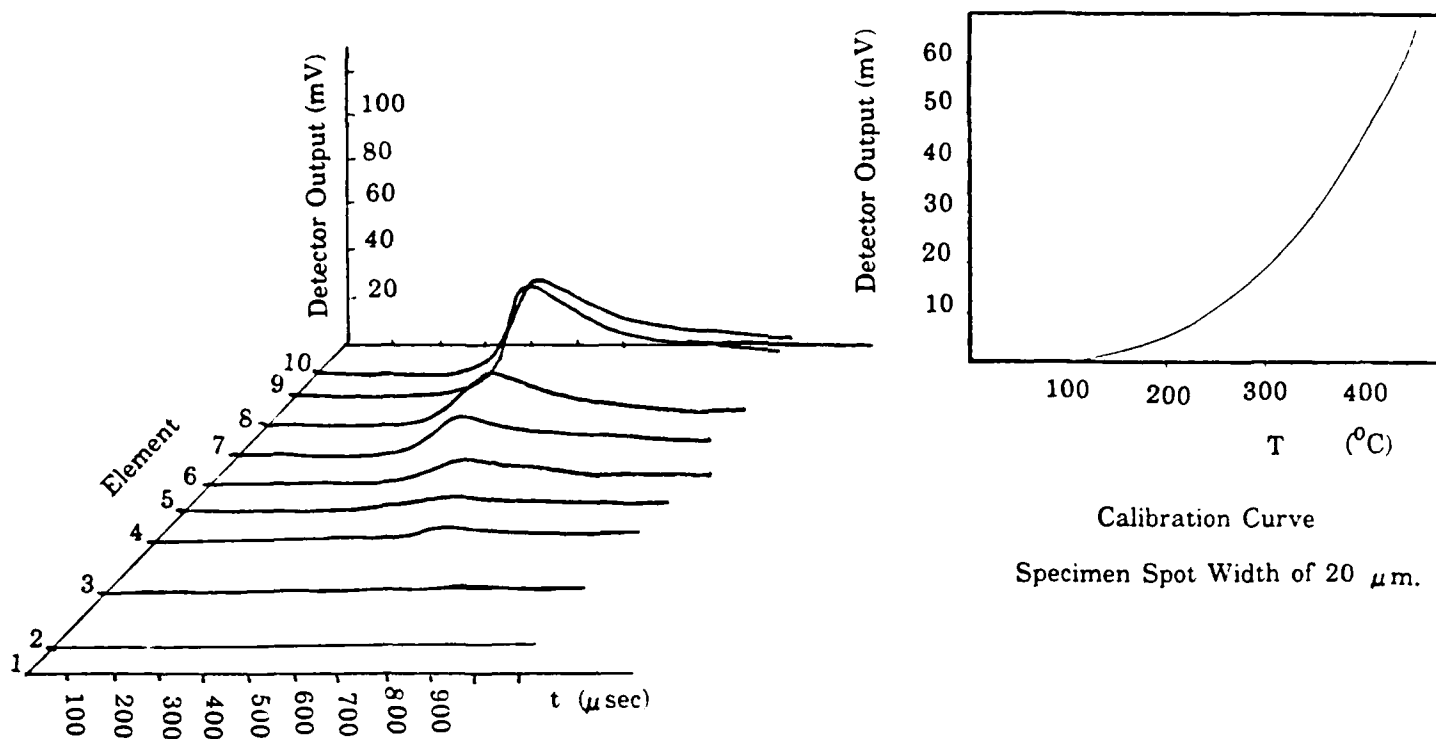


Figure 2a: Temperature Profile Across the 1018 CRS Gage Section for a Specimen Spot Size of $20 \mu\text{m}$.

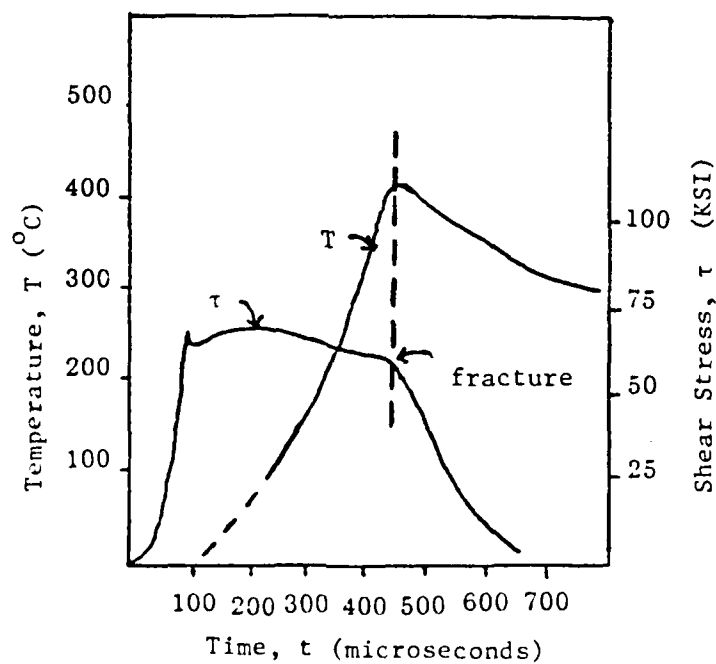


Figure 2b: Shear Stress and Shear Band Temperature as Functions of Time for 1018 CRS.

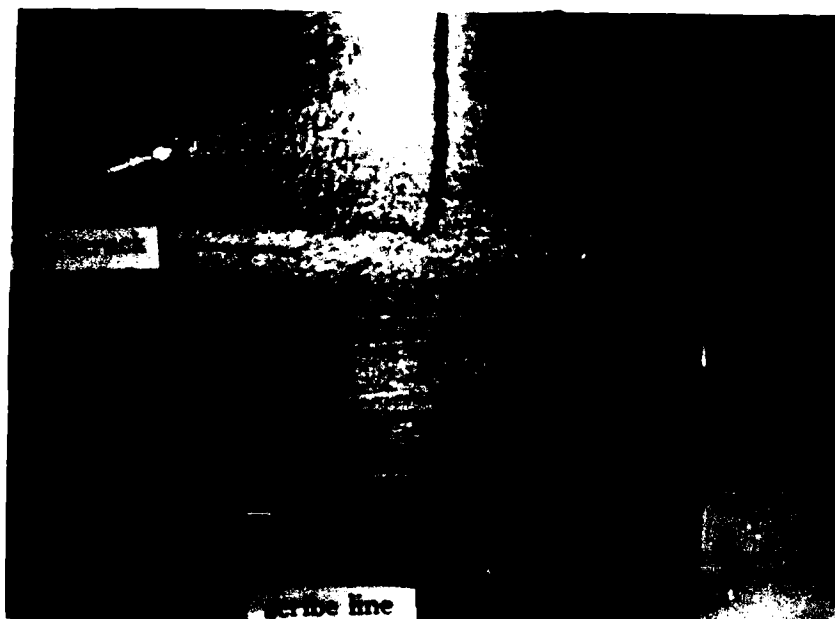


Figure 1a: Deformed Shear Band in 1018 CRS.

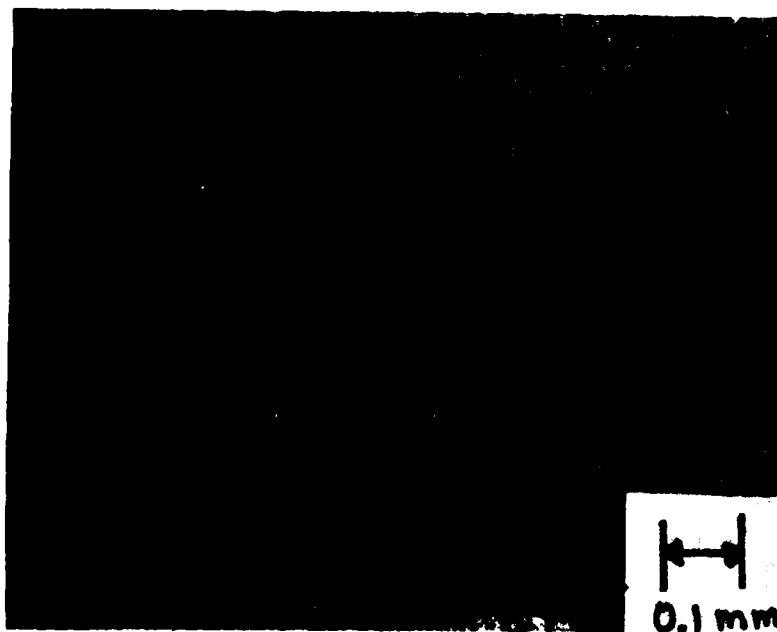


Figure 1b: Microstructure in the Shear Band Region (1018 CRS).

2. J. Duffy, "Temperature Measurements During the Formation of Shear Bands in a Structural Steel," Mechanics of Material Behavior, G. J. Dvorak and R. T. Shield (Eds.), Elsevier Science, Amsterdam, 1984, pp. 75-86.
3. R. J. Clifton, J. Duffy, K. A. Hartley and T. G. Shawki, "On Critical Conditions for Shear Band Formation at High Strain Rates," Scripta Met. 18, 1984, pp. 443-448.
4. K. A. Hartley and J. Duffy, "Measurement of Temperature During the Formation of Shear Bands in 1018 Cold-Rolled Steel," Brown University Report, in preparation.

To measure the temperature profile within the band, a greater magnification was used. It was found that, for a spot size of 20 microns, the maximum temperature rise within the band is about 440°C. A typical test result including the spatial temperature profile is given in Figure 2. Temperature measurements were also made for 4340 VAR steel, where transformed bands are formed. These have a width of less than 10 microns. At the smaller spot size, a temperature increase of 410°C was recorded. However, because our current spot size is larger than the width of the band, this suggests that the temperature rise within the shear band is probably much greater, as required if a phase transformation actually occurs in this steel. Figure 3 illustrates the spot size/shear band width relationship for the deformed bands in 1018 CRS and the transformed bands in 4340 VAR steel. We have received a ten-element infrared microscope that will allow finer temperature measurements in the future.

In addition to the temperature measurement work, tests have been performed on three AISI 1215 steels furnished by Inland Steel Corporation that contain MnS inclusions. The purpose of this work is the determination of the influence of inclusion shape, size and distribution on shear band formation. It has long been known that the addition of MnS improves the machinability of steels. However the mechanisms by which machinability improves is still not fully understood.

We have found that the addition of MnS inclusions does influence shear band formation in 1215 steel, with the smallest, mostly highly elongated inclusions leading to the formation of multiple bands. Only one band was observed after tests on 1018 CRS or 1215 steel with larger, rounder inclusions, although the stress-strain curves are almost identical. SEM fractographs reveal many deep voids on the fracture surface of the multiply-banded steel, while fewer, shallower voids were seen in the other steels. These results agree well with the machinability test results obtained at Inland Steel, which show the steel with the highly elongated inclusions to have the worst machinability. Additional tests are planned to further examine the mechanism by which inclusions influence machinability and shear band formation, including metallurgical examination for voids and microcracks.

References:

1. L. S. Costin, E. E. Crisman, R. H. Hawley, J. Duffy, "On the Localization of Plastic Flow in Mild Steel Tubes Under Dynamic Torsional Loading," Mechanical Properties at High Rates of Strain, J. Harding (Ed.), The Institute of Physics, Bristol and London, Conf. Series No. 17, 1979, pp. 90-100.

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

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

Personnel: K. A. Hartley, Graduate Student, Division of Engineering
R. H. Hawley, Senior Research Engineer, Div. of Engineering
E. E. Crisman, Sr. Research Engineer, Div. of Engineering
G. J. LaBonte, Technical Assistant, Div. of Engineering

Sources of Support: MRL, ARO

Objectives and Approaches:

We are continuing our effort to understand the development of non-homogeneous deformation, or shear bands, during the dynamic deformation of steel (1-4).

One important area in this research involves measurements of the temperature rise in steel resulting from the relative large plastic deformation within the shear bands. Our experiments are conducted with thin-walled tubular specimens deformed in torsion. For the dynamic tests a torsional Kolsky bar is employed to give strain rates to 2000 s^{-1} while furnishing a measure of shear stress as a function of average shear strain in the specimen. The infra-red radiation from the metal surface is focused on an array of ten separate indium-antimonide detectors to provide a temperature profile of the shear band during its formation. These experimental data, including the temperature distribution, are essential to analyses into the mechanisms of shear band initiation and growth. Metallurgical evidence provided by numerous other investigators suggests that the temperatures that are reached within some bands are great enough to cause a material phase transformation, which, however, results in a much thinner shear band. By adjusting the optics in our experiment it is possible to vary the magnification and hence the size of the observed area on the specimen. To obtain the profile across the entire gage length, an initial spot size of 0.25 mm was chosen. This is approximately equal to the width of the deformed-type shear band in 1018 cold-rolled steel (CRS), as seen in Figure 1. We have also employed much smaller spot size, as detailed below.

Research Achievements:

It was found that the average temperature measured in a deformed band in the 1018 CRS (no phase transformation) is about 220°C . This is consistent with a calculation of the heat that is generated by the plastic work at the band. To either side of the band, the temperature was found to fall off rapidly along the gage length.

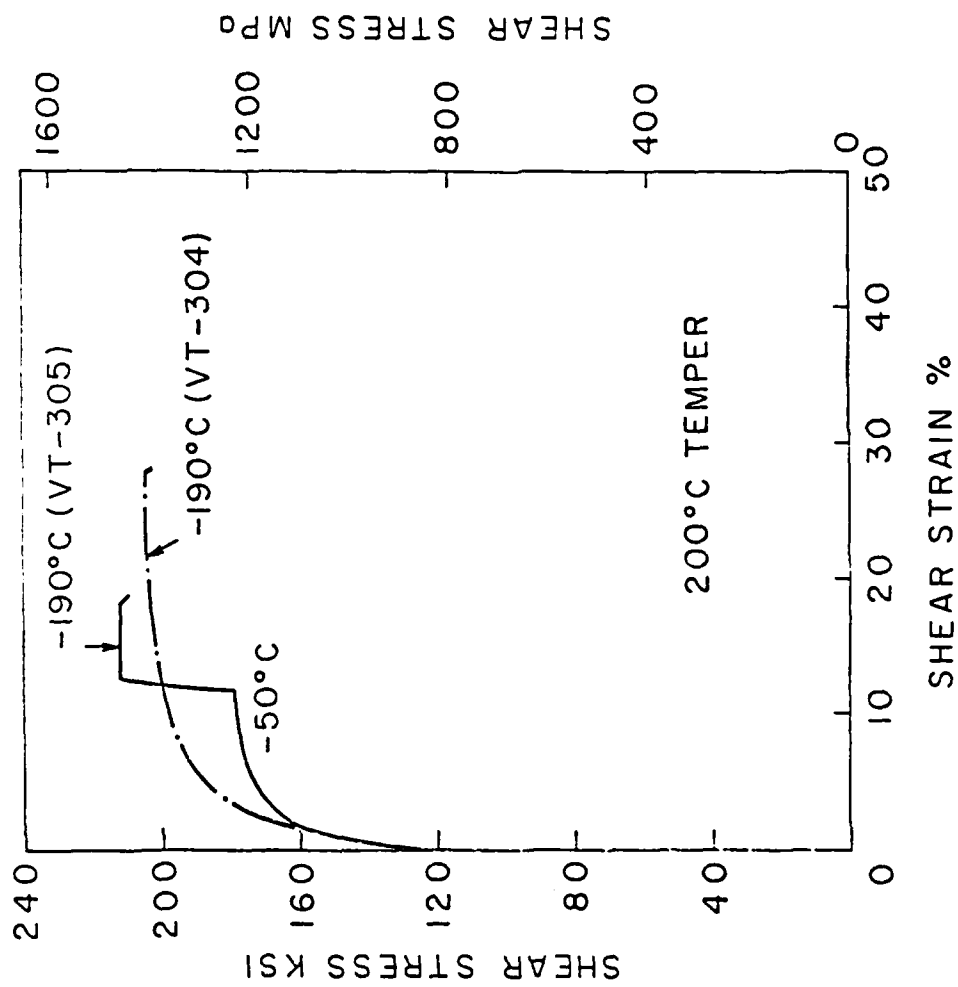


Figure 6b: Incremental Temperature Tests at $\dot{\gamma} = 6 \times 10^{-4} \text{ s}^{-1}$, 200°C Temper.

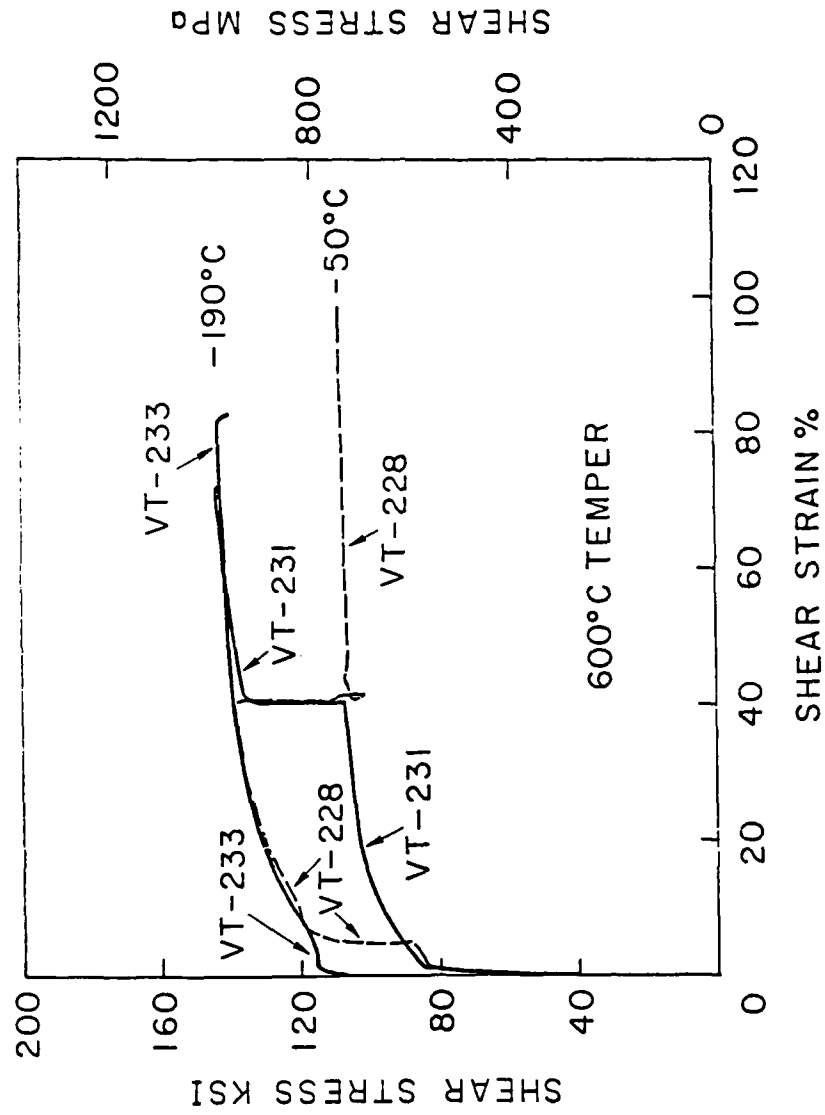


Figure 6a: Incremental Temperature Tests at $\dot{\gamma} = 6 \times 10^{-4} \text{ s}^{-1}$, 600°C Temper.

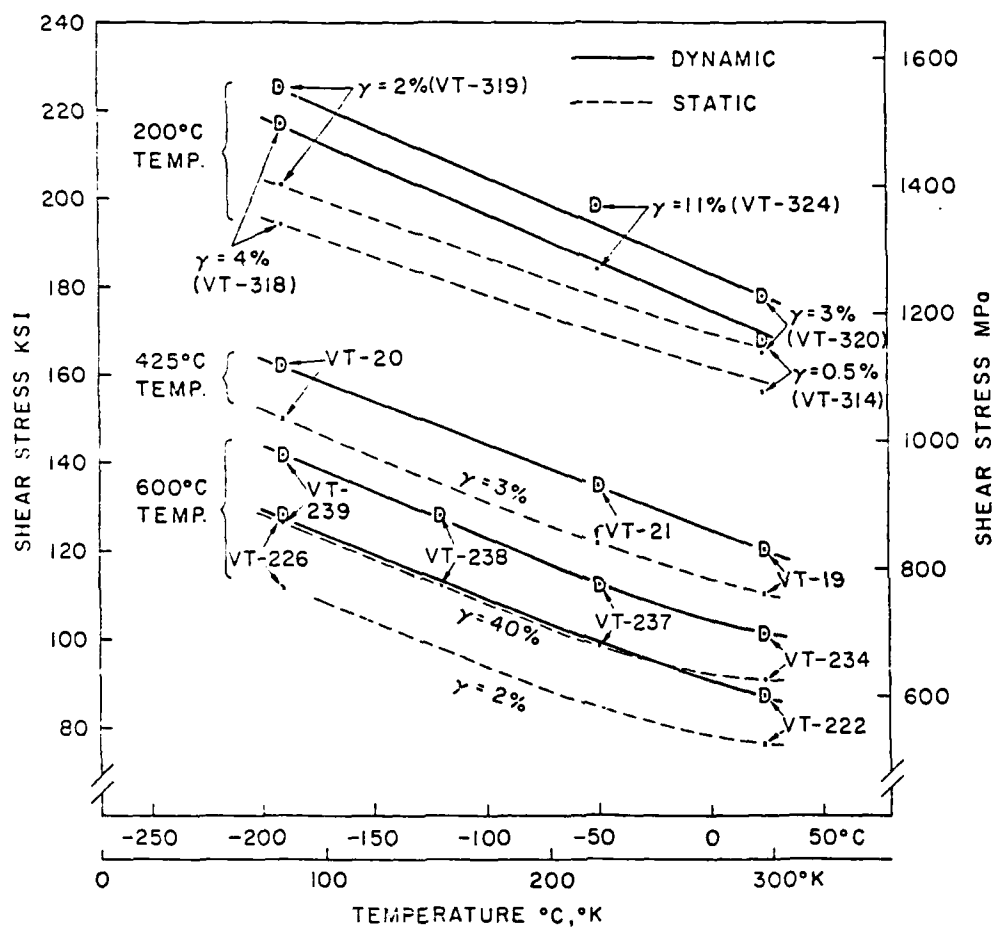


Figure 5: Results of Incremental Strain Rate Tests. Dashed lines show stress values just before increments in strain rate and solid lines just after. Increments in strain rate are imposed at strain values indicated on curves.

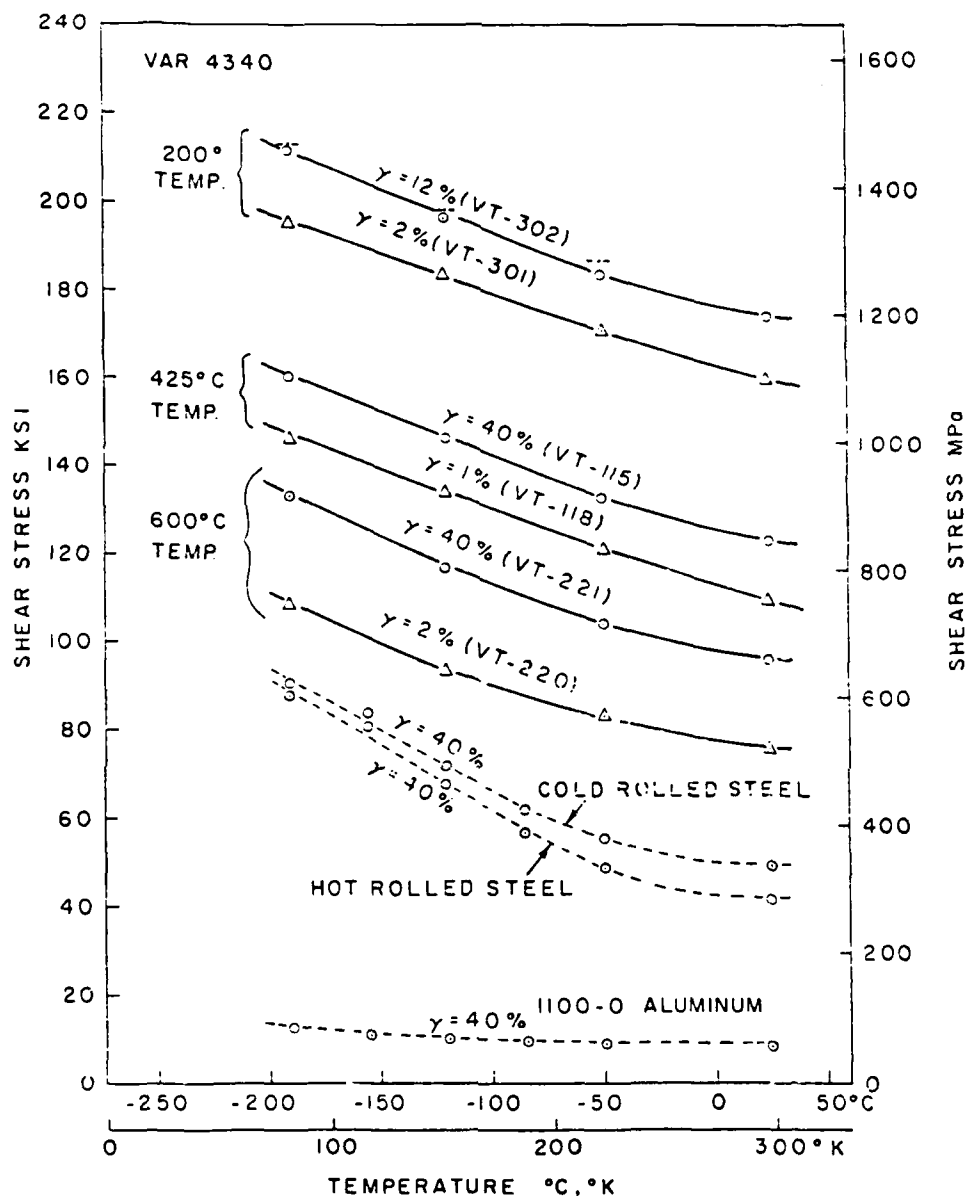


Figure 4: Flow Stress as a Function of Test Temperature. Results of Tests Involving Multiple Decrements in Temperature. All Tests Start at Room Temperature. The Strain at Which the Temperature Decrements Occur is Indicated on Each Curve. $\dot{\gamma} = 6 \times 10^{-4} \text{ s}^{-1}$.

Strain rate sensitivity for all three tempers of the 4340 VAR steel is about the same as found in mild steel and considerably greater than that seen in aluminum or other FCC metals. For the 425°C and 600°C tempers it is nearly independent of test temperature in the range -190°C to room temperature, although there is a small relative maximum at about -120°C. For the 200°C temper, the strain rate sensitivity is considerably greater at -190°C than at room temperature (see Figure 5). Based on these results, an activation volume was calculated and, for the 600°C temper, its value was found to agree closely with the results of other experiments on iron and steels. For an increase in applied stress, the numerical values of activation volume were found to decrease from about $50 b^3$ to about $10 b^3$, where b is the Burgers vector. According to published data this indicates that the dominant deformation mechanism is overcoming the Peierls-Nabarro stress.

The effects of temperature history and strain rate history on the subsequent flow stress are complicated, but at the same time are characteristic of BCC metals. For the 200°C temper the effects of a prior deformation are pronounced, whereas they are small for the other two tempers. For the 600°C temper, for instance, history effects appear negligible, although there is some evidence that the work-hardening rate may be slightly lower following an increase in temperature from -190°C to -50°C during deformation (see Figure 6a). It is clear, however, that the 200°C temper does not behave in the same way as the other two tempers. For instance, while a sudden drop in temperature from -50°C to -190°C during deformation results in a flow stress somewhat lower than found in a specimen loaded entirely at -190°C in the 600°C and 425°C tempers. In the 200°C temper the subsequent flow stress exceeds considerably that found in a like specimen deformed entirely at -190°C (see Figure 6b). An overshoot of this nature has not been seen in FCC or HCP metals but is quite characteristic of deformation in BCC metals, and generally is limited to certain temperature and strain rate ranges. It now turns out to be limited to certain tempers of 4340 VAR steel.

The fact that these experiments included increments in both temperature and strain rate, in addition to the more conventional tests under constant temperature and strain rate conditions, should make it possible to develop uniaxial constitutive equations for different hardnesses of AISI 4340 VAR steel that include temperature, strain rate and their history.

References:

1. S. Tanimura and J. Duffy, "Strain Rate Effects and Temperature History Effects for Three Different Tempers of 4340 VAR Steel," Brown University Technical Report #DAAG29-81-K-0121/4, 1984 (submitted for publication).

Strain Rate and Temperature History Effects on the Stress-Strain Behavior of 4340 VAR Steel

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

Personnel: S. Tanimura, Visiting Assoc. Professor, Div. of Engineering
K. A. Hartley, Graduate Student, Division of Engineering
R. H. Hawley, Senior Research Engineer, Div. of Engineering
G. J. LaBonte, Technical Assistant, Div. of Engineering
P. Rush, Technical Assistant, Division of Engineering

Sources of Support: MRL, ARO

Objectives and Approaches:

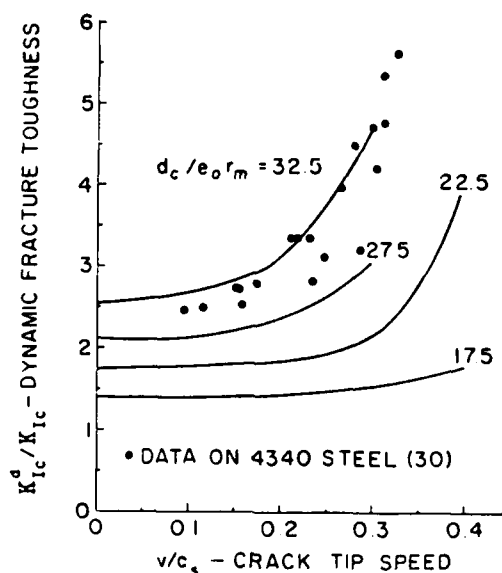
An extensive series of experiments was performed to determine the quasi-static and dynamic stress-strain behavior in shear of specimens of AISI 4340 VAR steel, tempered at temperatures of 200°C, 425°C and 600°C resulting in hardnesses of 55, 44 and 33 on the Rockwell C scale respectively (1). For this purpose short tubular specimens were loaded in a torsional Kolsky bar at strain rates in shear of $6 \times 10^{-4} \text{ s}^{-1}$ and 400 s^{-1} and over the temperature range -190°C to room temperature. In addition, temperature history effects were examined by deforming the specimen first at one temperature up to a given value of strain, and then imposing a rapid decrement or increment in temperature and allowing deformation to continue to fracture. A few specimens were also subjected to multiple increments in temperature during deformation. Similarly, incremental strain rate experiments were conducted in which the strain rate was increased rapidly from the quasi-static to the dynamic rate.

Research Achievements:

As expected, these results show that the quasi-static room temperature flow stress level in 4340 VAR steel depends quite strongly on the temper. At yield in shear for instance, it increases from about 520 MPa for the 600°C temper to 760 MPa for the 425°C temper to 1140 MPa for the 200°C temper. The change in flow stress with test temperature, in the range -190°C to -50°C is about the same for all three tempers even up to large strains. Furthermore, for this range of temperatures it appears that flow stress decreases linearly with an increase in temperature. However, the rate of change is smaller in the range -50°C to 20°C, particularly for the 200°C temper. This is probably due to the effects of dynamic strain aging and is in agreement with the general trend seen by others for plain carbon steels (see Figure 4).

same relationship was measured during rapid crack propagation in 4340 steel plate specimens, and the agreement between the theoretical prediction and the observation was very good as indicated in the attached Figure. In the course of doing the experiments, it was found to be necessary to re-examine the analysis underlying the optical shadow spot method in fracture mechanics to assess the influence of crack tip plasticity on the observations being made, even though light reflected from the elastic part of the specimen is used in the technique. We were also able to determine an analytical description of the stress and deformation fields very near to the crack tip compared to the size of the crack tip plastic zone which agreed very well with the results of the finite element numerical simulation.

The results resolved a long-standing paradox in this field. Experiments have typically yielded a variation of crack driving force with crack tip speed that is fairly strong for low crack speeds, say above 20% of the elastic shear wave speed. Elastic models, on the other hand, could not account for this strong variation, even though the process is of the small scale yielding type. The inclusion of plasticity in the analysis brought the theory and experiment into closer harmony, and it clearly demonstrated the significant role played by material inertia on the microscale in determining the dynamic fracture resistance of materials. Further work is directed toward determining the role of material rate sensitivity in the process. The results of a preliminary study completed during the year in collaboration with Professor J. W. Hutchinson, a colleague at Harvard University, on high strain rate crack growth in materials make clear the very important role played by strain rate in controlling the microstructural separation mechanism in materials (such as structural steels) which can undergo a mechanism transition with changes in temperature and/or rate of crack growth.



Prediction of dynamic fracture toughness of an elastic-plastic material vs. crack tip speed based on a local ductile growth criterion. The data points are values inferred by means of the shadow spot method from experiments on 4340 steel.

Publications:

L. B. Freund and A. S. Douglas, "Dynamic Growth of an Antiplane Shear Crack in a Rate-Sensitive Material," in Elastic-Plastic Fracture Mechanics ASTM-STP 803, edited by C. F. Shih and J. P. Gudas, ASTM (1983), p. 5-20.

L. B. Freund, "The Mechanics of Dynamic Crack Growth in Solids," in Fundamentals of Deformation and Fracture, edited by K. J. Miller, Cambridge University Press (1984) to appear.

A. J. Rosakis, J. Duffy and L. B. Freund, "The Determination of Dynamic Fracture Toughness of AISI 4340 Steel by the Shadow Spot Method," Journal of the Mechanics and Physics of Solids 32 (1984), pp. 443-460.

P. S. Lam and L. B. Freund, "Analysis of Dynamic Growth of a Tensile Crack in an Elastic-Plastic Material," Journal of the Mechanics and Physics of Solids (1985), to appear.

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 (1985), to appear.

C. C. Ma and L. B. Freund, "The Extent of the Stress Intensity Factor Field in Dynamic Crack Growth," Brown University Report, September 1984.

The Formation of Shear Bands in High Rate Deformation Fields

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

Personnel: M. Toullos, Research Associate, Division of Engineering
F. H. Wu, Graduate Student, Division of Engineering

Sources of Support: MRL, ARO

Objectives and Approaches:

The localization of plastic strain in materials into narrow layers of intense shear, i.e., the so-called "shear bands", is an undesirable mode of deformation in numerous applications. For example, it accounts for poor finish of metals in machining operations, it sets the limits on permissible shape change in metal forming operations, and it represents a low energy deformation mode in armor plating or other energy absorbing system. Consequently, it has become necessary to understand the conditions under which such bands can form, and the properties of materials that contribute to their formation.

Research Achievements:

Our work is based on the view that it is most likely that shear bands are initiated at material defects, natural inhomogenieties or geometrical stress concentrators, and that they subsequently grow in a crack-like manner. Stress is intensified at the front of the band, and the material instability condition in this region becomes the condition for sustained growth of the band. In initial work, the transient growth of shear bands in nonlinear elastic materials for which the stress-strain curve has a local maximum was analyzed. This provides a simple material model for the situation when strain hardening is dominated by thermal softening beyond some strain level under adiabatic conditions. To examine the mechanism of shear band formation, analyses have been made of the process of steady overall shearing of a large block of material containing a small region less resistant to deformation than the rest of the block. It was found that the shear strains are first concentrated around the defect, and then a shear band begins to grow into the otherwise homogeneous material at a speed that is a significant fraction of the elastic wave speed of the material and at an overall strain that is far below the critical strain for the whole sample. The irreversibility of plastic deformation has also been taken into account in more recent calculations involving multiple defects. A band is observed to form at the weakest defect, and then to propagate through the otherwise homogeneous material at a material specific speed. If the band approaches a second defect, then several different phenomena have been

observed. The main outcomes of the interaction are: (i) the primary band arrests and a secondary band grows unilaterally from the second defect in the same direction as the primary band, (ii) the primary band grow beyond the second defect and, in so doing, screens the second defect from the applied loading so that a secondary band is never formed, or (iii) the defects precipitate shear bands independently if their mutual spacing is large enough. In future work, we intend to pursue these issues along similar lines, but on the basis of a more realistic material model.

Publications:

F. H. Wu and L. B. Freund, "Deformation Trapping Due to Thermoplastic Instability in One-Dimensional Wave Propagation," Journal of the Mechanics and Physics of Solids 32, pp. 119-132 (1984).

J. H. Wu, M. Toullos and L. B. Freund, "Initiation and Propagation of Shear Bands in Antiplane Shear Deformation," Brown University Technical Report, March 1984.

M. Toullos, "The Wavefront Induced in a Homogeneously Shearing Solid by a Localized Material Imperfection," Quarterly of Applied Mathematics (1985), to appear.

Fracture Toughness of Cemented Carbides

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

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

Sources of Support: MRL

Objectives and Approaches:

The aim of the project is to elucidate the effects of microstructure and constituent properties on the fracture toughness of two-phase aggregates consisting of hard particles and ductile matrix. The experimental work is restricted to cemented carbides, but the theoretical analysis will have relevance to the fracture of heterogeneous alloys in general.

Cemented carbide tool materials are now generally coated by refractory films which greatly improve the wear resistance. The massive substrate consists of sintered tungsten carbide, WC-Co. The fracture toughness of the substrate is an important design variable since it is a measure of the tool's resistance to failure by crack growth from flaws which either exist in the substrate material or might form in the coating. The understanding of the fracture process is required for further alloy development, especially in the search for hard phase and binder substitutes for WC and Co, respectively.

In contrast to previous work, this study will be extended to a very wide range of compositions and microstructures, including a number of different carbides (WC, TiC, TaC, etc.) and a variety of binder metals (Co, Ni and Fe-C steels).

The theoretical analysis will focus on the application of fracture mechanics to the stress state and observed fracture processes at the crack tip, with special consideration of the heterogeneity of the microstructure.

Research Achievements:

The preliminary work, now in progress, deals with the selection and development of a suitable fracture toughness testing method. No single procedure has as yet been accepted as a standard method, the principal problem being the difficulty of reproducibly introducing the required starting cracks. Several methods are being investigated, among them 1) single-edge notched beam (SENB) specimens, with notch produced by spark cutting (EDM) with very thin foils, 2) SENB specimens pre-cracked by wedge indentation with subsequent removal of the plastically strained material, 3) chevron-notched specimens loaded in bending, and 4) surface indentation cracking, now widely used in the industry as a screening method for evaluation of relative fracture resistance. WC-Co tool grade specimens are used for the above purpose.

Determination of fracture toughness by the SENB-EDM and surface indentation cracking methods has also been carried out on a number of specimens from several alloy systems, namely, WC-Co, TiC-Mo-Ni and TiC-steel in order to determine some of the boundary conditions of the large scale study to follow. All indications to date show relatively small differences in fracture toughness between systems at similar binder ligament size, although large effects are introduced by varying the binder content. These results confirm the necessity for an accurate and precise fracture toughness testing method.

Publications:

J. Gurland, "Application of Quantitative Microscopy to Cemented Carbides," in Practical Applications of Quantitative Metallography, ASTM STP 839, J. L. McCall and J. H. Steele, Jr., Eds., Am. Soc. Testing and Materials, Philadelphia, 1984, pp. 65-84.

Strength and Fracture of Two-Phase Alloys

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

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

Sources of Support: U.S. Department of Energy and MRL Central Facilities

Objectives and Approaches:

Some of the important industrial alloys derive their strength from mixtures of hard and soft constituents. Examples of this type are the common steels which consist of hard pearlite and ductile ferrite, and aluminum-base casting alloys which contain hard silicon particles embedded in a matrix of soft aluminum. Although much is known empirically about the strength and deformation of each alloy, only limited work has been done on the general problem of predicting the yield strength and flow stress of two-phase materials over a wide range of compositions (except for the two special cases of dispersion hardening and fiber reinforcement).

As a contribution to the theory and design of two-phase alloys, the present study is concerned with the partition of stress and strain between the hard and soft constituents, and consideration of fracture processes in two representative alloy systems, namely, spheroidized carbon steels (iron carbide in ferrite) and dual-phase steels (martensite in ferrite). Together, the two systems cover a wide range of compositions, from about 6% to 70 volume % of the hard phase. In addition to their scientific interest the dual-phase steels have interesting technological properties, they are both very strong in use and easily deformable during processing (rolling and stamping). This unusual combination of properties makes them attractive to the automobile and transportation industries.

Research Achievements:

- 1) The magnitude of the back stress in a spheroidized steel has been determined indirectly by measurement of the Bauschinger effect and is being studied by residual strain determination by x-ray diffraction.
- 2) The stress-strain data for dual-phase steels has been obtained for specimens with martensite contents from 20 to 100 volume %. The fracture generally is ductile, with crack initiation at the martensite-ferrite interfaces, but little cracking of the martensite. Cleavage was observed in ferrite under conditions of high plastic constraint near coarse martensite grains.
- 3) A 30 mm grid superimposed upon the microstructure by photolithography permits direct measurement of strain in coarse martensite grains on the specimen surface. The results show a) that

there is a great variability of martensite grain deformation, b) that, on the average, the martensite deforms appreciably less than the alloy, and c) that the relative average martensite strain increases at high martensite volume fractions.

4) The relevant theoretical analysis is concerned with models for the description of the limits of ductility in uniform elongation and in post-uniform elongation to fracture. The former modifies the existing theory, based on equal strains, by taking into account the observed strain and stress differences between phases. The latter is based on an instability criterion applicable to porous solids, which includes, as a controlling parameter, the rate of void density increase with strain, at fracture.

Publications:

J. Gurland, "Some Aspects of the Plastic Deformation of Phase Mixtures with Coarse Microstructures," in Yield, Flow and Fracture of Polycrystals, T. N. Baker, Ed., Applied Science Publishers, Ltd., (1983), pp. 51-67.

Analysis of Deformation in Two Phase Alloys

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

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

Sources of Support: DOE

Objectives and Approaches:

This work is part of a research program aimed at understanding strengthening and failure mechanisms in two-phase alloys. The specific aim of this project is to study the effects of geometric and material properties of the phases on internal deformation and macroscopic behavior in the plastic range. A finite element analysis of a regular array of hard inclusions embedded in a continuous soft matrix was carried out which addressed itself mainly to the influence of volume fraction and shape of the hard phase on overall strain hardening behavior.

Research Achievements:

The finite element results clearly show the importance of hard phase geometry on overall strain hardening behavior. When the matrix material is only lightly hardening, deformation in the plastic range takes place mainly in narrow slip regions. Enhanced strain hardening occurs when the hard inclusions interfere with the slip patterns directly traversing the matrix.

Fully Plastic Crack Analyses

Principal Investigators: A. Needleman, Professor, Division of
Engineering
C. F. Shih, Associate Professor, Division of
Engineering

Personnel: B. Glicksman, Graduate Student, Division of Engineering
F.-Z. Li, Graduate Student, Division of Engineering

Sources of Support: DOE

Objectives and Approaches:

Fully plastic crack solutions are an essential ingredient in an approach to developing rational but simplified engineering procedures for assessing the integrity of structural components from a fracture mechanics viewpoint. The aim is to produce relatively accurate formulas useful for engineering design and safety assessment analyses that covers the range from small scale yielding to fully yielded conditions. A key ingredient of the engineering approach is fully plastic solutions to the crack configuration under consideration. We have developed numerical techniques that provide accurate solutions to two dimensional fully plastic crack problems. Our recent work has focussed on analysis procedures that can be used to extend this engineering methodology to three dimensional problems, for example to include technically important problems involving surface flaws in plates and shells.

Research Achievements:

We have developed a reduced integration penalty method for fully plastic crack problems. The computational implementation of the method was outlined for both two and three dimensional crack configurations. We also applied this method to two dimensional plane strain problems of an edge cracked panel subject to both tension and bending. In addition to being of interest in their own right these particular configurations are also of interest in connection with surface flaw problems, when those problems are analyzed using a line spring model. Furthermore, we have given a concise derivation of a volume integral expression for the energy release rate (the key fracture mechanics parameter obtained from the numerical solution) using a virtual work type identity for Eshelby's energy-momentum tensor. An accurate method of computing local values of energy release rate is needed to apply the engineering methodology to three dimensional problems. The resulting integral is identical to the one deLorenzi at General Electric Research Laboratory derived by direct calculation of the energy difference between configurations with slightly different crack lengths. This volume integral method

corresponds to a continuum formulation of the finite element virtual crack extension technique and provides an attractive approach for obtaining pointwise values of the energy release rate along a crack front. Our derivation provides a broader perspective on the virtual crack extension method, showing it to be an application of well founded energy methods of continuum mechanics and not tied to any particular numerical implementation.

Publications:

C. F. Shih and A. Needleman, Fully Plastic Crack Problems-Part I: Solutions by a Penalty Method. J. Appl. Mech., 48-56 (1984).

C. F. Shih and A. Needleman, Fully Plastic Crack Problems-Part II: Application of Consistency Checks. J. Appl. Mech., 57-64 (1984).

F. Z. Li, C. F. Shih and A. Needleman, A Comparison of Methods for Calculating Energy Release Rates. Eng'g. Frac. Mech., in press (1984).

Computational Modelling of Nonlinear Dynamic Fracture

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

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

Sources of Support: MRL, NBS

Objectives and Approaches:

Dynamic fracture results are relevant to technology concerned with fracture control or fracture promotion, e.g., fracture prevention design for load bearing structures (pressure vessels, piping systems, ship hulls), fracture promotion technology for recovery of oil, natural gas and geothermal energy, and to materials development as a means to characterize the fracture resistance of materials under dynamic conditions. Our objective is to develop a finite element method for the analyses of fracture initiation and propagation due to stress wave loading including dynamic crack propagation under steady state conditions. The emphasis is on elastic-viscoplastic (rate dependent) behavior and rate-independent elastic-plastic response is treated as a limiting case. We have developed an explicit algorithm for the finite deformation analysis of elastic-viscoplastic solids. The non-iterative one-step algorithm is obtained by the introduction of the effective tangent stiffness (Peirce, Shih and Needleman) into the so-called alpha method (Hilber, Hughes and Taylor). A totally explicit algorithm based on a centered difference scheme (with lumped mass) and a load vector based on a midstep integration for the constitutive equation is also being considered. The computational method will be employed to analyze and interpret dynamic fracture experiments by Asaro, Clifton, Duffy and Freund. These integrated investigations which include experimental, analytical and computational studies will serve to broaden the framework of nonlinear fracture mechanics to include aspects of high loading rates and rapid crack propagation.

Research Achievements:

The explicit one-step algorithm for transient analysis has been implemented into our finite element code. To test the accuracy and stability of the algorithm, we examined several problems on stress wave propagation in elastic-viscoplastic solids. Our numerical solutions agree in all aspects with the accepted solutions. We have also applied the computational approach to analyze several elastodynamic crack growth problems where exact solutions are available. In this connection, we obtain a line-integral expression

for crack tip energy flux in terms of near tip mechanical fields which is valid for general material response. A variety of seemingly path-independent integrals proposed in recent years can be extracted from this general result by invoking appropriate restrictions on material response and crack tip motion. From the general result, we obtain several domain integral representations for the energy flux by application of the divergence theorem over some part of the fracturing solid. The domain integrals computed during the simulation of crack propagation using the present algorithm are in good agreement with the exact solutions. These comparisons lend confidence to our computational algorithm and the use of domain integrals in dynamic fracture analysis.

We have also undertaken transient analysis of cracked elastic-viscoplastic bodies. While exact solutions are not available to gauge our algorithm and results, the trend of our solutions appears to be in accord with known behavior. Furthermore, results from a particular study into stress wave fracture initiation offers some insight into the accuracy of our computational approach. A deeply notched round bar is subject to a tensile pulse with a wave length which is long compared to the bar diameter. The dynamic J-integral obtained from a domain integral agrees well with values determined from a deep crack formula based on the transmitted load and notch opening displacement. The analysis reveals that for a more accurate measurement of the dynamic J-integral, the notch depth of the round bar specimen employed in the experiments by Duffy et al. should be increased. On the basis of this analysis, the experimental technique has been modified.

Publications:

T. Nakamura, C. F. Shih and L. B. Freund, "Computational Methods Based on an Energy Integral in Dynamic Fracture," to appear in a Special Issue of the International Journal of Fracture.

T. Nakamura, C. F. Shih and L. B. Freund, "Elastic-Plastic Analysis of a Dynamically Loaded Circumferentially Notched Round Bar," to appear in Engineering Fracture Mechanics.

Mechanics and Mechanisms of Fracture and Fatigue

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

Personnel: T. Christman, Undergraduate Student, Div. of Engineering

Sources of Support: MRL

Objectives and Approaches:

The objective of the research program, initiated in December 1983, is to examine the micromechanics of quasi-static and cyclic fracture in metallic materials. Specifically, attention is focused on the effects of microstructure on fracture path and the dependence of fracture toughness and fatigue crack growth rates on crack morphology. Simple micromechanical models are developed to estimate the improvements in crack growth resistance arising from microstructurally-influenced kinked crack growth (crack deflection). Concomitant with this general objective, a large research effort is under way, in collaboration with the Aluminum Company of America, to investigate the effects of compositional and microstructural variations on the micromechanisms of fracture and fatigue in new generation aluminum-lithium alloys. Such alloys are now known to have a strong potential for extensive use in aerospace applications because one weight percent of lithium added to an aluminum alloy reduces the density by approximately 3 percent and increases the elastic modulus by about 6 percent for lithium additions of up to 4 weight percent.

Research Achievements:

1. Novel descriptions have been developed for the effects of crack deflection (kinked crack growth) and closure processes on fatigue crack propagation behavior and are shown to provide a physically realistic rationale for microstructural effects on cyclic crack growth in a number of engineering materials. (See papers 1, 2 and 4 in the enclosed publications list). The relationship between microstructure and crack deflection mechanisms is now being studied in a wide variety of materials including new generation Al-Li alloys, Al-SiC composites and Ni-base superalloys.
2. Paper #2 cited in the enclosed publications list, the preparation of which is partially supported by MRL, represents an up-to-date and comprehensive state-of-the-art description of the role of crack closure in influencing fatigue crack growth resistance.

3. The applications of mechanisms associated with constant amplitude fatigue thresholds to the more realistic variable amplitude crack propagation behavior are established (in paper #1 cited in the enclosed publications list). Such concepts are used to rationalize the apparent anomaly that heat treatments, which promote resistance to constant amplitude fatigue crack propagation, often lead to detrimental fatigue characteristics under variable amplitude cyclic loading conditions.
4. Preliminary experiments have already been completed in the study of the influence of composition and aging treatment on the micromechanics of fracture in lithium-containing aluminum alloys, currently in progress with technical collaboration from Alcoa.
5. The articles cited in the enclosed publications list are part of a series of recent papers for which this principal investigator has been selected as a recipient of the 1985 Champion Mathewson Gold Medal by the Metallurgical Society of AIME.

Publications:

S. Suresh and A. K. Vasudevan, "Application of Fatigue Threshold Concepts to Variable Amplitude Crack Propagation," in Fatigue Crack Growth Threshold Concepts, edited by D. L. Davidson and S. Suresh, The Metallurgical Society of AIME, Warrendale, PA, pp. 361-378, 1984.

S. Suresh and R. O. Ritchie, "Near-Threshold Fatigue Crack Propagation: A Perspective on the Role of Crack Closure," in Fatigue Crack Growth Threshold Concepts, edited by D. L. Davidson and S. Suresh, The Metallurgical Society of AIME, Warrendale, PA, 1984.

D. L. Davidson and S. Suresh, editors, Fatigue Crack Growth Threshold Concepts, Proceedings of an International Symposium, published by The Metallurgical Society of AIME, Warrendale, PA, 1984.

S. Suresh, "Fatigue Crack Deflection and Fracture Surface Contact: Micromechanical Models," Metallurgical Transactions A, Vol. 16A, pg. 249, February, 1985.

rate sensitivity between strain rates of 10^4 sec^{-1} and 10^6 sec^{-1} . Above this transition the flow stress increases more nearly as a small power (say $n \approx 0.2$) of strain rate than as the logarithm of strain rate -- which is the approximate dependence below the transition. These results, which require more extensive investigation, are expected to have important implications for understanding the ductile-brittle transition in the fracture of metals and the localization of shear strain at high strain rates.

STRAIN RATE SENSITIVITY OF ALUMINUM

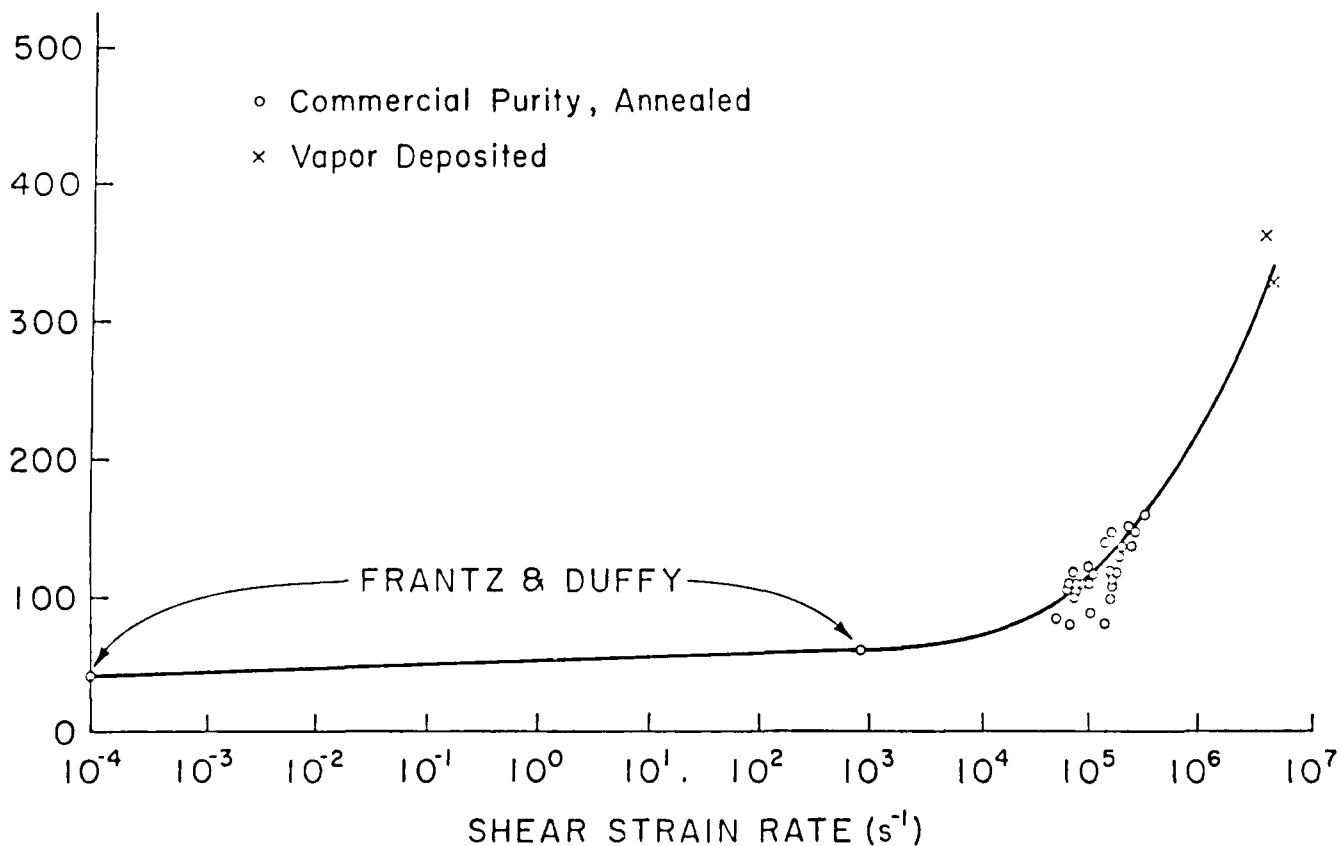


Figure 1

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

Sources of Support: ARO 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} . Until recently the highest strain rates at which flow stresses had been measured under well characterized conditions were approximately 10^3 sec^{-1} to 10^4 sec^{-1} , using Kolsky bar techniques. Then, we introduced the pressure-shear plate impact experiment and obtained the flow stresses of several metals up to strain rates of approximately $2 \times 10^5 \text{ sec}^{-1}$. In this experiment, sustained high strain rates are obtained by sandwiching thin-plate specimens between two, hard, parallel plates which are skewed relative to the direction of approach so that both normal and shear tractions are generated at impact. Shear stresses and nominal shear strain rates are obtained by using a laser interferometer to monitor the elastic waves transmitted through one of the hard plates. From these experiments initial insight was obtained into the plastic response of metals under conditions that are applicable for understanding mechanisms of shear band formation at high strain rates and dynamic, ductile fracture.

Research Achievements:

During the past year the general approach used for pressure-shear impact experiments at shear strain rates of 10^5 sec^{-1} was extended to shear strain rates of 10^7 sec^{-1} . These higher rates were obtained by reducing the specimen thickness from approximately 300 μm . Very thin specimens, 3-20 μm thick, were prepared by vapor deposition. Materials used for the deposition were commercial purity aluminum and high purity iron. The pressure-shear experiments on vapor-deposited specimens were supplemented by pressure-shear experiments on the bulk materials at strain rates of 10^5 sec^{-1} . From these experiments the dependence of flow stress on strain-rate, over 11 decades of strain rate, is shown in Figs. 1 and 2. Because of unknown differences between the plastic response of bulk materials and vapor deposited materials, caution should be used in drawing conclusions from these figures. Nevertheless, there appears to be a marked change in strain

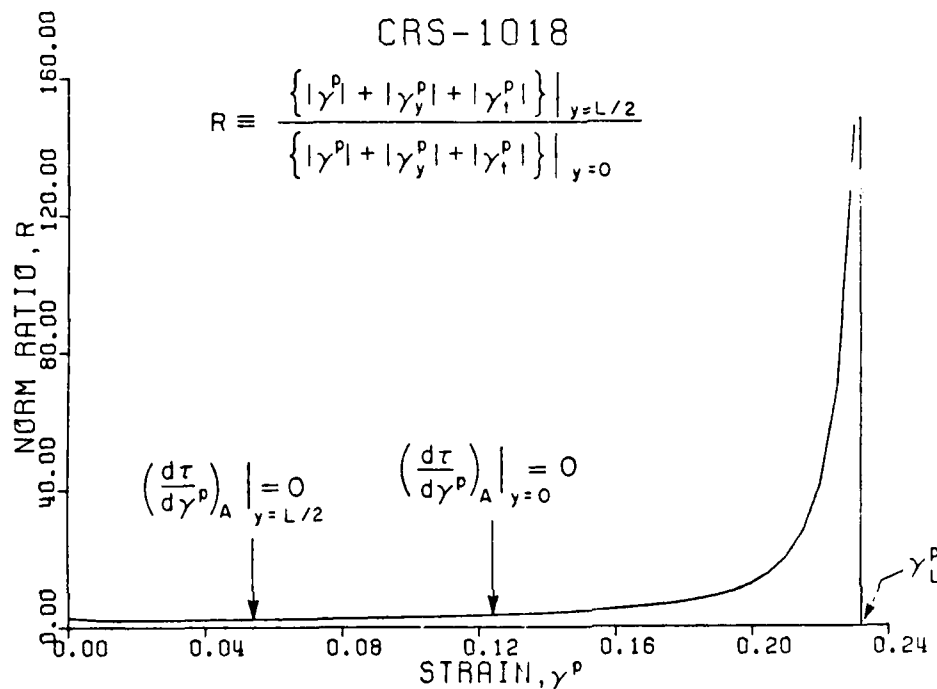


Figure 2: Growth of the Nonuniformity of Plastic Strain.

Publications:

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

nominal strain γ^P . Localization of the strain at the center of the notch is becoming evident at $\gamma^P = 0.2$. Localization increases rapidly for nominal strains greater than 0.2 as shown in Fig. 2. The ordinate in this figure is a measure of the nonuniformity of the plastic strain given by the ratio of the sum of the absolute values of the strain, strain-rate, and strain gradient at the middle of the notch divided by the same quantities evaluated at the ends of the specimen. Strong localization does not occur until after the strain everywhere outside the band has reached the critical strain at which the slope of the adiabatic stress-strain curve becomes zero. Nominal strains at which this critical strain is reached at the midpoint of the notch and at the ends of the specimen are marked on Fig. 2. As the limiting strain γ_L^P is approached the local strain rate outside the notch decreases requiring a strong increase in the strain-rate within the notch in order to maintain the imposed nominal strain rate. Ultimately, the strain-rate within much of the notch begins to decrease and the region of increasing strain rate is only a small, narrowing region near the center. This narrowing of the region of intense shearing is a fundamental feature of the thermoplastic instability.

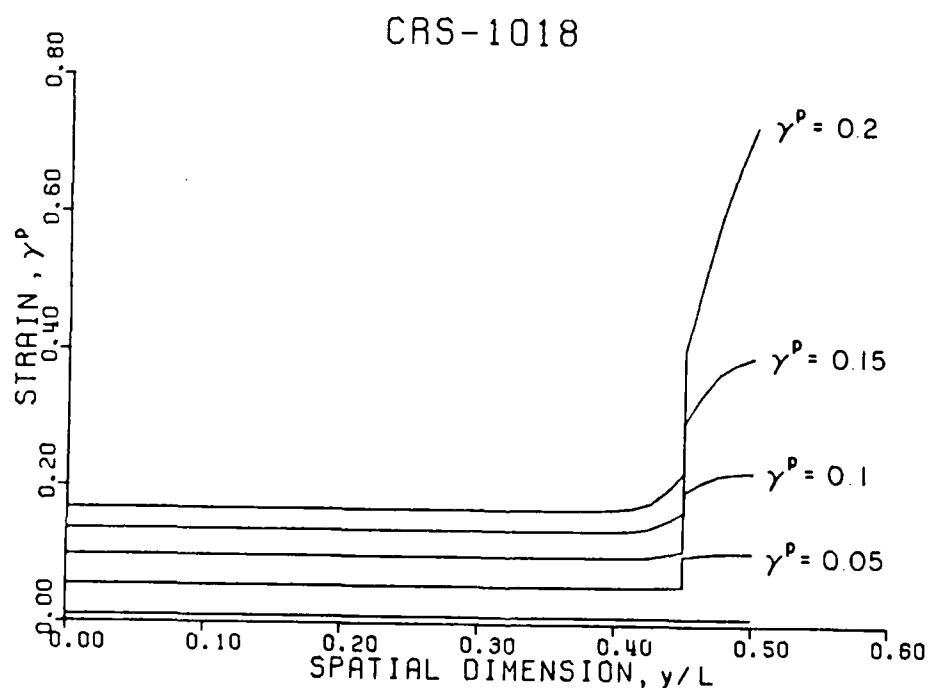


Figure 1: Plastic Strain Profiles.

Shear Band Formation at High Strain Rates

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

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

Sources of Support: ARO and NRL

Objectives and Approaches:

Shear band formation is generally enhanced at high strain rates because the lack of time for heat diffusion allows non-uniform straining to cause non-uniform heating. Thermal softening of the material can subsequently lead to a thermoplastic instability in which the shear strain localizes into narrow bands. Formation of such shear bands results in premature failure either by sliding along the shear bands or by the propagation of cracks initiated within the bands. Thus, the determination of critical conditions for the formation of shear bands is of central importance in predicting failure at high strain rates.

Determination of such critical conditions is being pursued through analytical and numerical investigations of shear band formation in the dynamic torsion experiments conducted by Duffy and co-workers. Previous investigations, including ours, have shown that strain hardening being more than offset by thermal softening is a necessary condition for shear band formation by the thermoplastic instability. The effect of strain-rate sensitivity on shear band formation has not been understood as well.

Research Achievements:

During the past year the influence of strain-rate sensitivity in shear band formation has been addressed through numerical simulation of shear band formation in simple shearing deformations. A principal conclusion of this research is that weak strain-rate sensitivity not only reduces the critical strain at which shear bands form, but effectively allows shear bands to form under conditions for which they would not form in materials which are more strain-rate sensitive, but otherwise identical.

The main features of shear band formation in strain-rate sensitive materials due to thermoplastic instability are illustrated in Figs. 1 and 2. Calculations reported here are for the simulation of dynamic torsion experiments on a cold-rolled steel, AISI 1018. The specimen has length L and a geometric imperfection in the form of a shallow circumferential notch of length $0.1 L$ centered at the mid-length of the specimen. The specimen is deformed at a constant nominal strain rate. Strain distributions for one half of the symmetrical specimen are shown in Fig. 1 at several levels of the

Fracture at Ultra-High Loading Rates

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

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

Sources of Support: ARO and MRL Central Facilities

Objectives and Approaches:

Under impact loading conditions the crack-tip loading rates at pre-existing cracks are much larger than obtained in quasi-static laboratory experiments. Thus, in order to understand fracture conditions in impact-loaded structures, new dynamic fracture experiments are being developed. These experiments, such as the notched bar technique developed by Duffy and co-workers, allow loading rates as high as $\dot{K}_I = 10^6 \text{ MPa m}^{1/2} \text{ s}^{-1}$ where $\dot{K}_I$ is the rate of change of the stress intensity factor for the elastic singularity at the crack-tip. Since still higher loading rates occur in high velocity impact, a plate impact experiment for studying crack initiation at loading rates as high as $\dot{K}_I = 10^8 \text{ MPa m}^{1/2} \text{ s}^{-1}$ is being developed. In this experiment the specimen consists of a circular disc with a mid-plane, prefatigued, edge crack that has propagated halfway across the diameter. 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. Solutions of 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 to be used to compare predictions based on various crack propagation models with the measured motion at the rear surface.

Research Achievements:

Several advances in the development of the technique have been made during the past year. One advance is the accurate location of crack front positions before and after impact by means of focussed ultrasonic waves. This step is essential if quantitative comparisons with theory are to be made since the rear surface motion depends significantly on the surface coordinate perpendicular to the crack front. Other advances include the development of a finite difference code for solving the elastic wave propagation problem, improvement of the technique for generating the fatigue crack (Central Facility for Mechanical Testing) and scanning electron microscope observations of the fracture surfaces (Electron Microscope Facility). Several experiments were conducted on 4340 VAR steel specimens, tempered at 200°C. Cracks advanced from 0.6 - 1.9 mm for tensile pulses with durations of 1.0×10^{-6} sec. The feasibility of the experiment and the existence of sub-microsecond crack propagation at velocities of one-half the elastic shear wave speed or higher have been established. Current research is directed towards relating predicted rear surface motions to those measured. Elastic analysis, even for the time before crack advance occurs does not appear to be adequate. This may be due to plastic flow near the crack tip since the scanning electron microscope observations indicate fully fibrous fracture surfaces at dynamic fracture initiation.

dislocation density. (High etch pit densities near the impact and rear surfaces indicate the effects of surface lapping and asperity contact since the specimen is not isolated by thin fluid layers in the soft recovery experiment.)

Inclusion of dislocation generation at sub-grain boundaries in the prediction of precursor decay make it possible to predict the measured precursor amplitudes at 3 mm and 6 mm from the impact face. Parameters used to characterize dislocation mobility, dislocation density and dislocation generation rates are reasonable values suggested from independent experiments. Thus, it appears that, at least for annealed, high-purity LiF, the longstanding precursor decay anomaly can be resolved by including dislocation generation at sub-grain boundaries. No extraordinary mechanisms, such as supersonic dislocation motion or homogeneous nucleation of dislocations, appear to be necessary.

SHOT 10-84GM (ROOM TEMPERATURE)
 IMPACT VELOCITY: $V_0 = 0.9146$ mm/sec TILT: 0.1 mrad
 NORMAL STRESS: 187 MPa (1.87 kbars) R.S.S: 40 MPa
 SPECIMEN THICKNESS: 3.546 mm

REAR FACE (MOMENTUM TRAP CONTACT)



Publications:

K. S. Kim and R. J. Clifton, "Dislocation Motion in MgO Crystals Under Plate Impact," *J. of Materials Science* 19, 1984, pp. 1428-1438.

P. Blinot, C. Y. Chiem, P. Kumar and R. J. Clifton, "Dislocation Configurations and Velocities in 3% Se-Fe Single Crystals Under Uniaxial Strain Impact," in *Proceedings of the Third Oxford Conference on the Mechanical Properties of Materials at High Rates of Strain*.

Dislocation Dynamics of Plastic Flow

Principal Investigator: R. J. Clifton, Professor,
Division 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. Because of the large differences between the microscopic scale of dislocations and the macroscopic scale of applied stresses, the relationships between quantities applicable at one scale and those applicable at another scale are difficult to establish. Experiments must be well designed to allow modeling of microscale phenomena to be used for predictions that can be compared with macroscale measurements. Two such experiments have been introduced at Brown for relating the dynamics of dislocations to dynamic plastic flow. One of these, a new precursor decay experiment designed to eliminate surface damage effects, consists of plate impact of a multi-layer sandwich in which the specimen surfaces are separated from other solid surfaces by thin fluid layers. The fluid cushions reduce surface damage effects by reducing the need for lapping to obtain flat surfaces and by eliminating damage due to asperity-contact during impact. Initial investigations showed that this reduction of surface damage reduced the decay of the stress amplitude at the leading elastic wavefront (the "precursor") but not sufficiently at distances of several millimeters to account for discrepancies between predicted and measured precursor amplitudes in high-purity single crystals of LiF. The second experiment is one 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.

Research Achievements:

Significant advances in the understanding of dynamic plastic flow have been obtained during the past year from the coordinated use of both of these two types of experiments on high purity LiF crystals. From the soft recovery experiment, subgrain boundaries have been identified as the primary source of mobile dislocations generated by a stress pulse. This observation is evident from Fig. 1 in which dislocations intersecting a plane perpendicular to the impact face are revealed by etch pits. Bands of closely spaced dislocations, emanating from the irregular contours which mark the sub-grain boundaries, were generated by the stress pulse. Except for these bands the dislocation density within subgrains is approximately the same as the initial

We have only partial results so far; these indicate that the answer to this question hinges on a delicate relation involving the observed transformation strain, the symmetry of the parent phase, and the orientation of the loads. Our calculations show that there can be significant differences among apparently similar alloys (or minerals) with regard to whether a certain phase or variant can be obtained by applying loads. Curiously, we find that the nature of the loading device also has an important effect; uniformly applied dead loads will generally produce a different arrangement of phases than a hydrostatic pressure.

Publications:

R. D. James, "A Relation Between the Jump in Temperature Across a Propagating Phase Boundary and the Stability of Solid Phases," *J. Elasticity* 13, (1983) pp. 357-378.

R. D. James, "Theory for the Cold-Drawing of Polymers," in Proceedings of the Workshop on Orienting Polymers, University of Minnesota, March 21-26, 1983, Springer-Verlag.

R. D. James, "On the Stability of Phases," *Int. J. Engng. Sci.*, Vol. 22, No. 8-10, pp. 1193-1197, 1984.

R. D. James, "Phase Transformations and Non-Elliptic Free Energy Functions," in New Perspectives in Thermodynamics (ed. J. Serrin & G. Sell), Springer-Verlag, 1984.

Mechanics of Multiphase Microstructures

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

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

Sources of Support: MRL, NSF

Objectives and Approaches:

The basic objective of this research is to provide a fundamental, predictive understanding of the effect of stress on phase transformations in solids. The main focus is presently on displacive transformations in metals (shape memory materials), minerals (quartz, calcite), ceramics (partially stabilized ZrO_2) and the high temperature superconductor V_3Si . We are particularly interested in the effect of non-hydrostatic stress on transformation temperatures and on the arrangement of the phases. These displacive transformations are primarily responsible for the fracture resistance of some ceramics, the shape memory effect, the remarkable damping characteristics of some martensitic alloys, the substantial attenuation of large amplitude stress waves in rock and occurrence of ferro-electric solids. Nonhydrostatic stress plays an essential role in most of these effects. We are modelling these transformations using highly nonconvex (and nonelliptic) free energy functions which account for three dimensional and nonhomogeneous changes of shape.

Research Achievements:

We have based our studies on a free energy function which accounts for three dimensional changes of shape in a transforming body. The free energy is a function of the local change of shape and the temperature. Properties of this function reflect the underlying symmetry of the parent and product phases, and the idea that there is an exchange of stability from parent to product phase as the body is cooled through the transformation temperature. This free energy function turns out to be highly nonconvex; each of its minima corresponds to a phase which is stable under zero stress. Mechanical considerations imply that the free energy, expressed as a function of the deformation gradient and temperature, has an infinite number of minima in all cases. We have calculated a variety of stable arrangements involving the parent phase and symmetry-related variants of the product phase. These consist of two or more variants arranged coherently in needle-like regions which protrude into the parent phase; they agree well with observed arrangements in alloys with mobile phase boundaries. We have also studied dead-loaded states at temperatures below the transformation temperature, with particular attention to the question of whether the parent phase alone can be recovered by applying some system of dead loads to a transformed body.

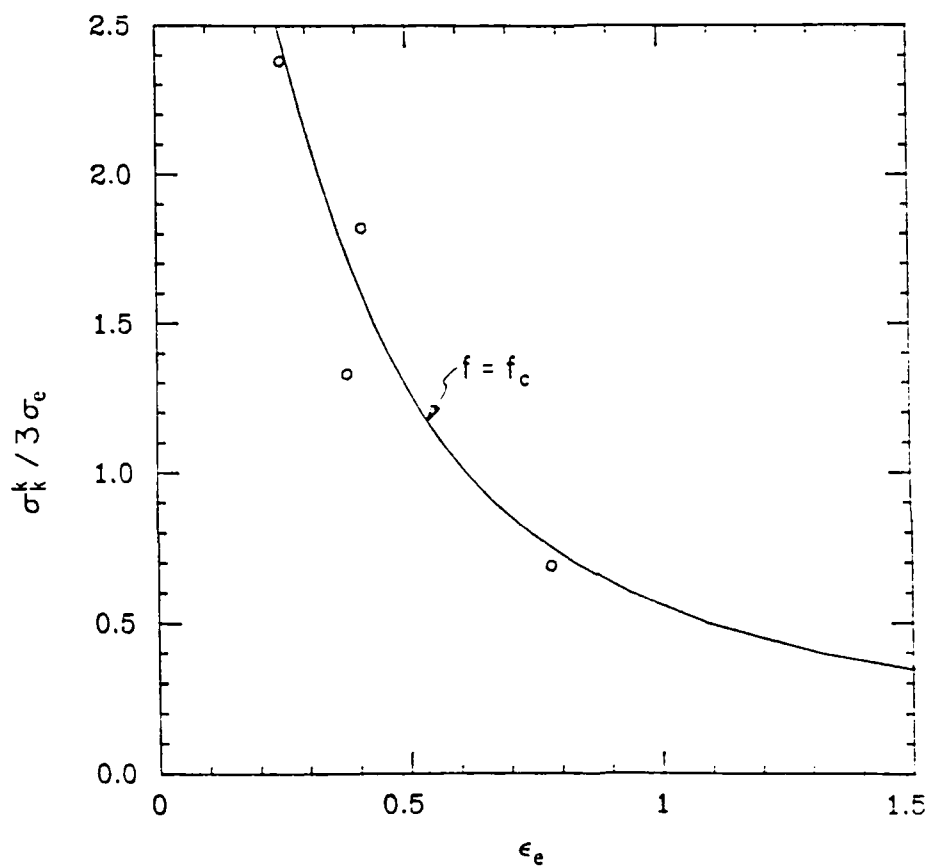


Figure 1

Publications:

V. Tvergaard and A. Needleman, Analysis of the Cup-Cone Fracture in a Round Tensile Bar. *Acta Metall.*, 32, 157-169 (1984).

A. Needleman, The Numerical Analysis of Necking Instabilities. *Unification of Finite Element Methods*, (ed. by H. Kardestuncer), North-Holland Elsevier, 249-273 (1984).

A. Needleman and V. Tvergaard, An Analysis of Ductile Rupture in Notched Bars. *J. Mech. Phys. Solids*, 32, 461-490 (1984).

Analysis of Ductile Rupture

Principal Investigator: A. Needleman, Professor, Division of Engineering

Personnel: V. Tvergaard, Visiting Professor Division of Engineering

Sources of Support: NSF, ARO

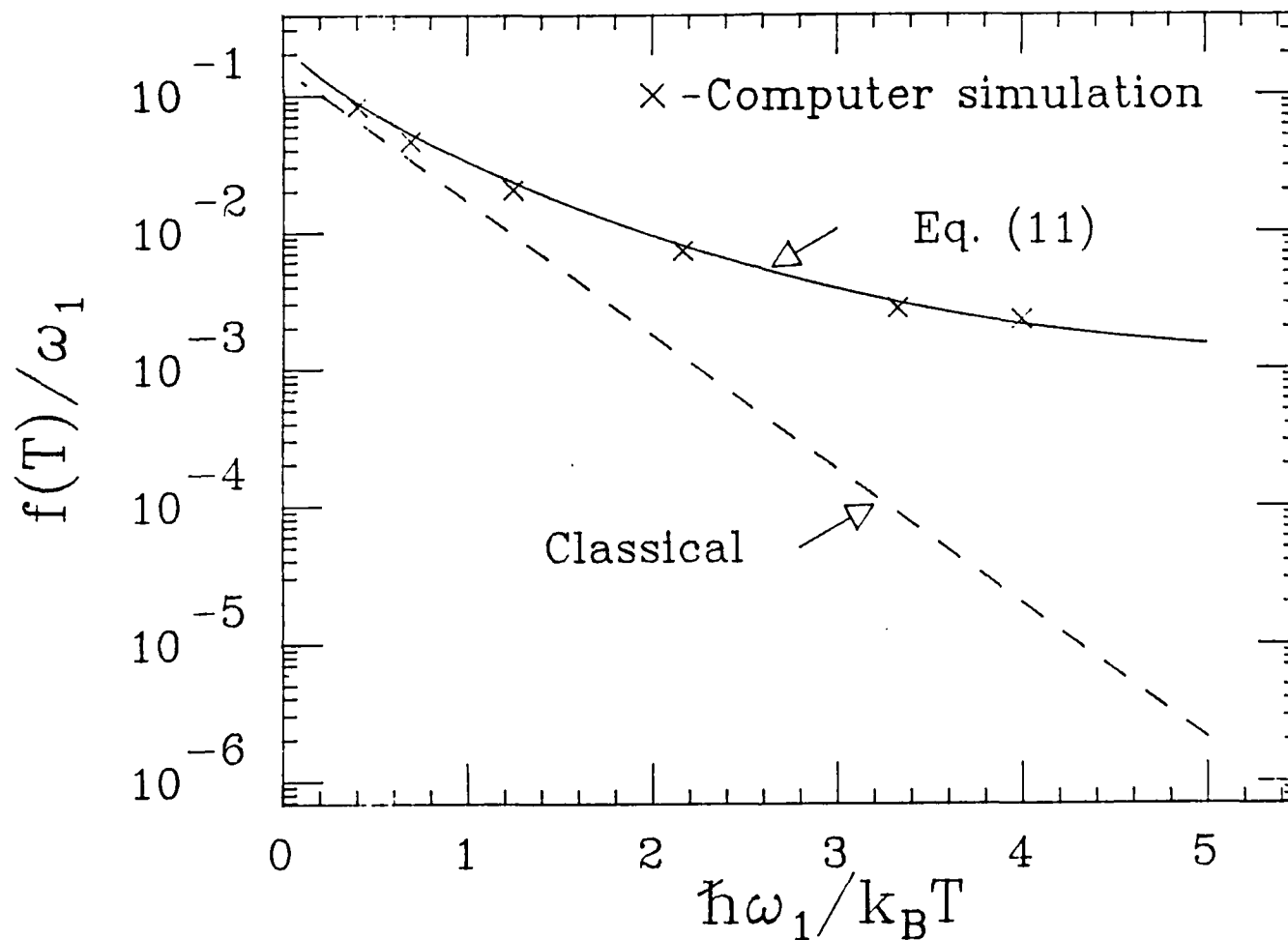
Objectives and Approaches:

Ductile rupture in structural metals mainly occurs by the nucleation of micro-voids at second phase particles and the subsequent growth of neighboring micro-voids to coalescence. Our present work is aimed at providing a bridge between continuum descriptions of stress and deformation fields and microstructural processes of ductile rupture. We have analyzed notched and un-notched tensile specimens using a constitutive relation which represents the micro-voids in terms of a single parameter, the void volume fraction. The material description incorporates the complete loss of stress carrying capacity due to the coalescence of micro-void voids - no separate failure criterion is imposed. These studies build on our development of finite element methods for analyzing highly localized deformation modes and material failure. Using this framework, we have carried out the first analysis of the common tensile test that exhibits the cup-cone fracture so typically observed in ductile metals.

Research Achievements:

We have studied the influence of stress state on ductile failure by analyzing the onset of ductile failure in blunt notched and sharp notched round and plane strain (thick) specimens. One issue addressed in our analysis stems from the fact that experimental studies, reported in the literature, have inferred local failure conditions from calculations based on classical plasticity theory. Since classical plasticity theory cannot account for stress redistributions due to progressive micro-rupture, an important question is the extent to which stress and deformation fields based on using classical plasticity theory are representative of local conditions at the failure site. Another issue concerns the role of shear band localizations in setting local conditions at fracture initiation in these notched bar specimens.

One of our results is shown in Fig. 1, where the strain to fracture initiation is plotted against stress triaxiality (hydrostatic tension divided by Mises effective stress). The solid curve shows the failure locus for a special proportional triaxiality history which serves as a reference curve. The points are values taken from the failure site in our finite element calculations for four specimen geometries and using a particular set of material constants. The difference between the reference curve and the points is a consequence of the history dependence of the fracture strain. Our calculations showed a systematic trend in the deviation from a history independent failure curve due to the effect of shear localization. While the initial interpretation of the experiments had led to the suggestion of a history independent fracture strain curve, our calculations and an experimental study reported in the literature at about the same time, both showed that such a concept is appropriate only for nearly proportional histories.



Publications:

K. F. Lau and J. H. Weiner, "Computer Simulation of Temperature Effects on Tunneling Rates," Chemical Physics Letters (in press).

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 works on the rates of potential barrier crossings are based on classical mechanics. However, it is recognized that quantum mechanical effects may become significant at low temperature levels and for light atoms. For example, experimental evidence for quantum-mechanical tunneling effects on the viscoelastic relaxation in poly(methyl methacrylate) has been reported.

Direct comparison of theory with experiment is difficult for this process because the tunneling rates are very sensitively dependent on the potential barrier details and these cannot yet be determined from first principles. 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:

In order to treat a case with known potential, we are currently studying temperature effects on this process 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.

Short-term tunneling rates, those which apply during a single classical period of oscillation of the tunneling particle in its well, have been determined by computer simulation of this model. We find that they agree well with the predictions of a previously-developed theory¹. An example is shown in the accompanying figure in which $f(T)$ is the tunneling rate at temperature T , ω_1 is the classical circular frequency and Eq. (11) refers to the theory of Ref. 1; the dashed line is the classical Arrhenius relation which would apply in the absence of any quantum effects.

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

SHEAR STRAIN RATE SENSITIVITY OF HIGH PURITY IRON (Fe 99.99 %)

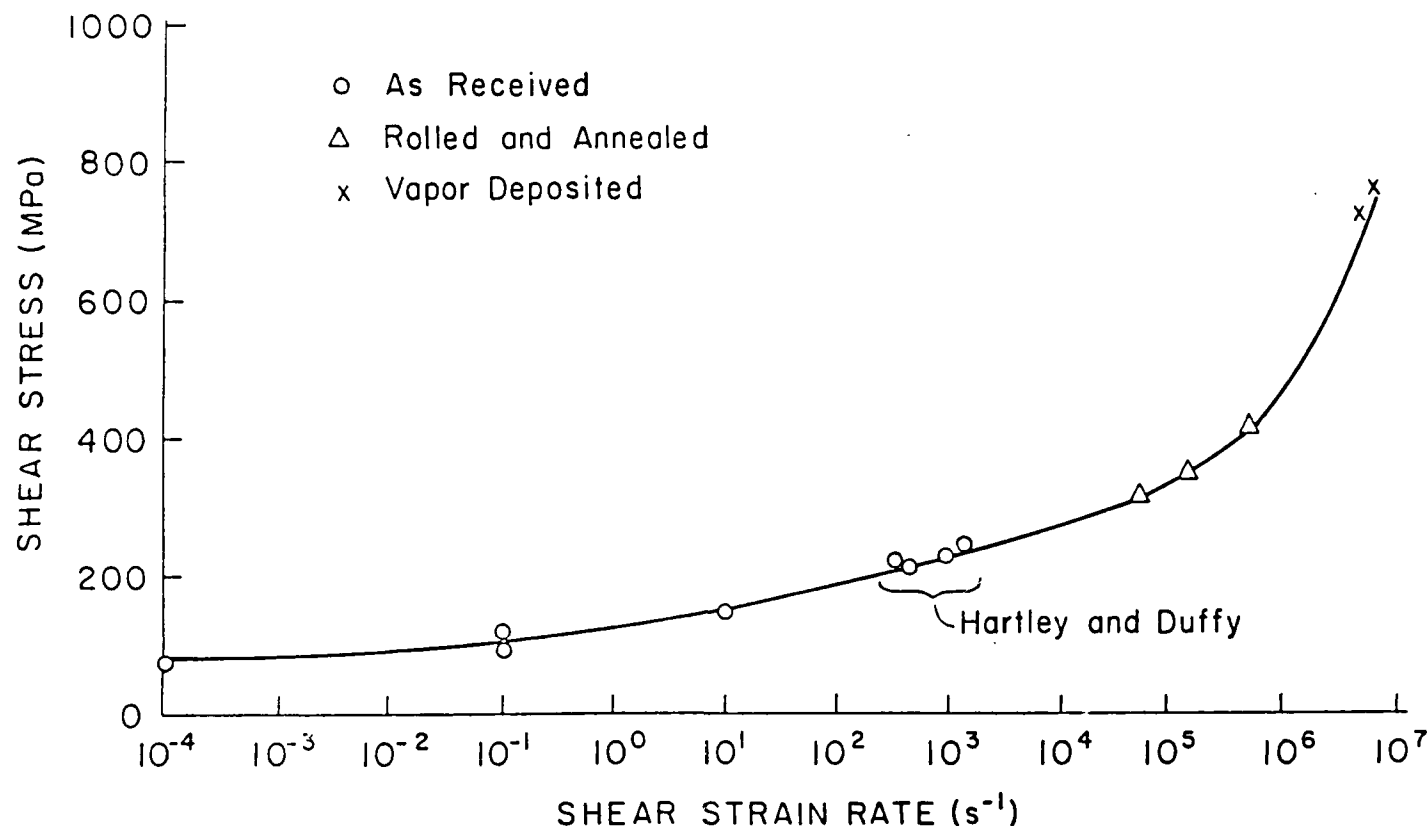


Figure 2

Publications:

R. J. Clifton, "Pressure-Shear Impact and the Dynamic Plastic Response of Metals," in Proceedings of the American Physical Society 1983 Topical Conference on Shock Waves in Condensed Matter, (ed. by J. R. Asay, G. K. Straub, and R. A. Graham).

R. J. Clifton, "Dynamic Plasticity," J. of Appl. Mechs. Vol. 105, 50th Anniversary Issue, 1983, pp. 941-952.

R. J. Clifton, "Experiments and the Micromechanics of Viscoplasticity, in Plasticity Today: Modeling, methods and Applications, (ed. by A. Sawczuk and G. Bianchi), Applied Science Publishers.

Ultrasonic Studies of Plastic Deformation of Metallic Glasses

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

Personnel: A. Hikata, Professor (Research), Applied Mathematics
W. Myung, Visiting Associate Professor
Physics Department

Sources of Support: MRL

Objectives and Approaches:

The aim of this research is to clarify the mechanisms of plastic deformation in metallic glasses, with special emphasis on the stress-strain behavior and its relation to microscopic processes. To this end, attenuation changes of ultrasonic waves are studied during plastic straining of samples deformed in compression. These measurements are carried out as a function of strain rate and "ageing" under constant stress. For comparison, and as a reference for the results on metallic glasses, crystalline samples of the same shape and composition, obtained by annealing glass samples above T_g (the glass transition temperature) were studied by the same methods. All the deformation experiments were conducted on the alloy PdSiCu, at room temperature.

Research Achievements:

A prominent feature of plastic deformation of many metallic glasses are "serrations" in the stress-strain relation. These serrations display considerable uniformity of height, spacing and shape. Moreover, the average value of stress remains essentially constant over the range of serrated stress-strain curves (i.e., there is no strain hardening, on average). These characteristics indicate that each serration is the result of an event, or set of events, that occur in an environment which is similar to that at the start of the preceding serrations. Our ultrasonic studies further strengthen this view, as each serration is accompanied by an increase in ultrasonic attenuation, $\Delta\alpha$. α remains unchanged during the rising stress portion of each serration. On the other hand, a rapid increase in α is associated with the stress decrease (of each serration). Thus, the attenuation increases with every serration and there is no evidence that it diminishes (i.e., that "recovery" of attenuation occurs) on the time scale of the experiment. These observations are interpreted as evidence that each serration is due to the formation of internal features that cause (elastic) scattering of the ultrasonic waves, which, in turn, appears as an increase in attenuation.

A possible model for this behavior is as follows. The increasing stress part of each serration corresponds to the accumulation of free volume regions in the bulk of the deformed specimen, along a plane (or

"slab") of high resolved shear stress (approximately at 45° to the longitudinal stress direction). When the maximum stress is reached, a shear band is formed, resulting in a stress relaxation (decreasing stress portion of the serration). Such a shear band contains locally a higher concentration of free volume than the average concentration in the bulk and results in a region of acoustic impedance that is different from that of the surrounds. This, in turn, results in scattering of the ultrasonic wave and a rapid increase in the attenuation. The process is repeated for each serration.

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:

A new feature of rapid deformation, not anticipated by existing models or theories, has been observed in this work, as follows. Under certain conditions of prior deformation in aluminum and of irradiation in lithium fluoride double peaks in ultrasonic attenuation were found, corresponding in time to the rise and fall portions of the stress pulse. The shape and duration of these peaks closely resembles those of the time derivatives of the stress pulse. Possible interpretations of this novel result in terms of instabilities of the dislocation network during rapid stress changes, or of dislocation pile-up formation and release are being examined.

Correlation of Microstructure and Micromechanics of Fracture with Macroscopic Fracture Toughness

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

Personnel: S. Lee, Graduate Student, Division of Engineering

Sources of Support: DOE

Objectives and Approaches:

Our studies, supported by the Department of Energy, over the past five years on the fracture behavior of quenched and tempered ultrahigh strength steels have been concerned with experimental observations of microfracture processes at crack tips and with correlating these processes with macroscopic fracture. To this end an experimental program has been carried out on a series of steels with compositions corresponding to AISI 4140 and 4340 steels which has explored the effects of heat treatment and microstructure on ductility and fracture toughness. Our most recent studies have focused on two special steels of 4340 composition, one of which was deoxidized by aluminum-silicon additions and the other by titanium-aluminum additions. These two chemistries led to steels with very good overall mechanical properties at room temperature ($\sim 20^\circ\text{C}$) and allowed an interesting study to be made of the effects of grain refinement on ductility and fracture. The ultimate aim of this project is to provide a comprehensive understanding of how heat treatment and microstructure influence the micromechanics of fracture and thereby affect macroscopic ductility and fracture.

Our early work was concerned with the correlation of simple high temperature quench and temper heat treatments, and microstructure, with uniaxial and plane strain ductility as well as plane strain fracture toughness. The high temperature heat treatments consisted of high austenitizing temperatures which ranged from the usual 870°C , to 1200°C . More recent work has focused on the effects of tempering and on developing models for the initiation of fracture.

One of the major differences between the aluminum and titanium-aluminum killed steels was the degree of grain refinement achieved. Figure 1 illustrates this by showing the prior austenite grain size versus austenitizing temperature over the austenitizing temperature range of 870°C to 1200°C . The general effect of the higher heat treatment temperatures is to increase grain size and decrease both uniaxial and plane strain tensile ductilities. For the microstructures produced by simple quench and temper heat treatments, with tempering done at 200°C , the higher heat treatment temperatures led to an increase in plane strain fracture toughness as illustrated in Fig. 2. This difference in the trends of ductility and fracture toughness has been reported on in earlier literature and was studied in some detail in the present work.

Again for the microstructures produced by simple quench and temper heat treatments a significant microstructural difference was found to be the spacing between undissolved carbides and other second phase particles. For example, for the aluminum killed steel the spacings between the larger alloy and iron carbides (i.e. with diameters greater than $0.1\text{ }\mu\text{m}$) were found to be approximately $3.3\text{ }\mu\text{m}$ and $7.5\text{ }\mu\text{m}$ when the steels were austenitized at 870°C and in the range 1150°C to 1200°C respectively. It was further shown, through careful fractographic study, that these particles control the process of microfracture at the tips of pre-fatigue cracks in the plane strain fracture toughness specimens. In the cases studied, fracture initiated by void growth at the submicron particles and by the coalescence of these voids with the blunting crack tip. In some cases voids grew essentially on the crack line and coalesced with the crack tip by direct impingement and in other cases void growth took place off the crack line and coalescence involved localized deformation between the void and the crack tip.

Following these observations a fracture model was developed which correlated the measured particle spacings with ductility and the finite strain field of a blunted crack. By using this model a consistent picture was obtained for the variation in fracture toughness with microstructure. The results of this study indicated that a major influence of high temperature heat treatments was to produce a more effective solution treatment and finer dispersion of void initiating particles. To explore this further a second set of tests was carried out on specimens given step quench and double austenitizing heat treatments. The purpose of these was to see if the benefits of using high temperature heat treatments for solution treatment could be combined with the grain refining of subsequent lower temperature heat treatment. The results showed this approach to be partially successful in that increases in K_{IC} were obtained in fine grain steels that also showed good ductility properties.

More recent work has explored the effects of tempering on ductility and fracture toughness. Preliminary studies have been carried out on the aluminum and titanium killed steels used in our previous studies of the effects of austenitizing temperature on fracture toughness. In these studies we have measured plane strain toughness and Charpy impact energy for specimens tempered in the range 200°C to 500°C . When the two steels are austenitized at 870°C they display very shallow energy, or toughness, troughs. However, when austenitized at 1150°C the K_{IC} values display pronounced troughs in the temperature range 200°C to 350°C . We are currently in the process of characterizing these tempered microstructures and making detailed studies of the fracture mechanisms.

In order to obtain a more quantitative understanding of the micromechanics of fracture initiation, we have initiated a series of tests aimed at measuring the critical strains required for void

formation at fine particles. Axisymmetric tensile tests to various strain levels, up to fracture, are conducted on initially smooth and circumferentially notched specimens. The specimens are then examined at high magnification in the SEM and quantitative stereology performed on the generated void distribution. The heat treatments to be examined will include both high and low austenitizing temperatures and step quench treatments. Our results, obtained by interpreting the measured variations in fracture toughness using the model developed by Lee, Majno and Asaro, have suggested that the critical strains required to initiate voids at submicron size particles is affected by heat treatment. The experiments proposed here are designed to quantify the effects of heat treatment on these critical strains. An important part of this continuing effort will be the development of more accurate mechanistically based models for crack tip rupture which account for the large and localized strains which occur at the crack tip. We have been able to explain a good part of our observations on the basis of rather simple phenomenological models which account for the observed mechanisms of void initiation and growth. These models are, however, based on crack tip patterns which do not usually correspond to those observed. More accurate analyses of crack tip deformation which can account for the influence of material constitutive behavior and crack tip geometry and, in particular, provide a description of localized deformation modes (e.g., crack tip shear bands) are required in order to formulate models which can describe the micromechanics of microfracturing. This is the aim of the research described in the section on crack tip mechanics.

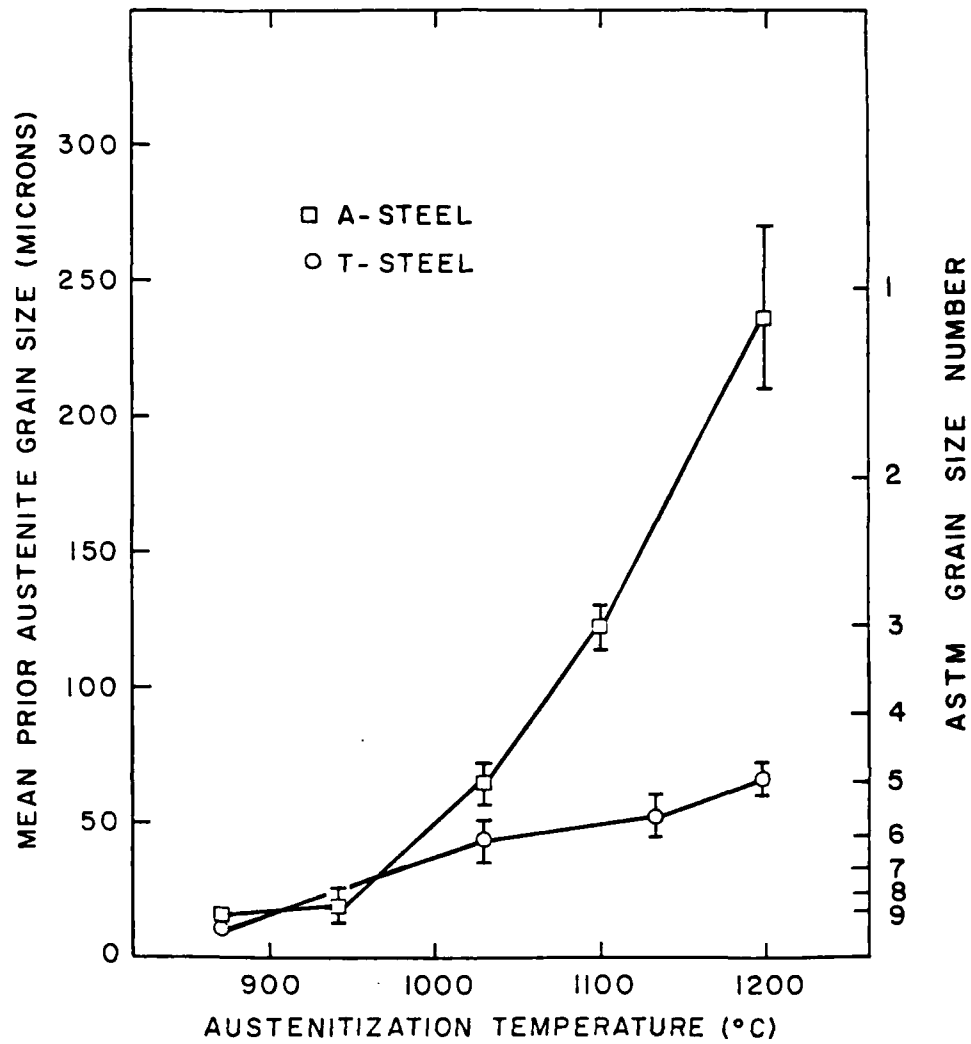


Figure 1: Prior austenite grain size vs. austenitizing temperature.

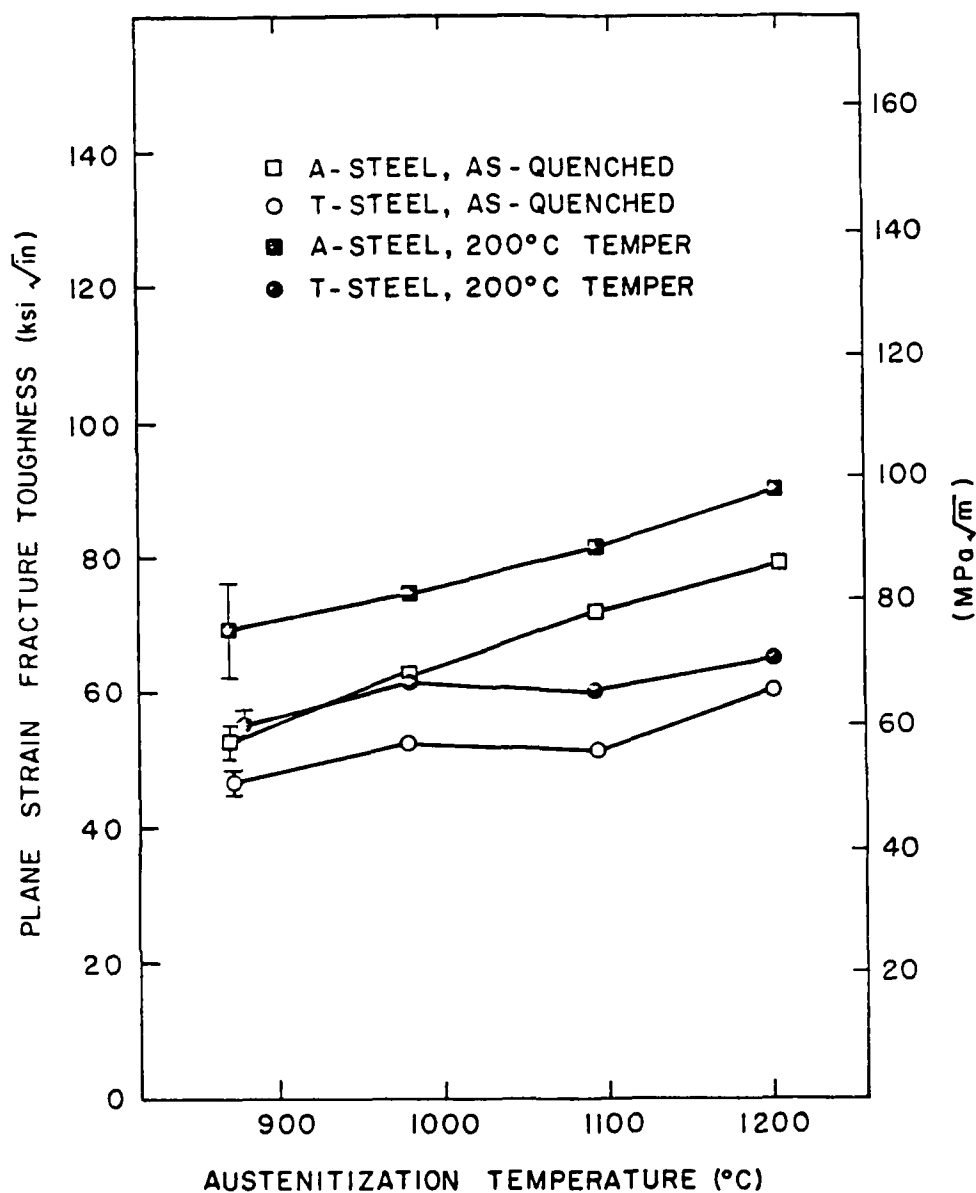


Figure 2: Plane strain fracture toughness vs. austenitizing temperature.

Publications:

S. Lee, L. Majno and R. J. Asaro, "Correlations of Microstructure and Fracture Toughness in 4340 Steel," to appear in Metallurgical Transactions A, 1985.

Finite Element Studies of Crack Tip Deformation Fields

Principal Investigators: R. J. Asaro, Professor, Div. of Engineering
A. Needleman, Professor, Div. of Engineering

Personnel: V. Tvergaard, Visiting Professor, Div. of Engineering
R. Becker, Graduate Student, Division of Engineering

Support: DOE

Objectives and Approaches:

Analyses of crack tip and deformation fields, especially those that account for the finite strains and geometry changes associated with blunting, are necessary in order to relate the micromechanics of fracture to macroscopic toughness. For assessing fractures in high strength materials, for example in steels with yield strengths larger than 200 ksi but with plane strain fracture toughness K_{IC} values less than 100 ksi in. it is necessary to accurately describe the deformation field within a zone at the crack tip that extends over a distance of only one to two times the crack tip opening displacement. In particular, this is the case for the steels described in the section dealing with Correlation of Microstructure and Micromechanics of Fracture with Macroscopic Fracture Toughness. Crack growth initiates by microfracture within this zone, often by a process of void development and growth at second phase particles. Furthermore, observations such as those described in the above mentioned section, have shown that the deformation field at a crack tip is typically highly nonuniform and involves intensely localized shearing within bands. The large strains within these shear bands, which are often accompanied by large triaxial stresses, serve to both initiate and coalesce voids. Thus what is required to construct accurate micromechanical models of fracture which can be used to predict macroscopic toughness are descriptions of crack tip plasticity that account for the development of localized deformation modes. In the present work we have extended some calculations performed by Needleman and Tvergaard in which rate independent constitutive laws that incorporate yield vertex structure, and the associated stress-strain path dependent material stiffness, were implemented. These "corner" theories are known to lead to predictions of localized shearing in plane strain tensile states that are in good qualitative agreement with experiment. The specific plan of the present research is to explore the effects of notch and crack tip geometry, and of constitutive description, on stress and deformation patterns at blunting crack and notch tips. Two constitutive laws have been used to date along with two crack and notch tip geometries. In addition an experimental program has also been initiated to directly observe the deformation patterns and notch tip profiles that develop in the 4340 steels described. The geometries and material properties used in our calculations are matched to those of the steels studied experimentally. Some example results are described below.

Figures 1a and 1b show the specimen geometry and finite element grid used. In the calculations and experiments two notch radii were used, viz. $R_0 = 0.005$ in. and $R_0 = 0.002$ in. However, in what follows only results for notches with a radius of 0.005 in. are presented. Figures 2a and 2b show deformed notch profiles predicted using a finite strain version of J_2 flow theory and the finite strain version of " J_2 corner theory" proposed by Christoffersen and Hutchinson (J. Mech. Phys. Solids, 1979). When the initial notch profile is smooth, as is the present case shown in Fig. 1b, J_2 flow theory predicts a smooth deformed notch profile. Consistent with this is the smooth contours of principal strain shown in Fig. 3a. On the other hand, the corner theory predicts the development of localized deformation modes as evidenced by the notch tip "sharpening" seen in Fig. 3b; Fig. 2b shows contours of principal logarithmic strain for this case which corresponds to a nearly identical state of loading (as measured by the far-field value of the J integral) to the case shown in Figs. 2a and 3a. Figure 2b shows that the corner theory predicts much more intense straining at the notch. At the notch tip itself the plastic strains are nearly 50 percent larger than predicted from J_2 flow theory. Another representation of this difference in plastic strain level is given in Figs. 4a and 4b which show the von Mises effective plastic strain plotted on the crack line. Here again the much larger strains at the notch tip predicted by the corner theory are evident.

Calculations at blunted crack tips (with $R_0 = 0.002$ in.) show similar trends except that the more intense straining predicted by the corner theory appears to take on the character of shear bands extending from a point just removed from the crack line and on the crack surface to the crack line. Again the peak strains are much larger for the corner theory calculations and do not occur on the crack line itself. Instead they occur at points within the shear bands.

Some implications of these results regarding fracture initiation have been discussed by Becker, Needleman, Tvergaard and Asaro. For one thing they noted that models such as that proposed by Rice and Johnson generally tend to overestimate toughness. These models are partly phenomenological and generally rely on notions such as a critical fracture strain or critical fracture stress. Becker et al. have used the same basic idea along with the new results including those outlined here on crack tip fields and found that the larger strains predicted in the regions of intensely localized straining do indeed lead to reduced estimates of toughness. When applied to the experimental studies of fracture toughness in 4340 steels by Lee and Asaro (described in the section on Correlation of Microstructure with Fracture Toughness) this new modelling yields a quite favorable description for how fracture toughness changed with microstructure and ductility. Both the experimental and theoretical aspects of this work are continuing. Our most recent experimental studies have included

measurements of the plastic strains at which voids initiate in the various microstructures produced by quench and temper heat treatments in 4340 steels. We are also planning to extend our calculations to include descriptions of void growth and thus directly link the calculations to our experimental studies of fracture toughness.

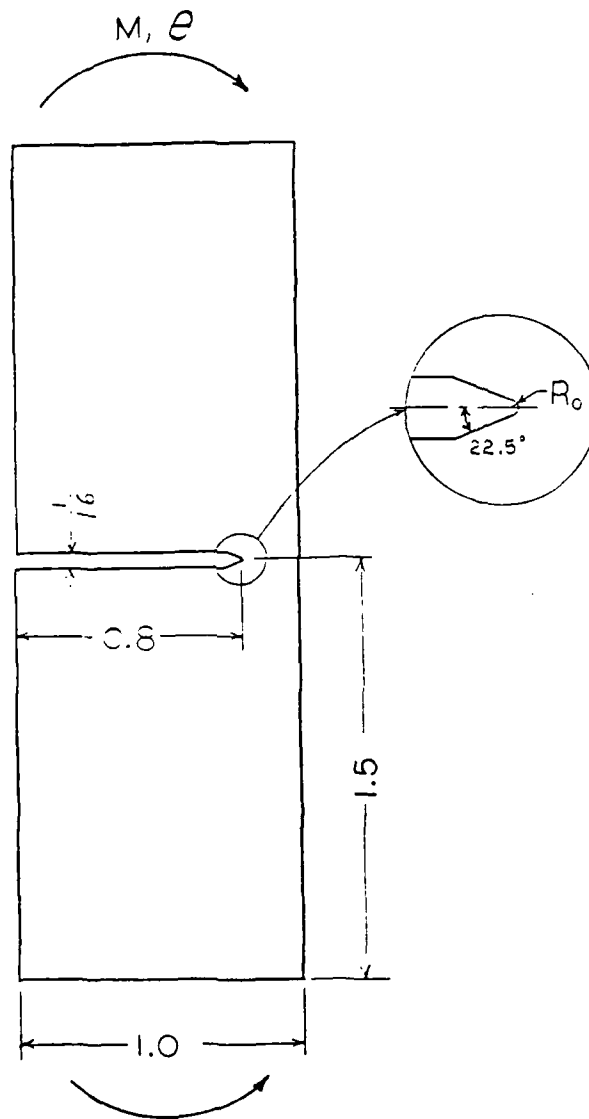


Figure 1a: Specimen geometry used in the finite element calculations described here and in the experimental studies of notch tip blunting.

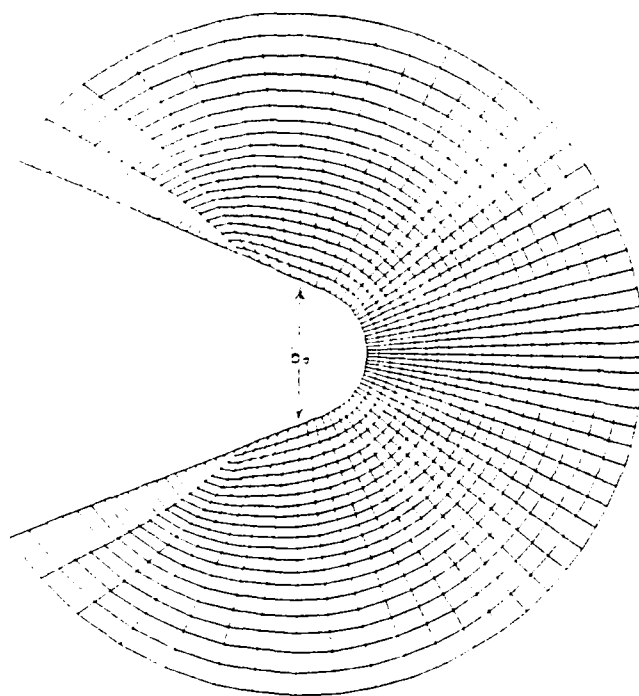


Figure 1b: Finite element grid used for the calculations described here.

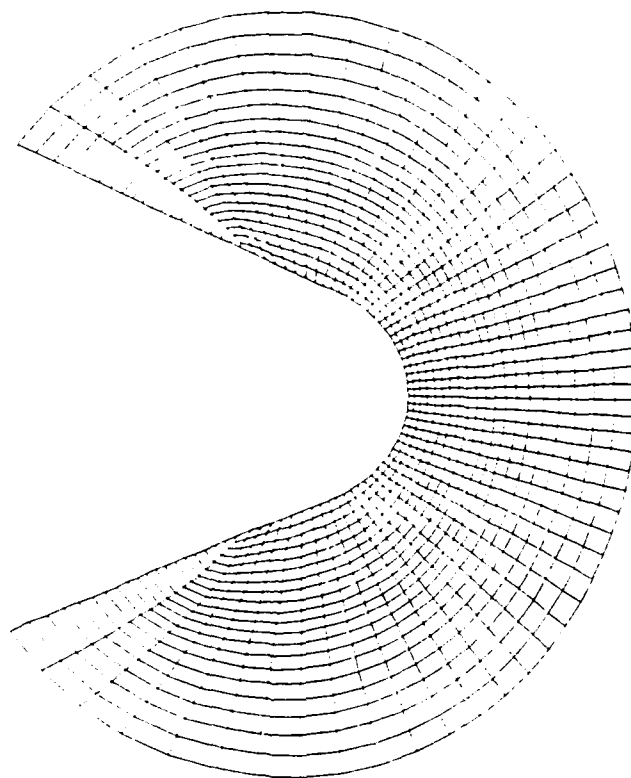


Figure 2a: Deformed finite element grid as predicted by " J_2 flow" theory. This calculation corresponds to an applied J integral loading level of $J/b_0 = 1.2$ where b_0 is defined in Fig. 1b.

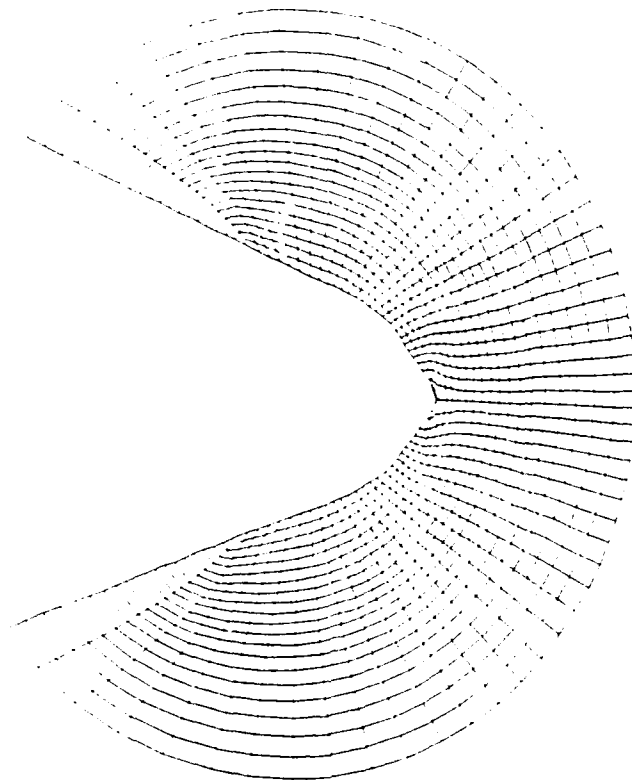
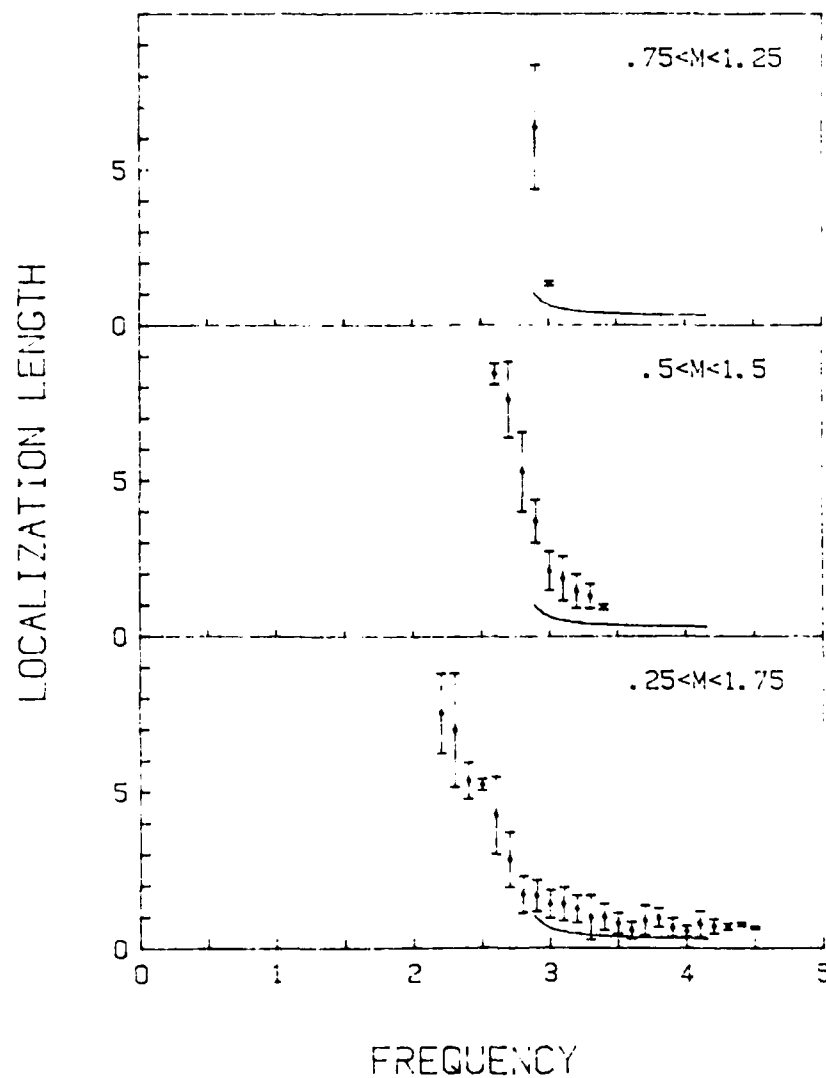


Figure 2b: Deformed finite element grid as predicted by "J₂-corner" theory. This calculation corresponds to an applied J-integral level of $J/b_0 = 1.24$. Note the flattening of the blunted notch tip as compared to that in Fig. 2a.



Publications:

M. L. Williams and H. J. Maris, "Numerical Study of Phonon Localization in Disordered Systems," Physical Review, April 1985.

Phonon Transport in Dielectric Glasses

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

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

Sources of Support: MRL

Objectives and Approaches:

The thermal conductivity K of a dielectric glass is very different from that of the corresponding crystalline material. K_{glass} is smaller than K_{crystal} by a factor which is typically 10 at room temperature, and which increases to $\sim 10^4$ at 10 K. In qualitative terms, the fact the $K_{\text{crystal}} > K_{\text{glass}}$ is not unexpected. The structural disorder in the glass will cause extra scattering of the thermal phonons. This gives a reduced phonon mean-free path Λ and a lower thermal conductivity. Many theoretical models of phonon scattering have been proposed but, although they all predict $K_{\text{glass}} < K_{\text{crystal}}$, the theoretical value for the thermal conductivity is always considerably larger than the experimental value. We believe that this discrepancy may occur because some of the phonons in the glass are localized excitations, and hence do not contribute to the thermal conductivity. Consequently we are investigating theoretically phonons localized in simple models of glasses.

Research Achievements:

We have used a new computer algorithm to investigate phonons in glasses and other disordered systems. Our method can find the normal mode vibrational patterns (phonon eigenfunctions) in any dimensionality. Even on a small computer one can handle systems made up of a fairly large number of particles. The algorithm can also be used to find the density of phonon states. We have used the method to study several disordered systems. They include systems in which the atoms have random mass, systems for which the vibration is pinned at a set of random points, and systems which have topological defects (missing atoms and dislocations). As an example of our results we show the localization length for phonons in a system where the mass of each atom is random within a certain range.

This experiment suggests that it may be possible to study the propagation of coherent acoustic phonons in thin films. The acoustic phonons have frequencies up to approximately 14 GHz. As a first step we have used our method to measure the sound velocity in a 6000 angstrom film of α -SiO₂ which was deposited on top of the α -As₂Te₃ film. We believe that our method will make possible acoustic measurements in a range of amorphous materials which can only be prepared as thin films.

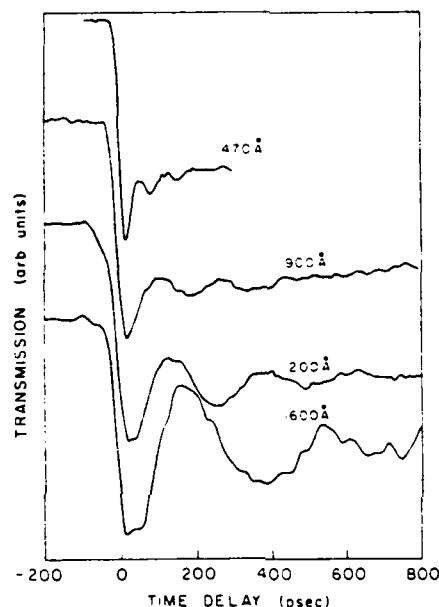


FIG 1 Photoinduced transmission in α -As₂Te₃ for films of different thickness at room temperature.

Publications:

C. Thomsen, J. Strait, Z. Vardeny, H. J. Maris and J. Tauc, "Coherent Phonon Generation and Detection by Picosecond Light Pulses," *Phys. Rev. Lett.*, **53**, 991 (1984).

C. Thomsen, J. Strait, Z. Vardeny, J. Tauc and J. J. Hauser, "Picosecond Optical Generation and Detection of Phonon Waves in α -As₂Te₃," in *Ultrafast Phenomena IV* (ed. by D. H. Auston and K. B. Eisenthal), Springer Series in Chemical Physics, Vol. 38, (Berlin, 1984), p. 133.

C. Thomsen, J. Strait, Z. Vardeny, J. Tauc and J. J. Hauser, "Picosecond Optical Excitation of Phonons in Amorphous As₂Te₃," *American Institute of Physics Conference Proceedings*, No. **120**, 102 (1984).

Research Results

Optical Studies of Amorphous Semiconductors by Picosecond Pump and Probe Spectroscopy

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

Personnel: J. Strait, Graduate Student, Physics Department
C. Thomsen, Graduate Student, Physics Department
Z. Vardeny, Visiting Associate Professor, Division of
Engineering

Sources of Support: MRL

Objectives and Approaches:

We are studying the optical properties of amorphous semiconductors. In our method a "pump" pulse of duration of approximately one picosecond is absorbed in the sample. This pulse causes transient changes in the optical properties of the sample. These changes are detected by measurements of the reflection and transmission coefficients for a small "probe" pulse. The probe pulse can be delayed relative to the pump pulse by a time ranging from approximately one picosecond up to several nanoseconds. There are several mechanisms which can give rise to the induced changes in optical properties. The photons in the pump pulse have energy greater than the band gap, and when the pump pulse is absorbed electrons and holes are produced. This change in the number of carriers produces a change in optical absorption. After generation, the electrons and holes relax to the bandgap, or to defect states within the gap. This process gives a further change in absorption. The electrons emit phonons during this relaxation process, and these phonons can also alter the optical properties. Our overall aim in this research is to measure the induced changes in reflection and transmission, and use these changes to extract information about electron and phonon relaxation processes in amorphous semiconductors.

Research Achievements:

We have studied photo-induced changes in thin films of $a\text{-As}_2\text{Te}_3$ and cis-polyacetylene. We have discovered a remarkable oscillatory change in transmission and reflectance. The oscillation period is in the range 100-350 picoseconds, and increases linearly with the film thickness (Fig. 1). We have shown that these oscillations are caused by the following mechanism. The pump pulse is absorbed in a thin layer (approximately 300 angstroms) near the surface of the film which is in contact with the substrate. The electrons, holes, and phonons produced in this layer set up a stress. This stress propagates into the film as a coherent acoustic phonon. When it reaches the free surface it is reflected, and at the time that it returns to the substrate surface it causes the observed change in reflectance.

SECTION 2 INORGANIC GLASSES

Introduction

This section reports advances made by the Inorganic Glass Group in elucidating the nature of disordered systems experimentally and theoretically. In this program the relationships between projects with collaborative or related objectives has proven particularly productive. For example, the optical studies of amorphous semiconductors by picosecond pump and probe spectroscopy carried out by Tauc and Maris lead to the discovery of remarkable photo-induced oscillatory changes in transmission and reflectance of thin films. The phenomena were shown to be associated with this generation of coherent acoustic phonons. They can be used to measure the sound velocity and attenuation in thin films. This was demonstrated in an initial study on $\alpha\text{-SiO}_2$ deposited in $\alpha\text{-As}_2\text{Te}_3$, which opens the way for acoustic measurements in amorphous materials which can be prepared only as thin films.

The structure and behavior of ionic and other oxide glasses are actively studied in the Group by Bray, Cole and Risen. Extensive spectroscopic work by NMR, infrared, Raman and Time Domain Reflectance methods at frequencies ranging from 10^6 to 10^{14}Hz were carried out on related series of glasses. Ion motion and structural relaxation in lithium borate glasses were studied by Bray using NMR and by Cole and Risen using Raman, IR and TDR. Of particular interest is the discovery of the fact that the application of an electric field has a disordering effect on fast ionic conducting glasses based on the lithium borate system. Together with Bray's elucidation of the structures formed in a range of borate-based glasses, and the effects of thermal and preparative history in complex ionic oxide glasses, as well as model studies on ionomers, the work reported here introduces new insights into the formation and nature of oxide glasses.

Theoretical studies on disordered systems have been carried out by Houghton, Kosterlitz, Maris and Pelcovits on a variety of systems. Several of the materials, on which investigations are reported were selected for the insights they give about the way effects of disorder are manifested. This approach was particularly valuable in Houghton's and Pelcovits' studies of Ising models with random fields, and in Pelcovits' results on the structure factor in amorphous magnets. Other theoretical results, particularly those of Houghton on ultrasonic attenuation and related phenomena in bulk and thin film metals and those of Maris on phonon transport in dielectric glasses, are of importance in connection with the experimental results of Elbaum and Tauc, respectively.

Elbaum's experiments on the low temperature properties of amorphous solids produced important insight into the nature of the tunneling entity in amorphous and crystalline metal alloys. By showing that the same value of the two-level tunneling system density can be obtained for both a metallic glass and a crystalline phase prepared from it, the range of possible explanations for the TLS phenomena was severely constrained.

W. M. Risen, Jr., Coordinator

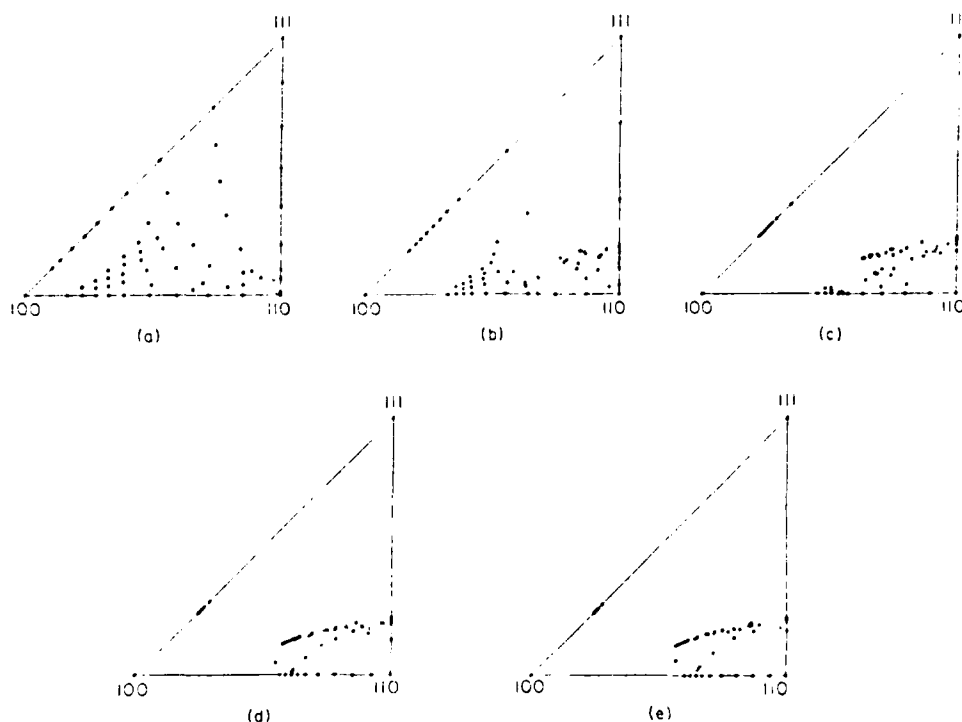


Figure 2: "Inverse pole figure" for the compression axis following axisymmetric compression to five different strains. The single crystal strain hardening displays strong latent hardening; the effective strain levels are a) $\epsilon_e = 0.23$, b) $\epsilon_e = 0.50$, c) $\epsilon_e = 0.89$, d) $\epsilon_e = 1.25$ and e) $\epsilon_e = 1.38$. The effect of strong latent hardening is to suppress the stronger 110 texture component evident in Figure 1.

Publications:

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

R. J. Asaro, "Crystal Plasticity," J. Appl. Mech. **50**, 1, 1983.

R. J. Asaro and A. Needleman, Flow Localization in Strain Hardening Crystalline Solids, Scripta Metall., **18**, 429-435, 1984.

R. J. Asaro and A. Needleman, Texture Development and Strain Hardening in Rate Dependent Polycrystals, Acta Metall., to appear as an Overview Article.

Research Achievements:

We have developed a polycrystal model based on the constitutive framework for crystalline slip that we developed and used to solve complete boundary value problems in single crystal plasticity, Peirce et al., *Acta Metall.*, 1983. Our analysis of polycrystal behavior uses a simple model similar to that introduced by Taylor in 1938, but differs from Taylor's in several important respects. Our rate dependent constitutive framework overcomes the well known problem of non-uniqueness in the choice of "active" slip systems and therefore in the prediction of lattice rotations that is inherent in the rate independent theory. In addition strains are not all prescribed a priori but instead boundary value problems for homogeneous deformations are simulated incrementally using, at each increment, the current averaged polycrystal constitutive laws. In this way textures and constitutive response can be calculated following complex stress and strain histories without introducing ad hoc and possibly erroneous assumptions concerning the incremental strains and trends toward texture development. Furthermore, since our analyses of texture development are carried out within a comprehensive constitutive framework which has been used to solve full boundary value problems for non-homogeneously deforming crystals, we can use this constitutive formulation to analyze limitations of models of polycrystal response that presume homogeneously deforming grains, such as Taylor and self-consistent averaging methods. Indeed a series of large strain finite element calculations have been undertaken for model bi-crystals for the express purpose of studying the effects of grain boundaries on the development of localized deformation modes, LeMonds, M.S. Thesis 1983.

Because, in our formulation, the slipping rates on all systems within each grain are unique, we believe our results to be the first unambiguous derivation of texture development and strain hardening from single crystal properties. For example, we obtained results on the path dependence of strain hardening in various deformation histories, we have analysed the development of vertex like reductions in stiffness to a change in loading path, which are often crucial to the development of shear localization and we have obtained the first quantitative results on the effect of latent hardening on texture development. Figures 1 and 2 show inverse pole figures for the compression axis in axisymmetric compression. The difference in behavior is because in Fig. 1 the latent hardening is isotropic, while in Fig. 2 the latent hardening is stronger than isotropic, which has the effect of suppressing the strong $\{110\}$ texture component.

Since we do not prescribe strains a priori and since we have a complete constitutive formulation, we are able to analyze complex non-proportional deformation histories. As an example, we have carried out an analysis of the effects of texture on sheet necking, within the framework of the "long wavelength" approximation. Our results show a strong effect of texture on ductility and we plan to pursue further detailed investigations of this topic.

Polycrystal Plasticity

Principal Investigators: R. J. Asaro, Professor, Div. of Engineering
A. Needleman, Professor, Div. of Engineering

Personnel: J. LeMonds, Graduate Research Assistant, Div. of Engrg.
S. Harren, Graduate Research Assistant, Div. of Engrg.

Sources of Support: MRL, NSF

Objectives and Approaches:

The overall aim of our work is to develop rate dependent polycrystalline constitutive models that rigorously account for arbitrarily large strains and rotations of both the material and the lattice within individual grains. More specific aims include the prediction of deformation induced textures and anisotropy following arbitrary stress and strain histories, including those characterized by abrupt changes in path, and to evaluate the stress-strain response of polycrystalline aggregates that accompany such histories. Input to the models include descriptions of single crystal strain hardening and latent hardening, along with material strain rate sensitivity, on the individual slip system level. One application of the models is to provide accurate physically based large strain constitutive laws to interpret experiments on large strain metal strain hardening behavior. Another is to provide a basis for formulating phenomenological constitutive laws for the solution of boundary value problems in metal plasticity.

An accurate description of metal strain hardening under conditions of arbitrary strain and stress states, and following arbitrary strain and stress histories, is necessary to assess the plastic response of metals deformed well into the plastic range. Common examples of processes where material strain hardening and rate dependence play important roles in determining response include large strain structural deformations in beams or pipes, the complex finite non-proportional strain histories imposed during metal forming, metal cutting and penetration, along with finite deformations that occur on a scale of a few multiples of grain size such as at crack tips or between voids or microcracks. In all these examples experiment has shown that the deformations inevitably become highly non-uniform and localized where the localization can play the role of a "failure mode." Our previous finite deformation analyses of particular cases, e.g. Tvergaard, Needleman and Lo, J. Mech. Phys. Solids, 1981, has shown that details of the multi-axial constitutive description are pivotal in determining the qualitative patterns of deformation and their development with subsequent deformation. Yet despite this understood necessity for accurate large strain constitutive models what is available at present are mainly extensions of rather simple small strain (and mostly isotropic) models into the finite strain range.

rotations and a "textural" or "geometric softening" of the slip systems that are most active in the bands.

Finite deformation and localized deformation in crystalline materials has been studied theoretically by both analytical and numerical techniques. Finite element calculations of full boundary value problems for single crystals subjected to tension have been carried out using rate independent and rate dependent constitutive theories. These calculations represent the first complete solutions to full boundary value problems for single crystals, in particular for processes involving highly nonuniform and localized flow ever attempted. The calculations followed the crystal through necking and localized shearing and describe the full kinematics of nonuniform lattice rotations and anisotropic elastic-plastic response.

It was found that the nonuniform deformation associated with necking causes nonuniform lattice rotations that, in turn, cause selected slip systems to be aligned in orientations more favorable to slip, i.e. to become "geometrically softened." This is a nonuniform process and causes localized deformation to occur preferentially on those slip systems leading eventually to bands of localized deformation. These calculations, carried out by D. Peirce, R. Asaro and A. Needleman are in very good agreement with our experimental studies and provide a rather comprehensive framework for correlating the effects of material properties, including strain hardening, latent hardening, and strain rate sensitivity along with effects of stress and strain state on the localization process.

Publications:

L. L. Lisiecki, D. Q. Nelson and R. J. Asaro, *Scripta Metall.*, 16, 441 (1982).

T. Goto and R. J. Asaro, in proceedings of the conference on 50th Anniversary of the Discovery of Dislocations, ASME, ed. X. Markenscoff, 1984.

Experimental Studies of Crystal Plasticity and Localized Plastic Flow

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

Personnel: Y. W. Chang, D. Q. Nelson, L. L. Lisiecki and T. Goto,
Former Graduate Students, Division of Engineering
H. Deve, Graduate Student, Division of Engineering

Sources of Support: NSF Metallurgy Section, MRL

Objectives and Approaches:

Over the past 5 years an experimental program concerned with the study of strain localization in ductile single crystals has been conducted. In particular, the process of shear band development in single crystals of precipitation hardened alloys of Al-Cu and Cu-Co and in pure single phase Cu has been studied. The experiments documented the conditions of stress, temperature, and strain hardening levels at which shear bands formed. In addition the kinematics, including crystallography, of shear band development were studied. These experiments have been extended to single crystals of BCC Fe-Ti-Mn alloys.

Our experimental studies of FCC single crystals have shown that the formation of shear bands in tension is an inherent feature of the deformation process which is linked to the crystallography of slip and to the nonuniform lattice rotations that accompany nonuniform deformation modes such as necking. Localized shearing occurred in all cases while the materials were strain hardening and without evidence for prior microfractures-in-progress. The general pattern for macroscopically localized shearing was for necking to precede localized shearing; shear bands formed just after a maximum load was achieved and led to ductile fracture through void initiation and coalescence.

There were several important differences in the way that shear bands developed in the age hardened alloys than in the single phase crystals. The alloy crystals were characterized by higher strength and lower strain hardening rates. This difference seemed to have the effect of causing the shear bands to form more abruptly with strain and to be more sharply delineated. The single phase crystals of Cu underwent much deeper necking prior to shear band formation and the shear bands were initially diffuse and gradually sharpened with continued straining. An additional difference was that in the Al-Cu alloys shear bands were preceded by heavy bands of concentrated slip, i.e. "coarse slip bands." These bands are aligned with one of the active slip systems and appear to serve as imperfections within which macroscopic shearing develops. Macroscopic shear bands are, on the other hand, characteristically misaligned with the octahedral slip systems; the lattice kinematics of these shear bands involve lattice

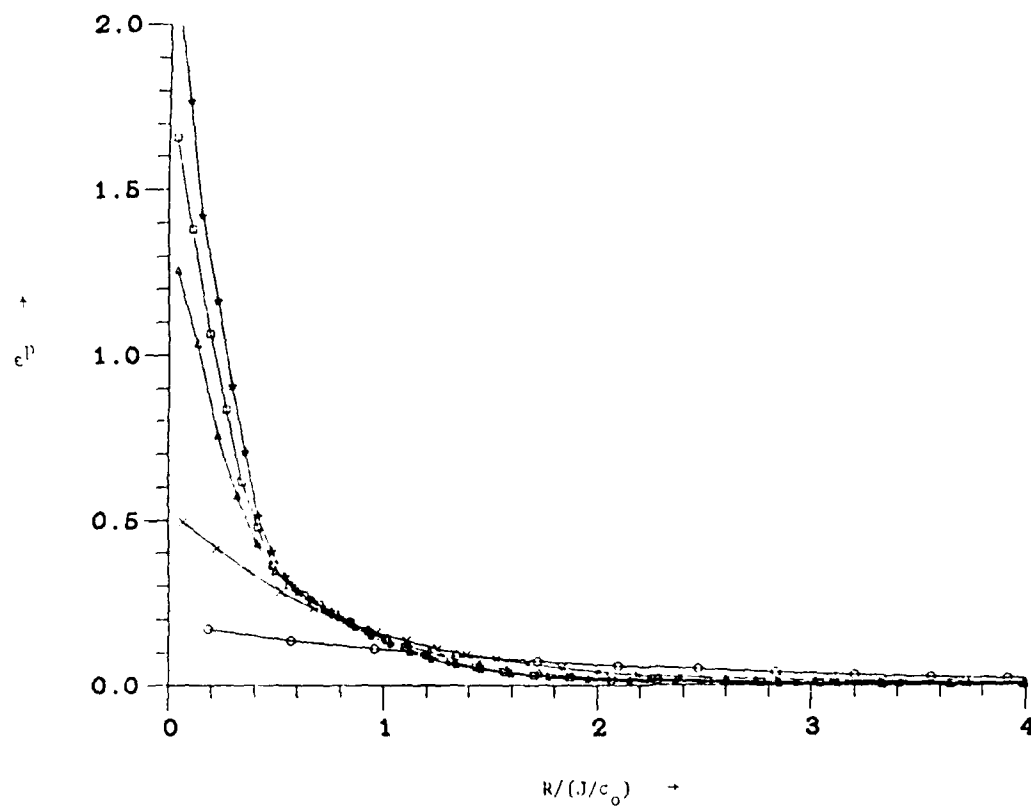


Figure 4b: Plots of Von-Mises effective plastic strain versus normalized distance for various applied J-integral load levels. The symbols correspond to the following: 0-0.210, X-0.536, Δ -0.882, $\bullet$ -1.03 and *-1.24.

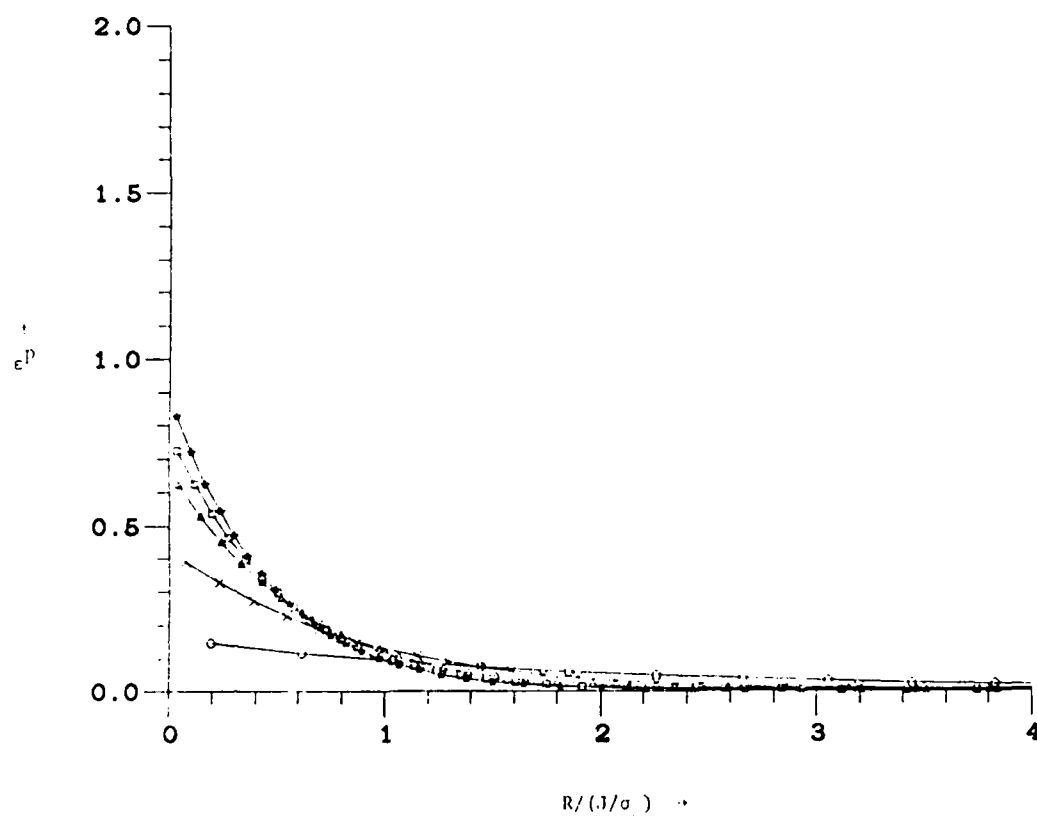


Figure 4a: Plots of Von-Mises effective plastic strain versus normalized distance ahead on the notch tip and on the crack line; symbols correspond to the following values of J/b_0 : 0-0.195, X-0.518, Δ -0.859, $\square$ -1.03, and *-1.20.



Figure 3b: Contours of principal logarithmic strain as predicted by "J₂-corner" theory. This calculation corresponds to an applied J-integral value of 1.24 as in Fig. 2b.

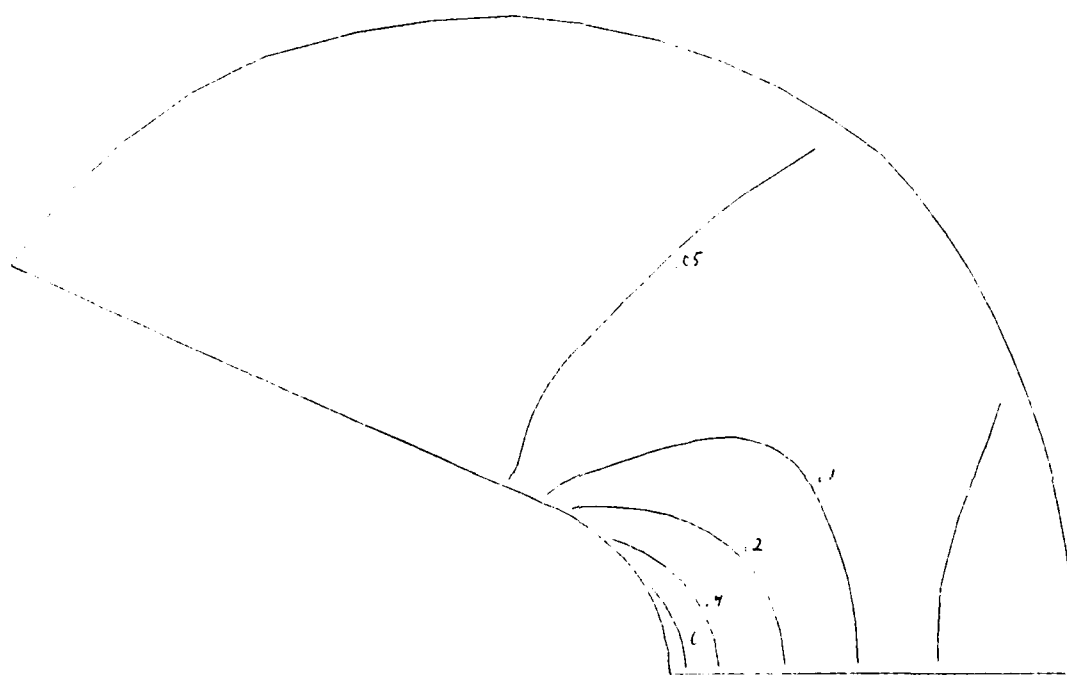


Figure 3a: Contours of principal logarithmic strain predicted by " J_2 -flow" theory. This calculation corresponds to an applied J-integral level of 1.20 as in Fig. 2a.

Disordered Systems Theory

Principal Investigator: A. Houghton, Professor, Physics Department

Personnel: A. Khurana, Research Associate, Materials Research
Laboratory
F. Seco, Graduate Student, Physics Department

Sources 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 attempt to understand (i) the propagation and attenuation of phonons in very dirty metallic systems, both in the bulk and in thin films. (ii) the competition between localization and superconductivity in these systems.

(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. At this time the lower critical dimension is still uncertain, the nature of the phase boundary between paramagnetic and ferromagnetic phases and the critical exponents unknown. We have shown how one can study critical phenomena in this system by means of high temperature series: preliminary results, reported below, give us confidence that the approach will allow us to answer the questions posed above. Work continues to generate longer series so that we may probe deeper into the asymptotic critical regime.

(2) Ultrasonic Attenuation, Superconductivity and Anderson Localization

There is very little detailed work aimed at understanding the effects of strong disorder, $\sigma \approx \sigma_{\min}$, on phonon propagation and sound attenuation in either bulk metals or thin films. Our starting point will be to study the effect of Anderson Localization and Coulomb interaction on the ultrasonic attenuation in the 'weak localization' limit. The long term aim will be to probe the 'strong localization regime.' Significant corrections to simple conventional theory are expected due to anomalous diffusion of the conduction electrons when $\sigma \approx \sigma_{\min}$. Knowing the attenuation coefficients, and hence the electron phonon coupling the effect of disorder on the superconducting transition temperature can be predicted. Preliminary results show that the attenuation of both longitudinal and transverse waves is enhanced:

$$\alpha = \alpha_0 \left[1 - \frac{3\sqrt{6}}{4(k_F \ell)} 2\sqrt{\tau} \right]; \text{ in 3D.}$$

and

$$\alpha = \alpha_0 \left[1 - \frac{1}{\pi k_f \ell} \ln |\omega \tau| \right]; \text{ in 2D}$$

Research Achievements:

A formalism has been developed whereby high temperature series for the random field Ising model on a d-dimensional hypercubic lattice can be obtained by partitioning vertices of the diagrams for the pure Ising series. High temperature series for the susceptibility in which order by order the disorder is treated exactly have been analysed by Dlog Pade methods. In d=3 there is clear evidence of a phase transition, in contradiction to the $d \rightarrow d-2$ rule, with an exponent γ which crosses over from a value of 1.24 in the pure limit to 1.40 as the disorder increases. In two dimensions we find no region in which γ is independent of disorder indicating that d=2 is likely to be the lower critical dimension. In higher dimension, $4 < d < 6$, our results are consistent with the $d \rightarrow d-2$ rule once corrections to scaling are taken into account. The crossover exponent in d=3 is found to be 1.23 in excellent agreement with the predicted value. The location of the tricritical point is given for various dimensions, in d=3,4 good agreement with Monte Carlo renormalization group calculations is found.

Publications:

A. Khurana, F. J. Seco and A. Houghton, "The Ising Model in a Quenched Random Field: Critical Exponents in 3 Dimensions from High Temperature Series," Phys. Rev. Letters 54, 357 (1985).

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

Theoretical Studies of Amorphous Magnets and Charge Density Wave Systems

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

Personnel: S. Heinekamp, Graduate Student, Physics Department
B. Minchau, Graduate Student, Physics Department
P. De, Graduate Student, Physics Department
J. Smith, Undergraduate Student, Physics Department

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

Objectives and Approaches:

Our objective is to understand the large-scale behavior of disordered systems such as amorphous magnets and impure charge density wave systems. These are challenging systems because of their lack of translational symmetry. The loss of this symmetry leads to unusual physical behavior and requires the development and use of new theoretical techniques. We are using techniques such as the replica method, renormalization group scaling, and exact solutions of one-dimensional systems to elucidate the behavior of these systems. The questions of interest to us in the study of amorphous magnets include: a) the destruction of magnetic ordering by the disorder; b) the dynamical behavior of the magnets; and c) the properties of the structure factor which is measured by neutron scattering. The description of charge density wave systems bears some mathematical resemblance to that of amorphous magnets. Of particular interest are quasi-one-dimensional metals with charge density wave states in the presence of impurities. We have been using exact solutions of one-dimensional models of this system in an attempt to understand the unusual electrical transport properties. In all of the above work, we hope to develop techniques and physical insight which might be useful in understanding a much larger class of disordered systems.

Research Achievements:

We have solved the one-dimensional XY magnet in a random field in the limit of infinitely strong fields with dilution p . This solution indicates that while the model is disordered, there are nevertheless two different regimes corresponding to weak and strong (our solution) pinning. We have calculated various correlation functions and the susceptibility and examined the dynamical behavior. Upon application of an external magnetic field, the magnetization relaxes to zero in a fashion identical to the Kohlrausch law for ordinary glass. This behavior arises here due to the spectrum of relaxation times in the system.

A related calculation concerns the AC conductivity of a one-dimensional charge density wave system interacting with impurities. We solved exactly for the conductivity in the limit of infinite pinning and found that as a function of the frequency of the external field, the conductivity behaves as a devil's staircase function. Qualitative features of this behavior are expected to persist even when the pinning is large but finite.

We have also studied the Ising model in a random field in an attempt to understand the discrepancy between previous theoretical analyses. Of particular interest is the value of the spatial dimensionality below which the random field destroys magnetic order. We constructed a rigorous inequality for the width of domain walls in the model and were able to focus in on the critical assumptions made by earlier authors.

Finally, we studied the structure factor in amorphous magnets with bond or site dilution using renormalization group scaling methods. The disorder leads to the presence of an additional term in the structure factor which we analyzed with the aim of aiding experimentalists in fitting their data to theoretical models of these systems.

Publications:

R. A. Pelcovits and D. Mukamel, "Exact Solution of a One-Dimensional XY Model in a Random Field," Phys. Rev. (RC) B28, 5374 (1983).

R. A. Pelcovits and B. J. Minchau, "Lower Bounds for the Width of Domain Walls in the Random Field Ising Model," Phys. Rev. B29, 6059 (1984).

R. A. Pelcovits and D. Mukamel, "Dynamics of Charge-Density Waves Pinned by Impurities," Phys. Rev. (RC) B29, 5972 (1984).

R. A. Pelcovits, D. Mukamel and G. Forgacs, "Glauber Dynamics for One-Dimensional Spin Models with Random Fields," Phys. Rev. B30, 205 (1984).

R. A. Pelcovits and A. Aharony, "Structure Factor for Dilute Magnetic Systems," Phys. Rev. B, January 1985.

Time Domain, Raman and Infrared Spectroscopy of Fast Ionic Conducting Glasses

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

Personnel: G. Chryssikos and D. Turcotte, Graduate Students,
Chemistry Department
P. Winsor IV, Research Associate, Chemistry Department

Sources of Support: MRL/NSF

Objectives and Approaches:

Fast ionic conducting (FIC) glasses hold promise as isotropic ionic conductors capable of bearing high currents under extreme chemical and temperature conditions. This is a key requirement for electrolytes in high power batteries needed for mains-system load-leveling and for mobile power sources. While the glassy state gives the isotropy and inorganic oxide compositions promise chemical stability in the case of FIC glasses, their structures, relaxation phenomena, stabilities, and other properties are not well enough understood to permit their use or optimization.

The key problems involve understanding the structures and relaxations of FIC glasses and their relationships to composition, temperature, and preparation. This joint project is designed to address these problems. Raman and infrared spectroscopy are used to determine the nature of the glass network and how alkali compounds added to increase the conductivity to FIC levels change the structure of the glass. Time domain spectroscopy is used to measure the dielectric behavior of the materials over a range of frequency and temperature in order to understand the relaxation phenomena exhibited by FIC glasses. The high frequency TDS loss and far infrared absorbance measurements are used together to help understand the energy loss mechanisms at low values of kT .

Research Achievements:

In this period several key results were obtained on FIC glasses in the $x \text{LiF} \cdot y \text{Li}_2\text{O} \cdot \text{B}_2\text{O}_3$ system. The role of fluorine in the structure has been studied by Raman spectroscopy. It was shown that addition of LiF results in important structural changes, compared to binary glasses of the same O/B ratio. These results are consistent with the participation of fluorine in the network, which may be expected on thermochemical grounds but is different from previously reported results. This means that the glass network is modified by the added LiF and that new local structures involving B-F bonds, probably BO_3F and BO_2F_2 -containing moieties, exist, but it does not eliminate the possibility that some fraction of the LiF is interstitial. These results lead to feasible models for the sites at which Li^+ ions are localized.

Based on this work and the development of powerful techniques to correct for small residual effects in TDS, measurements were made in the 0.1-10 GHz region at temperatures from 25 to 340°C on these FIC glasses. While further measurements are in progress, several key results were obtained. The most important is that the permittivity equivalent to the static permittivity increases significantly with temperature in this range. The implications of this can be seen by recognizing that, through Maxwell relations, the quantities $(\partial S / \partial E^2)_T$ and $(\partial \epsilon_s / \partial T)_{E^2}$ have the same sign. Since we found the latter to be positive, the former must be as well. This means that the entropy increases with electric field. This is quite extraordinary, since the normal expectation is that the field would have an ordering effect and lower the entropy. Work on these systems is continuing by both spectroscopic and TDS methods to develop an understanding of the microscopic structures and processes of importance to the behavior of FIC glasses.

Publications:

D. E. Turcotte, E. I. Kamitsos and W. M. Risen, Jr., "A Raman Study of Lithium Fluoride Containing Fast Ionic Conducting Glasses," *Solid State Communications*, 51, 313 (1984).

^{11}B 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

Objectives and Approaches:

Using ^{11}B 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 $\text{BaO-B}_2\text{O}_3\text{-SiO}_2$ is being determined. The fraction (N_4) of boron atoms that are four-coordinated to oxygen was measured by conventional lock-in as well as fast-passage methods. The fraction of borons that exist in the trigonally symmetric and asymmetric environments (N_{3S} and N_{3A}) is 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 X, Y, and Z; for $\text{X}(\text{BaO})\text{-Y}(\text{B}_2\text{O}_3)\text{-Z}(\text{SiO}_2)$ $\text{X}+\text{Y}+\text{Z}=1.00$, $\text{R}=\text{X}/\text{Y}$, and $\text{K}=\text{Z}/\text{Y}$. In particular the behavior of N_4 is studied and modeled as a function of R and K.

Research Achievements:

It is found that the N_4 versus R data are qualitatively similar to the alkali borosilicate analogues. That is, we find a linear relationship between N_4 and R for small R ($0 < \text{R} < 0.5$). N_4 behavior breaks at about $\text{R}=0.5$ ending the linearity, and N_4 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. That is, 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 covalent character 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 $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ and $\text{CdO-B}_2\text{O}_3\text{-GeO}_2$ systems. (J. Chem. Phys. 64, 4459 (1976)) and (Bull. Am. Ceramic Soc. 63, 1108 (Sept. 1984) Abstract 38-G-84F)).

NMR Study of the Mixed-Alkali Effect in Borate Glasses

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

Personnel: J. Zhong, Graduate Student, Physics Department

Sources of Support: MRL

Objectives and Approaches:

The mixed-alkali effect in glass refers to large, order of magnitude changes in properties of glasses caused by introducing more than one kind of alkali ion into the glass system. The study of the mixed-alkali effect is significant for two major reasons. First, it is an effect commonly met in many glass systems. Second, there are many properties (electrical, thermal, chemical, etc.) of glasses which are closely related to the motion and pairing of alkali ions, and it is the motion and (probably) the pairing that are involved in the mixed-alkali effects. Studies of the mixed-alkali effect may lead to an understanding of ionic motion and coordination in glasses and provide guidance for production of glasses with desired properties. NMR methods can be used to measure the activation energy of ionic motion and monitor the environment of alkali ions. Hence, it is a useful technique for study of the mixed-alkali effect.

Research Achievements:

The spin-lattice relaxation times T_1 of Li^7 and B^{11} ions have been measured in lithium, sodium, mixed lithium-sodium and mixed lithium 6-lithium 7 isotope borate glass systems. It is found that there is a mixed-alkali effect in the mixed Li-Na system (shorter T_1 and larger activation energy than for pure lithium or sodium borate glasses of the same total alkali content) but there is little evidence of the effect in the mixed Li^6 - Li^7 system although the two isotopes have different masses. These observations are in accord with the results of other studies of the mixed-alkali effect.

A systematic study of the coordination of boron due to the introduction of mixed-alkali ions into borate glasses is now in progress in this laboratory. The initial results show that there is a decrease in N_4 , the fraction of 4-coordinated borons in mixed-alkali glasses. This effect would be consistent with the mixed-alkali model (proposed by scientists at the Grebenshchikov Institute in Leningrad and most recently elaborated by Klonkowski in Poland) in which unlike alkalis pair at non-bridging oxygens (NBO's). If this configuration is favored by energy considerations, the competition between the formation of NBO's and 4-coordinated borons (i.e. BO_4 units) when alkali oxide is added to the glass may be biased in favor of the NBO's when the alkalis are mixed.

Publications:

J. Zhong and P. J. Bray, "New Evidence for the Pairing of Different Alkali Ions in Mixed-alkali Borate Glasses," submitted for presentation at the 87th Annual Meeting of the American Ceramic Society, Cincinnati, Ohio, April 1985.

Observation of Glass-like Behavior in Solutions of Polymer Molecules

Principal Investigators: William M. Risen, Jr., Professor
Chemistry Department
Richard M. Stratt, Assistant Professor
Chemistry Department

Personnel: J.-M. Y. Ha, Graduate Student, Chemistry Department

Sources of Support: NSF/MRL and NSF

Objectives and Approaches:

The conjugated electronic structure of polydiacetylene (PDA) molecules changes with their conformations. Such changes affect both the vibrational and electronic spectra of the species and can be probed by resonance Raman Spectroscopy. When PDA molecules are placed in a solvent, the interactions of their substituent side-groups with solvent molecules can effect dissolution without loss of all of the order the PDA species have in the crystalline state. However, after such solutions have had sufficient time for further side group-solvent interaction at elevated temperature, more of this order will be lost. When these solutions are cooled, the PDA molecules (1) can retain the disordered conformation characteristic of the higher temperature, (2) return to the relatively highly ordered state of the initial solution, or (3) they can be temporarily frozen into a conformation at low temperature with an intermediate order which is higher than that of the high temperature solution but lower than that of the initial solution at the lower temperature. The possibility of observing such a frozen disordered molecular conformation, which can be interconverted with the higher temperature form on a short time scale but not with the ordered form at short times, led to this study.

Research Achievements:

The Resonance Raman spectra of the PDA known as poly-3BCMU in mixtures of chloroform and n-hexane were studied as a function of temperature in the 25-55° range. The region of the PDA spectra that is characteristic of $\nu(\text{C}=\text{C})$ vibrations is sensitive to the electronic structure along the PDA backbone and thus to the backbone conformation. As shown in A of the accompanying figure, the spectra show that there are several vibrational entities that scatter light in this region and that their relative amounts change with temperature as the conformation of the PDA changes. Moreover, the spectra at 25°C before and after heating are different, so a new conformation is achieved after heating. However, this conformation is not simply a frozen arbitrary high temperature configuration which depends on the time of heating. Rather, as shown in B of the figure, the system can be cycled between it and the high temperature solution form. Thus, the disordered lower temperature solution form contains molecules

which are glass-like in the sense of having a configuration which is long-lived and can be reached through a more disordered state with which it can be cycled. This glass-like state must have a number of interesting characteristics and undergo relaxations. These are under investigation experimentally and theoretically.

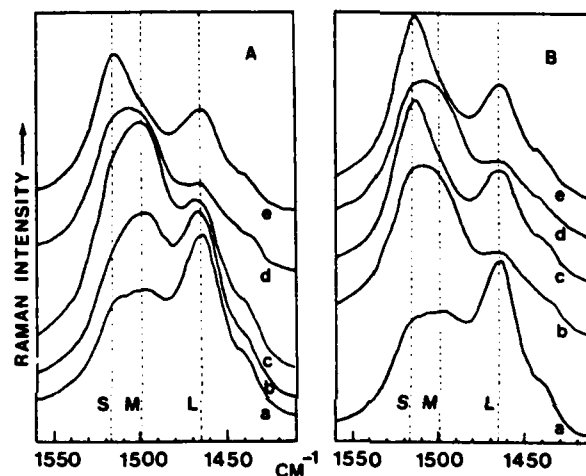


FIG. 1. Resonance Raman spectrum of poly-3BCMU solution as a function of temperature and history showing the C = C stretching region. (A) The progression of (a) 25 °C → (b) 35 °C → (c) 45 °C → (d) 55 °C → (e) 25 °C. (B) The progression (a) 25 °C → (b) 55 °C → (c) 25 °C → (d) 55 °C → (e) 25 °C. The small peaks at 1445 and 1455 cm^{-1} are due to the hexane in the solvent mixture.

Publications:

Jung-Mi Ha, Richard M. Stratt and William M. Risen, Jr., "Observation of Glass-like Behavior in Conjugated Polymer Molecules," J. Chem. Phys. 81, 2855 (1984).

Compositional Dependence of the Glass Transition Temperature of Metal Ionomers

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

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

Sources of Support: ONR and MRL/NSF

Objectives and Approaches:

Our work on ionic oxide glasses has led to observation of cation-motion vibrations in their far infrared spectra, and, from them, evaluation of cation-anionic site force fields. In the studies of alkali metaphosphate and mixed alkali silicate glasses, in particular, relationships between these forces and the processes leading to glass formation and glass transition have been indicated. To explore these relationships it is useful to investigate model systems in which the network forces are quite different from those due to cation-anionic site forces and their roles in glass formation are distinguishable. Metal ionomers, whose cation-anionic site forces are similar to those in other ionic glasses but whose network rearrangement forces are characteristically weaker, provide such a system. Thus, the cation-dependence of T_g and of cation-site forces in several series of metal ionomers were investigated.

Research Achievements:

The far infrared spectra of both M^+ and M^{+2} PSSA ionomers were determined in rigorously dried condition and from them the cation-sulfonate ion motion vibrations were measured. It was shown, as expected, that the force fields relevant to these vibrations are greater in the case of the M^{+2} cations. However, the glass transition temperatures of these M^{+2} ionomers were found to be lower than those of the M^+ ionomers. Moreover, T_g for the latter systems varies significantly as the concentration of anionic sites is changed while those of the M^{+2} ionomers do not. The interpretation of these facts is complex because of the thermodynamic factors favoring ionic domain formation at certain compositions, but the overall picture that emerges is the following. The attractive ionic forces in the M^{+2} ionomers are strong enough that the ionic crosslinking between network segments is not significantly altered thermally before other network moieties become mobile, so T_g is determined largely by the network and this temperature is not a strong function of the anionic site concentration until it is very high. Thus, these ion-site forces are not overcome until the temperature is well above T_g . In the case of the M^+ ionomers, however, the analogous forces and those in ionic clusters are on the same order of magnitude as those overcome in

network rearrangement. Thus, the cation-dependence of T_g is significant. The implication for ionic oxide glasses is that for systems with the same network the observation of a significant dependence of T_g on the nature of closely related cations of the modifiers requires the network rearrangement and cation-site forces to be of similar magnitude.

Publications:

V. D. Mattera, Jr. and W. M. Risen, Jr., "Far Infrared Study of Ionic Interactions in PSSA Ionomers," J. Polym. Sci. (Polym. Phys.) 22, 67 (1984).

V. D. Mattera, Jr. and W. M. Risen, Jr., "Composition Dependence of Glass Transition Temperature in PSSA Ionomers," J. Polym. Sci. (Polym. Phys.), in press (1985).

V. D. Mattera, Jr., S. L. Peluso, A. T. Tsatsas and W. M. Risen, Jr., "Spectroscopic and Thermal Studies of Ionic Interactions in Ionomers," Chapter in Coulombic Interactions in Polymers, A.C.S. Symposium Book Series, American Chemical Society.

Two-Level Tunneling Systems in Disordered Solids

Part I:

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

Personnel: A. Hikata, Professor (Research) Division of Applied
Mathematics
G. Cibuzar, Graduate Student. Physics Department

Sources of Support: MRL

Objectives and Approaches:

The nearly universal low temperature properties of amorphous solids have been successfully explained 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 in 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.

The structure of a metallic glass obtained by fast quenching of the liquid can be altered through heat treatments. By annealing at a temperature below the glass transition temperature, T_g , changes in atomic configuration occur which lead to relaxation to a more stable amorphous state. It is important to note that this structural relaxation does not lead to the formation of long-range, crystalline order. By annealing at a temperature above T_g , crystallization can occur which may bring about large structural changes as well as large changes in local composition. The process may proceed to the final stable structure via several increasingly stable (but still metastable) crystalline structures. The purpose of this work is to determine, in the structures resulting from these two types of heat treatment, the occurrence and the nature of features believed to be characteristic of the glassy state. This is done by measurements of ultrasonic propagation at low temperatures.

Research Achievements:

I. The Nature of the Tunneling Entity in Amorphous and Crystalline Metal Alloys:

Specifically, the density of TLS was determined in the metallic glass PdSiCu for several stages of annealing carried out at temperatures below T_g . A monotonic decrease of this number was found for increasing annealing temperature. The annealing was then extended to temperatures above T_g . First, a treatment was carried out to transform the amorphous solid, in several stages, into a crystalline, Pd-rich solid solution. A second recrystallization was then carried out to allow the formation of a crystalline silicide phase out of the solid solution.

The results on TLS density following these treatments were surprising. For all stages of recrystallization leading to a Pd-rich solid solution a substantial (over 50% of the value in as-quenched glasses) density of TLS remained, despite the change from the amorphous to the crystalline state. Following the second recrystallization, however, all evidence for the presence of TLS disappears.

The fact that the same value of TLS density is found in a metallic glass and in a crystalline phase obtained therefrom severely restricts the possible configurations for the TLS. For the amorphous state one could conjecture that for each TLS fairly large numbers of atoms are involved in the tunneling over very short distances d . In a crystalline phase, however, this is not possible without seriously disrupting the long-range order (translational invariance). It follows that most likely single atoms are involved in the tunneling process. The evidence for the presence of TLS in a crystalline solid solution containing Si and their absence when Si is in the form of silicides, indicates that in this case the TLS consist of individual Si atoms. In view of the similarity in TLS density this may also be the case in the amorphous phase.

Publications:

Cibuzar, G., Hikata, A. and Elbaum, C., "Two-Level Tunneling Systems in Amorphous and Crystallized Metal Alloys," Phys. Rev. Letters, 53, 356 (1984).

AD-A156 214

ANNUAL TECHNICAL REPORT MATERIALS RESEARCH LABORATORY 1 2/2
JULY 1983 - 30 JUNE 1984(U) BROWN UNIV PROVIDENCE RI
MATERIALS RESEARCH LAB 30 JUN 84 NSF-DMR82-16726

UNCLASSIFIED

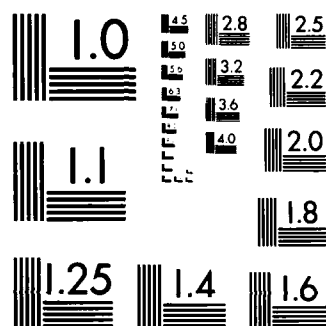
F/G 11/7

NL

END

FILMED

DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963-A

Part II:

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

J. R. Beamish, Research Associate - MRL

Sources of Support: MRL, NSF

II. Relaxation Rates of Two-Level Tunneling Systems in Porous Vycor Glass; Effects of Helium

One approach to studying the nature of the TLS in glasses is through effects of size and of relaxation processes. In this connection, several workers have measured the specific heat and thermal conductivity in amorphous powders and porous materials with particle and pore sizes as small as 70 angstroms. These materials still exhibit glass behavior, but effects such as excitation of surface and single particle modes in powders, and phonon scattering by pores become important.

We have made ultrasonic velocity measurements on porous Vycor glass (A silica glass with an interconnected network of pores, which may be characterized as a random collection of silica spheres about 300 angstroms in diameter) at low temperatures ($T \gtrsim 1K$). By filling the pores with helium-three and helium-four the effects of helium on the nearby TLS could be studied. The results indicate that the presence of helium increases dramatically the relaxation rate of the TLS and that superfluid helium-four has a particularly large effect. From the frequency and temperature dependence of the sound velocity in these experiments the estimated increase of the relaxation rate due to the presence of liquid ^3He , solid ^4He and a film of nonsuperfluid ^4He is about a factor of 15. The presence of superfluid ^4He causes an additional increase of the rate by at least another factor of 8.

The proposed explanation of these results is that in the absence of helium, the phonons resulting from the relaxation process are unable to escape from the glass and slow down the relaxation process. The presence of normal helium phases allows for a relief of this "bottleneck" by the propagation of phonons with wavelengths not exceeding the diameter of the pores. The presence of superfluid helium provides an additional channel of escape through the propagation of fourth sound.

Publications:

Beamish, J.R., Hikata, A. and Elbaum, C., "Effects of Helium on Two-Level Systems in Porous Vycor Glass," Phys. Rev. Letters, 52, 1970 (1984).

A 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: Supported in part by the Materials Research Laboratory. (Mr. Szu is also supported by a teaching assistantship from the Department of Physics.)

Objectives and Approaches:

A ^{11}B NMR study of boron coordination in the lithium borosilicate glass system and the sodium borosilicate glass system has been performed in the past. It has been shown that, initially, the N_4 value (the fraction of boron atoms in BO_4 units) of both systems increases linearly with increasing alkali 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 alkali oxide content to boron oxide content is higher than some critical value R_c , which increases linearly with the SiO_2 content of the glass. Beyond R_c , N_4 decreases while N_{3A} , the fraction of boron atoms in asymmetric BO_3 units, increases with higher alkali oxide content. Although the systems are qualitatively similar to each other, there are significant quantitative differences showing that the microstructure in the two glass systems is different. A natural extension of the above studies is a ^{11}B NMR investigation of potassium borosilicate glasses. Will these be the same as the sodium borosilicates, or the same as the lithium borosilicates, or will they exhibit a third type of structure?

Various potassium borosilicate glass samples have been made. They were grouped into five families, each family having the same K value but different R values where $K = \text{mole}\%\text{SiO}_2/\text{mole}\%\text{B}_2\text{O}_3$, $R = \text{mole}\%\text{K}_2\text{O}/\text{mole}\%\text{B}_2\text{O}_3$. 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 estimate N_4 . The technique of adiabatic 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, allows for 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} .

Research Achievements:

The $K=0.5, 1, 2$ families of potassium borosilicate glasses have been studied. We have found that the values of N_4 , N_{3A} , and N_{3S} behave qualitatively like those of the sodium and lithium borosilicate glass systems. More samples ($K=3,4$) will be studied to obtain a better understanding of the micro-structure of potassium borosilicate glasses.

Statistical Mechanical Models of Boron Coordination

Principal Investigator: P. J. Bray

Personnel: R. Mulkern, E. Holupka, B. Minchau, Graduate Students,
Physics Department

Sources of Support: NSF and Sandia Laboratory

Objectives and Approaches:

For over twenty years, boron coordination in a variety of borate glasses has been quantitatively catalogued. N_4 , N_{3S} , and N_{3A} , which are respectively the fraction of tetrahedral borons, symmetric BO_3 units and asymmetric BO_3 units (boron bonded to one or two non-bridging oxygens), are all quantities accessible to ^{11}B NMR. A wide variety of empirical models have been employed to explain the boron coordination in various glass systems as a function of glass composition. For instance, Dell and Bray (W. J. Dell, Ph.D. Thesis, Brown University, 1983) explained N_4 , N_{3S} and N_{3A} data in the sodium borosilicates as functions of R , $(\text{mol}\%Na_2O/\text{mol}\%B_2O_3)$, for several K families, $(K=\text{mol}\%SiO_2/\text{mol}\%B_2O_3)$, in terms of postulated chemical reactions which associate the alkali with various structural groupings (diborate groups, reedmergnerite units, etc.) which appear in the crystal chemistry of this ternary system. The fits to the experimental data using this technique, which may be referred to as "Krogh-Moe modeling" are often found to be quite good (J. Krogh-Moe, Phys. Chem. Glasses, 6, 46, 1965). However, there are other approaches to the modeling of glass structure which can offer valuable insights.

Within the last decade, several statistical mechanical models have been presented, primarily motivated by the work of Roger Araujo (R. J. Araujo, J. Non-Cryst. Sol., 55, 257, 1983). A theoretical study is currently underway at Brown in order to determine whether the statistical mechanical models proposed can actually predict boron coordination in alkali-borates. The problem of finding appropriate degeneracies and energies to use in a partition function for the alkali-borates, considered to consist of the units BO_4 , BO_3 , and BO_3 , is a fundamental one in that its success would justify the use of a quantity defined only for an equilibrium state, (the partition function), to determine the properties of a glass, considered to be an object that has not yet achieved thermal equilibrium.

Research Achievements:

We have succeeded in finding in closed form, an analytical solution to the partition function which Araujo originally proposed for this system. Araujo had only found an approximation, i.e. the largest term, in his partition function. Our solution is in qualitative agreement with the experimental data as found in earlier studies (R. J. Araujo, Phys. Chem. Glasses, 21, 193, 1980). More general models, based again on the ideas of Araujo, are being considered and computer techniques for solving the resulting equations are being employed.

Cadmium Borogermanates and Silicates

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

Personnel: R. Mulkern, Graduate Student, Physics Department and
S. J. Chung, Visiting Scientist

Sources of Support: NSF and MRL central facilities

Objectives and Approaches:

Several years ago, Strickler and Roy discovered a new family of photoconducting glasses (D. W. Strickler and R. Roy, J. Mat. Sci., 6, 200, 1971). These are the cadmium borogermanates and cadmium borosilicates. The glasses are of considerable theoretical interest since electronic conduction cannot occur via a change in valency of the cations, i.e., they are the first monovalent amorphous conductors. Several propositions have been put forward concerning the microscopic mechanism of conduction. These range from postulating non-stoichiometric regions of CdO in which conduction takes place via charged defects, Cd^{++} interstitials or doubly ionized oxygen vacancies, to a d-band overlap mechanism as proposed by Goodenough and requiring a substantial covalent character of the Cd-O bonds (J. B. Goodenough, "Magnetism and the Chemical Bond," J. Wiley and Sons, N.Y., 1963).

Research Achievements:

A ^{11}B and ^{113}Cd NMR study to determine overall structural aspects throughout the glassforming region has been undertaken. The NMR study has found that although the covalent nature of the cadmium bonding in the glass increases approximately linearly with the addition of CdO, the bond is still less covalent than that of a polycrystalline sample of CdO, in which the Cd-O bond has been estimated to be 80% ionic (J. C. Philips and J. A. Van Vechten, Phys. Rev. Letters, 22, 705, 1969). The data will help place severe restrictions on the types of mechanisms proposed to explain the electronic conductivity. In addition, the boron coordination throughout the glassforming region has been ascertained and N_4 vs. R , ($\text{mol}\% \text{CdO}/\text{B}_2\text{O}_3$), for all K , ($\text{mol}\% \text{Ge}(\text{Si})\text{O}_2/\text{B}_2\text{O}_3$), families has been empirically fit using a model previously employed to fit successfully the N_4 data of the lead borosilicates (K. S. Kim, P. J. Bray and S. Merrin, J. Chem. Phys., 64, 4459, 1976). This model assumes a linear increase of the percentage of cadmium bonded covalently in the network, an assumption entirely consistent with the ^{113}Cd NMR results.

In order to learn more about the glass structure of this system, especially the germanium network, a complete near and far infrared and Raman study is underway in a collaborative effort with Professor William Risen's group of the Brown Chemistry Department. The near

infrared studies so far have been consistent with the NMR results and have indicated a predictable growth of the B-O-B stretching mode as R decreases. Future far infrared and Raman studies performed with the equipment available at Brown should help distinguish 4- and 6-fold coordinated germanium. A complete vibrational analysis of all the spectra should add greatly to the burgeoning knowledge of germanate glasses (M. K. Murthy and E. M. Kirby, Phys. Chem. Glasses, 5, 144, 1964) and (I. N. Chakraborty and R. A. Condrate, Phys. Chem. Glasses, 25, 39, 1984).

Publications:

P. J. Bray, R. V. Mulkern and S. C. Chung, "An NMR Investigation of the Cadmium Borogermanates," Bull. Am. Ceram. Soc., 63, 1108, Sept., 1984, Abstract 38-G-84F.

Leached Glasses and Phase Separation

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

Personnel: R. Mulkern, Graduate Student, Physics Department

Sources of Support: NSF and MRL Central Facilities

Objectives and Approaches:

Liquid-liquid immiscibility of glass melts can lead to phase separation in the supercooled product. Vycor glass is a famous example of this phenomenon. An ordinary sodium borosilicate glass in which phase separation is enhanced by heat treatment is leached in an HCl solution. The borate phase is attacked leaving a porous silica skeleton which is sintered to yield the final product, a hard, mostly silica, glass.

Research Achievements:

A collaborative effort with Corning glass researchers was carried out in order to examine the effects of leaching a Vycor-like glass composition on the boron coordination. Chemical analyses of the original melts and the leached products were performed by Corning and ^{11}B NMR spectra were recorded at Brown. The R and K values, $\text{mol}\%\text{Na}_2\text{O}/\text{B}_2\text{O}_3$ and $\text{mol}\%\text{SiO}_2/\text{B}_2\text{O}_3$ respectively, of the original melt were 0.29 and 3.49 respectively. Values of R and K for the leached product were 0.05 and 24.5 respectively. An independent study of the sodium borosilicates by Bray and coworkers suggested that for R values less than 0.4 the relation $N_4=R$ was followed independent of K, implying that all the alkali is used to modify the borate network (W. J. Dell, P. J. Bray and S. Z. Xiao, J. Non-Crystalline Solids, 58, 1983) and (Y. H. Yun, P. J. Bray, J. Non-Crystalline Solids, 27, 1978). Based on these results, which did not include K families over 6.0, one would expect that leaching of the glass, resulting in the removal of alkali, would lead to a subsequent reduction in N_4 . This was found to be the case and, even for the extremely high K (24.5) of the leached product, N_4 was found to equal R (0.05) to within experimental error. Further, it was found that releaching in a basic (KOH) solution added alkali and increased N_4 .

More detailed studies of phases separation in other glass systems are being performed in conjunction with Dr. Bruce Bunker of Sandia National Laboratories. This type of work should prove of some interest to waste glass researchers in the effort to understand connections between glass microstructure and leaching processes.

Publications:

B. Mulkern, W. W. Wu, and P. J. Bray, "Boron Coordination at Various Manufacturing Stages of a Vycor-Type Glass," Bull. Am. Ceram. Soc., 62, 420, 1983, Abstract 97-G-83.

Thermal History

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

Personnel: E. Holupka, Graduate Student, Physics Department

Sources of Support: Sandia National Laboratories and MRL Central Facilities

Objectives and Approaches:

Very little is known about the microstructural changes which occur in a glass as a consequence of different quench rates of annealing times. Consequently, a program has been started to study the effects of thermal history on microstructure.

Presently, at Brown University, the change in the fraction of four-coordinated borons (N_4) in a variety of borate glasses is being compared for various quenching rates of the glass samples. Initial investigations have focused on the CABAL ($\text{CaO-B}_2\text{O}_3\text{-Al}_2\text{O}_3$) and Si-CABAL ($\text{SiO}_2\text{-CaO-B}_2\text{O}_3\text{-Al}_2\text{O}_3$) glasses. Glass samples of these two types were prepared in three different ways: i) bulk, ii) roller quenched and iii) drawn fiber. The bulk samples were simply removed as a melt from the furnace and allowed to cool in the air. The roller-quenched samples were prepared by pouring the melt through two rapidly rotating stainless steel cylinders, and the fiber-drawn samples, prepared by Owens-Corning Fiberglas Corporation, were prepared by drawing the melt into long fibers. The highest quench rate is obtained by the fiber drawing process.

Research Achievements:

N_4 was determined for bulk, roller-quenched and fiber-drawn samples of CABAL and Si-CABAL. The results appear in Table 1. It is noticed that the CABAL glass system shows no change in N_4 as a function of quench rate while the Si-CABAL glass system does.

wt. % $\text{SiO}_2 \cdot \text{CaO} \cdot \text{B}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$	N_4		
	bulk	fiber	roller
41.3-32.0-8.3-19.2	.26	-	.28
50.0-30.0-10.0-10.0	.18	-	.16
64.0-23.0-8.7-4.4	.12	.08	-
61.3-22.0-8.3-8.3	.16	.10	-
65.4-23.5-8.9-2.2	.09	.08	-
55.2-13.1-18.5-12.7	.16	.10	-
0.0-25.0-25.0-50.0	.09	-	.08
0.0-45.0-10.0-45.0	.23	-	.24
0.0-49.7-28.0-21.9	.17	.15	-

Table I

The CABAL glass system was previously studied by Bishop and Bray. It was established that the presence of aluminum alters the boron coordination in the glass and that at higher temperatures the aluminum competes with the boron for bonding with oxygens. Araujo has used a statistical mechanical model to calculate the fraction of 4-coordination in boron-containing glasses. It is predicted from this model that the fraction of borons in 4-coordination will decrease as the temperature increases. In consideration of Araujo's theory, one may postulate that since the roller quenched and fiberized samples have a higher fictive temperature T_f their N_4 values would decrease. This is observed in the fiberized Si-CABAL samples but not for the roller-quenched samples. The roller-quenching process may not produce a high enough quench rate for this effect to be observed. It is possible that a glass sample with a higher fictive temperature may have more aluminum atoms bonding in 6-coordination hence yielding a lower value for N_4 .

Future studies will include the determination of the fraction of 6-coordinated aluminums as a function of the fictive temperature. This will be done utilizing a technique called magic angle sample spinning (MASS). When the sample is spun at high speeds the quadrupole effects will be reduced and the dipolar effects will be averaged out allowing a determination of the chemical shifts for the 4- and 6-coordinated aluminums.

The Si-CABAL samples display a change in N_4 while the CABAL glass system does not. The silicon atoms may play a role in altering the boron coordination at higher fictive temperatures. The environment of the silicon will also be examined with MASS NMR of the ^{29}Si nucleus.

In order to explain the resultant change in N_4 between samples prepared by fiber drawing and bulk samples, calculations are in progress to modify Araujo's statistical model to incorporate the influence of the aluminum content of the glass on the resultant change in N_4 .

Publications:

P. J. Bray and E. J. Holupka, "The Potential of NMR Techniques for Studies of the Effects of Thermal History on Glass Structure," accepted for publication in the Journal of Non-Crystalline Solids.

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 Procedures:

Recently ^{10}B Nuclear Magnetic Resonance (NMR) has been used to determine the various structural groups found in the Sodium Borate and Lithium Borate glassforming systems. The different structural groups 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 crystalline compounds than 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, the double resonance technique cannot be used. We have been unable to detect ^{10}B or ^{11}B NQR signals 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 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:

The CW spectrometer has been built and is currently being tested. The design of the spectrometer is based on a recent design published by Robinson. The initial use of the new spectrometer will be for NQR studies. However, another unit of the same design will be developed into a sensitive NMR spectrometer for use with our recently ordered Bruker high field magnet and spectrometer.

The Placement 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 Procedures:

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 same 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 predominately ^7Li and in another it is mostly ^6Li . Since ^7Li has a magnetic moment about 6 times as large as ^6Li it will affect the dipolar interaction between the boron atom and the lithium atom more. 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 very close by, as is the case in the crystalline compounds known through x-ray diffraction studies.

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 are currently being fabricated and will be similarly measured.

Publications:

S. J. Gravina and P. J. Bray, Ceramic Society Bulletin 63, 1108, Sept. 1984, Abstract 39-G-84F.

SECTION 3 SURFACES

Introduction

The general aim of the Brown MRL program in surface research is to establish microscopic models of the structure of an interface and, on that basis, to develop a detailed understanding of the dynamics of surface processes. Studies are therefore carried out of static properties such as atomic geometry, electronic structure and bonding, and of kinetic phenomena such as scattering, molecular dissociation and desorption. During the period covered by this Technical Report, the specific projects have involved studies of surface phase transitions by Estrup, Ying and Greene; studies of structural effects on surface kinetics by Greene, Ying, Estrup, and Stiles; and studies aimed at the development of surface spectroscopic techniques by Diebold and Stiles. Progress and achievements are described in the following sections; they are listed according to the principal investigator, but in most cases the work has involved collaboration between several members of the thrust area. In addition, almost all the experimental investigations have benefitted from use of one or more Central Facilities, in particular the Electron Spectroscopy Facility, the Microelectronics Facility, and the Electron Microscope Facility.

P. J. Estrup, Coordinator

SECTION 4 NEW INITIATIVES

Introduction

The New Initiatives undertaken by the MRL are in the areas of structure-property relationships in polymeric molecules, surface treatment of polymers, and the preparation and study of the Ge_3N_4 -Ge interface for development of Ge-MISFIT based technology.

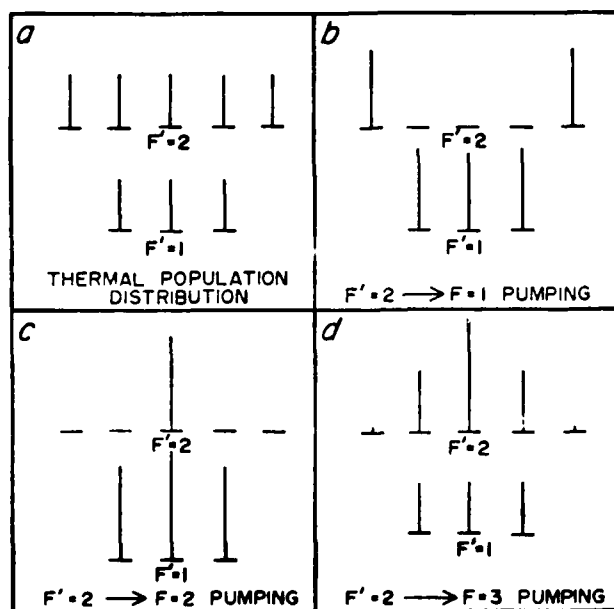
Novel approaches to studying structure-property relationships are being pursued by R. Stratt and J. Weiner. They depart from established methods in focusing on the role of electronic interactions. In examining the relation of such interactions to excluded volume in rubbery materials, Weiner adopted a kinetic approach and found that the intramolecular interactions contribute to stress transmission in a manner which depends on the state of strain. Stratt also is examining the role of electronic effects on polymers by studying electronic and conformational transitions in electron-delocalized materials, such as polydiacetylenes (PDA). This permits investigation of the ways in which the long ranged influence of the electronic structure can lead to cooperativity along the torsional angles in conjugated polymers. His prediction of mobile conformational defects has been invoked and is being refined and extended in the interpretation of novel resonance Raman work showing that PDA solutions exhibit glass-like behavior.

Rosenberg has constructed a nitriding facility and prepared Ge_3N_4 -Ge structures, which are under study. These materials demonstrated the facility's capability, and they form the basis for further materials development and for a wide range of optical, electronic and microscopic investigations now being undertaken to understand and develop the insulator needed for achievement of Germanium CMOS-type technology.

Suggs has initiated a program to modify organic polymer surfaces. The approach is to identify the way very reactive molecular oxidants react with hydrocarbons in order to understand the basic mechanisms of polymer surface functionalization. Initial model studies have shown that the oxidation is product-inhibited. This knowledge provides the basis for development of reactions that can achieve more efficient surface treatments of the types needed for improved adhesion and other specialized applications.

This result is not entirely surprising in view of the state multipole description of an optically pumped Na atom. The disequilibrium between hyperfine levels of Na produced by optical pumping is described by a zero rank tensor related to $\langle F^2 \rangle$. Relaxation of this disequilibrium is equivalent to a reversal of the net magnetic moment of the atom from a direction parallel to that of the total spin, F , to a direction antiparallel to the total spin. In contrast, D_2 pumping produces magnetic sublevel disequilibria described by a second rank tensor related to the quadrupole moment. Relaxation of this disequilibrium implies possible coupling of this moment to the surface during scattering. The inverse temperature dependencies of the relaxation of these two disequilibria seen in these experiments seems indicative of different coupling mechanisms of the Na valence electron to the surface during scattering.

Further work is in progress to determine the surface specificity of this technique, as well as to assess the surface relaxation of other atomic multipole moments that can be produced by different optical pumping schemes.



Ground state hyperfine sublevel populations produced by optical pumping. a) unpumped thermal distribution; b) D_1 pumping of the $F'=2 \rightarrow F'=1$ transition; c) D_2 pumping of the $F'=2 \rightarrow F'=2$ transition; d) D_2 pumping of the $F'=2 \rightarrow F'=3$ transition. All plots show distributions for $t \gg \tau$, where τ is the natural lifetime of the upper state.

Publications:

G. J. Diebold, P. R. Muessig, "Collisional Deexcitation of Optically Pumped Na on Surface Impact with LiF," (being submitted to Surface Science).

Surface Collisional Deexcitation of Optically Pumped Na on Impact with LiF

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 is centered upon the development of a laser probe of atom/surface impact which can give physical insight into the nature of surface scattering processes. 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. Two distinct disequilibria occur in the ground state energy levels as a result of pumping: one between the hyperfine level populations themselves and one between the magnetic sublevel populations of a given hyperfine level (see Figure 1). A non-thermal Na beam produced by optical pumping is scattered from a LiF surface, and the scattered atoms are probed with a laser for a change in hyperfine sublevel populations. Comparison of the scattered ground state population distribution with the incident (optically pumped) distribution provides insight into the relaxation behavior of the two disequilibria due to surface impact.

Research Achievements:

By pumping the $D_1 F'=2 \rightarrow F=1$, $F'=2 \rightarrow F=2$, or $D_2 F'=2 \rightarrow F=3$ hyperfine transitions, non-Boltzmann hyperfine ground state population distributions are produced as shown in Figure 1. If the density matrix formalism is applied to these distributions, and the population numbers are recast into the form of state multipoles, it can be shown that each of the $F'=2$ population distributions shown in Figure 1 corresponds to an "alignment," i.e., a second rank tensor directly related to the quadropole moment. Fluorescence intensity data obtained from the scattering of Na beams having the $F'=2$ ground state population distributions shown in Figure 1 show that relaxation of the $F'=2$ disequilibrium produced by D_1 pumping increases with surface temperature. Since D_1 pumping produces a simultaneous disequilibrium of the magnetic sublevels and hyperfine levels of the ground state, we probe here a simultaneous relaxation of these disequilibria. Preliminary data from the $D_2 F'=2 \rightarrow F=3$ pumping scheme, in which only a magnetic sublevel disequilibrium is produced, show a relaxation behavior which decreases with surface temperature, suggesting two fundamentally different relaxation mechanisms for an optically pumped atom on surface impact.

MOSFET's, have values that place them in the usable range (for silicon) and the surface mobility was shown to increase with decreasing temperature near room temperature, indicating that passivation was indeed being realized by the HPO technique. Preliminary evaluation of germanium nitride MIS structures has also been done showing, at room temperature, that nitrided surfaces have improved properties compared to the oxides from which they were formed. MRL facilities were used exclusively for analyzing the surface and interface conditions.

Publications:

O. J. Gregory and E. E. Crisman, "Review: Oxide and Nitride Passivation Layers on Single Crystal Germanium," American Chemical Society Symposium on Integrated Circuit Fabrication and Technology, March, 1984. To be published in J. Am. Chem. Soc.

E. E. Crisman, O. J. Gregory and P. J. Stiles, "The Nitridation of Thick Germanium Oxide Films on Single Crystal Germanium," J. Electrochem. Soc. 131 (8), p. 1896 (1984).

O. J. Gregory, E. E. Crisman and P. J. Stiles, "Structures and Formation Mechanisms of Germanium Nitride-Oxynitride Films on Single Crystal Germanium," presented at the November, 1984 meeting of the American Institute of Chemical Engineers, San Francisco, California.

E. E. Crisman, "The Construction and Characteristics of Native Insulators on Gallium Arsenide and Germanium," Ph.D. Thesis, Brown University, Providence, Rhode Island (1984).

Charge Transport at Semiconductor Surfaces

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

Personnel: E. E. Crisman, Sr. Research Engineer, Division of
Engineering and Department of Physics
B. Parker, Graduate Student, Department of Physics
J-I. Lee, Graduate Student, Department of Physics

Sources of Support: MRL, ONR, and University of Rhode Island,
Department of Chemical Engineering

Objectives and Approaches:

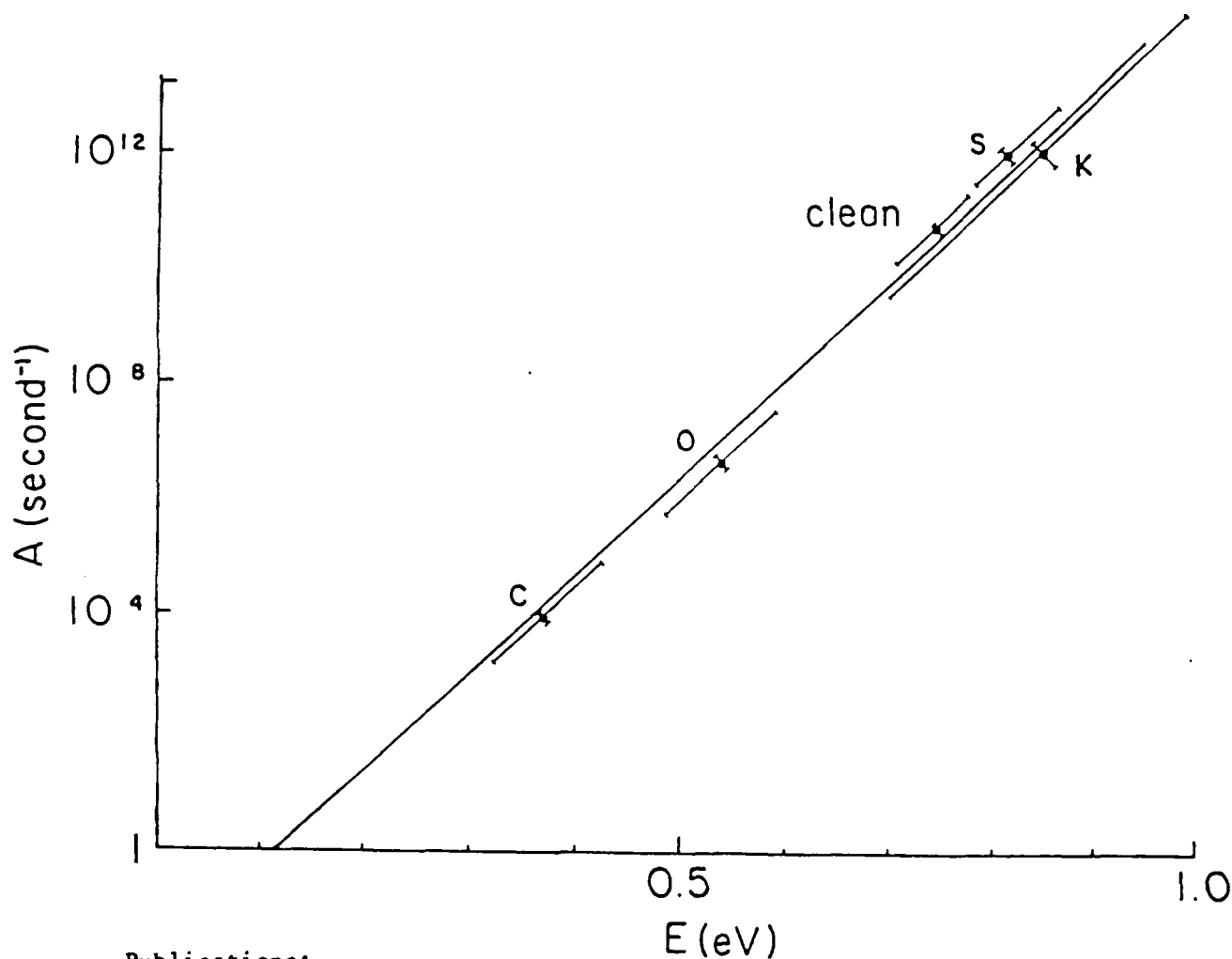
The purpose of this research is to develop methods of producing "passivating" layers on the surfaces of various semiconductors. The passivation (electrical) is required in order to reduce surface trapping and scattering mechanisms to the point where surface mobility approaches the mobility of the bulk. Surfaces, thus prepared, are used to explore the surface charge transport properties of two-dimensional electron gases at very low temperatures and high magnetic fields.

Research Achievements:

Preliminary studies of germanium oxides formed by high pressure oxidation (HPO) (up to 1360 atmospheres) have been extended to include morphological studies of the oxides per se and studies of nitrides formed by annealing the original HPO oxides in ammonia and hydrogen/nitrogen mixtures under a variety of gas flow conditions and temperatures. The production of both α -phase and β -phase by this manner has been demonstrated by SEM and IR-transmission analysis. Some of these specimens will be further analyzed by STEM. An extensive set of HPO oxides have been prepared at four temperatures from the three crystals with the lowest indice planes. These have been studied by IR-transmission and low angle X-ray diffraction to identify the phases that form and the conditions of formation. Four of the five known phases of GeO_2 have been identified in this manner, and conditions of temperature and pressure have been identified which give predominately hexagonal and predominately amorphous films (up to 5000 Å thick). Tetragonal GeO_2 has been observed but only in mixtures with other phases. These specimens are presently being analyzed by STEM techniques for details of the crystal structure of the various phases as well as the surface morphologies.

Specimens of germanium were processed in the MRL Microelectronics Facility into MOSFET structures using HPO as the "gate" insulator. These were analyzed at room temperature for surface fixed charge, interface state density distribution, and surface mobility. The "best" specimens, while not as good as the state-of-the-art silicon

decline in A is accompanied by a decrease in E , so that the net effect on k_r is relatively small. It seems clear that a microscopic model of the dissociation phenomenon must take this effect into account. Efforts to develop such a model are now underway.



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. (Proc. 31st National Symposium) (in press).

J. W. Erickson and P. J. Estrup, "Simultaneous Monitoring of Photoelectron Peaks," J. Vac. Sci. Technol. (submitted).

J. W. Davenport and P. J. Estrup, "Hydrogen on Metals," in Chemical Physics of Solid Surfaces and Heterogeneous Catalysis, Elsevier, (1984).

Studies of Chemisorption: Desorption and Dissociation Kinetics

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

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

Sources of Support: MRL

Objective and Approaches:

A central objective of the current studies of chemisorption phenomena is to reach an understanding of the fundamental physical interactions which govern dynamic processes such as scattering, adsorption, dissociation and diffusion on surfaces. The present work is focused on one of these, namely molecular dissociation, which is a basic step in almost all surface chemical reactions including catalytic processes. The experimental approach is to choose model systems in which variables such as structure and composition can be controlled, and to employ surface analytical methods that permit a characterization of the dissociation process at the molecular level.

Research Achievements:

Studies have been made of the kinetics of dissociation of carbon monoxide on a single-crystal molybdenum (110) surface. The reaction has been studied on both the clean substrate and in the presence of "modifiers" such as sulfur and potassium, which are prototypes of catalyst "poisons" and "promoters", respectively. The measurements were done by means of isothermal and temperature-ramped photoelectron spectroscopy (UPS and XPS) using techniques previously developed in this laboratory. In contrast to most previous studies of dissociation, both the activation energy E and the prefactor A were determined for the rate coefficient $k_r = A \exp(-E/kT)$.

The results show that the reaction poisons itself since the rate decreases as the products ($C + O$) accumulate on the surface. The special effectiveness of sulfur as a poison is found to be due to an increased desorption probability of undissociated CO. Similarly, potassium increases the adsorption probability but is not a very effective promoter on Mo(110), apparently because CO dissociation precedes desorption on this surface.

The figure shows representative values of E and A , for 25 percent completion of the dissociation on clean Mo(110) and in the presence of a co-adsorbed carbon, oxygen, sulfur or potassium. A remarkable result is that the prefactor falls by eight orders of magnitude, from the expected value of $\approx 10^{12} \text{ sec}^{-1}$ to 10^4 sec^{-1} . Another very surprising feature is a pronounced "compensation effect": the

Theoretical Study of Kinetic Processes on Solid Surfaces

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

Personnel: S. Tiersten, Graduate Student, Physics Department

Sources of Support: MRL and Office of Naval Research

Objectives and Approaches:

Surface adsorption, desorption and diffusion form a basis for understanding a number of issues of technological importance including mono-layer and interface formation, crystal growth, and surface phase transitions and chemical reactions.

The key to understanding these surface kinetic phenomena is the non-equilibrium transfer of energy between the phonon vibrations of the substrate and the adatom.

In the present work we use a generalized Langevin equation approach which includes fully the three dimensional microscopic dynamics of the substrate. The key quantities in this generalized Langevin equation are expressed simply in terms of the equilibrium displacement-displacement correlation functions $\langle u_i u_j(t) \rangle$ evaluated in the absence of the adatom. The evaluation of these correlation functions from the dynamical matrix of lattice elastic constants is formally analogous to the problem of the electronic properties of a tight binding Hamiltonian. We are using a powerful recursion method to evaluate these displacement correlation functions.

Research Achievements:

By taking advantage of the localized nature of the adatom substrate interaction, we have been able to express both the effective potential and the damping force on the adatom in terms of the clean substrate vibrational correlation functions. We have calculated these correlation functions for the reconstructed surface of W(100) and Si(100). It is found that lattice relaxation can greatly reduce the diffusion barrier. The other theoretical issue being investigated concerns the effect of three dimensional nature on the tunnelling probability of the adatom through the barrier. We find that a finite curvature of the reaction path can greatly enhance the tunnelling probability by reducing the effective mass of the adatom.

Publications:

S. C. Ying, "Effective Potential for Kinetic Processes on Semiconductor Surfaces," (with T. L. Reinecke), J. Vac. Sci. Tech. B2, 573 (1984).

An apparatus has been constructed to measure the diffraction and scattering of rare gas atoms from crystalline surfaces. It has been tested with He, Ne, and Ar beams on the (100) face of a LiF crystal. The most significant result is that for Ar beams the use of a velocity selector to pick out just the nearly elastic scattering reveals structure in the angular distribution almost completely obscured when molecules with the full range of scattered energies reach the detector. This suggests that phonon production in solids can be studied with beams of the heavier rare gases and promises to provide new insight into the nature of energy transfer that occurs when atoms strike surfaces.

Estrup and Greene have used a simple model to account for the compensation effect observed when desorption of atoms occurs from different surface phases. This compensation occurs when changes in the activation energy and preexponential factor in the Arrhenius form for the rate coefficient tend to occur together so their effects on the rate tend to counteract each other. Examples for which detailed results are available are the desorption of alkali metals from the Si surfaces mentioned above and the desorption of H₂ from W(100) as it varies with the temperature and fractional coverage of H₂ on the surface.

Publications:

E. F. Greene, J. T. Keeley, M. A. Pickering and D. K. Stewart, "Silicon (111) and (100) Surfaces and Their Interactions with Cs, K, Na and Li; Phase Changes and Kinetics of Desorption Studied by Surface Ionization," *Surface Sci.* 139, 185 (1984).

E. F. Greene, J. T. Keeley and D. K. Stewart, "Alkali Atoms on Semiconductor Surfaces: The Dynamics of Desorption and of Surface Phase Transitions," in Dynamics on Surfaces, B. Pullman and J. Jortner, eds, D. Reidel Publishing Co., 1984, p. 191.

The Scattering and Ionization of Atoms at Surfaces

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

Personnel: A. LeGrand, Graduate Student, Physics Department
D. Stewart, Graduate Student, Chemistry Department
J. S. Ha, Graduate Student, Chemistry Department

Sources of Support: DOE and MRL

Objectives and Approaches:

Molecular beams are used to probe the dynamics of surfaces. The angular and energy distributions recorded when well-collimated, nearly mono-energetic beams strike the outer layers of crystals give information about the structure of the surfaces and the amount of energy transfer between them and the bombarding molecules. In addition these molecules may be changed chemically. As a result of the impact they may be activated to decompose, they may be ionized by simply transferring an electron to the surface, or they may react with atoms on the surface.

Research Achievements:

Beginning with silicon, graphite, and silicon carbide we have started an extended study of the surfaces of semiconductors in the range 800-1200K as they are probed by beams of alkali atoms. Up to the present the most detailed results are for silicon.

The rates of desorption of Cs, K, Na, and Li from the (100) and (111) surfaces of silicon have been measured by surface ionization in the temperature range 800-1000K where the surfaces can be prepared in two forms. These are a stable form and another which is metastable below a surface phase transition. For the (111) surface this is a well known one at $1120 \pm 40\text{K}$ while for Si (100) it is a previously unreported one at $980 \pm 20\text{K}$. Below these temperatures the metastable forms convert spontaneously to the stable ones. On the metastable ones the desorption is first order and relatively rapid; comparison with a model suggests the atoms are highly mobile. In contrast, on the stable ones the desorption is slower and of mixed first and second order. A model having the adsorbed atoms concentrated at special sites such as ones along steps or edges on the surface can account for the results. The sticking probability is near unity on all the surfaces, and the smaller atoms, Li and Na, penetrate into the bulk to an appreciable extent.

Similar experiments on highly oriented pyrolytic graphite show that alkali atoms are bound on at least three kinds of sites between which the atoms are transferred at an appreciable rate but not rapidly enough to reach equilibrium.

Hamiltonian is derived starting from the usual lattice dynamic Hamiltonian. The soliton here represents an antiphase domain through which the in-plane displacement of W atoms go through a phase change of π . In the domain wall region, vertical components of displacements are mixed in, confirming the experimental results. Another important theoretical result concerns the effect of step boundaries on the phase transition. Due to the two component nature of the displacement, Monte-Carlo simulations show that there are a rich variety of displacement patterns possible near the boundary, depending on the orientation of the step boundaries.

Publications:

Ying, S.C., "Structural Phase Transitions on W and Mo Surfaces," to appear in Dynamical Phenomena in Surfaces, Interfaces and Superlattices, Springer-Verlag in Solid State Sciences (ed. M. Cardona).

Ying, S.C. and G. Y. Hu, "Theory of Commensurate-Incommensurate Transition on W(001)," to appear in Proceeding of First International Conference on Structure of Solid Surfaces, Berkeley, 1984.

Ying, S.C. and G. Y. Hu, "Effective Two-Dimensional Lattice Hamiltonian for Surface Structural Phase Transition," to appear in Surface Science.

Ying, S.C. and L. D. Roelofs, "Model for Surface Reconstruction Phase Transition for Clean and Hydrogen Adsorbed W(001) Surface: Low Coverage Solution," to appear in Surface Science.

Surface Structural Phase Transitions

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

Personnel: G. Y. Hu, Graduate Student, Physics Department

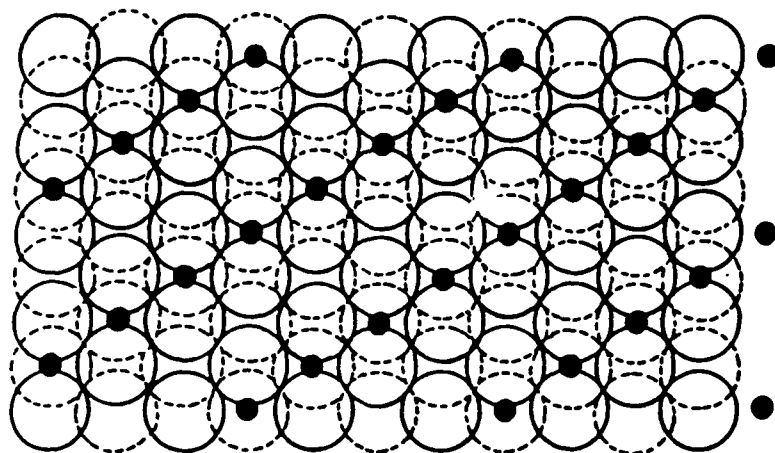
Sources of Support: MRL

Objectives and Approaches:

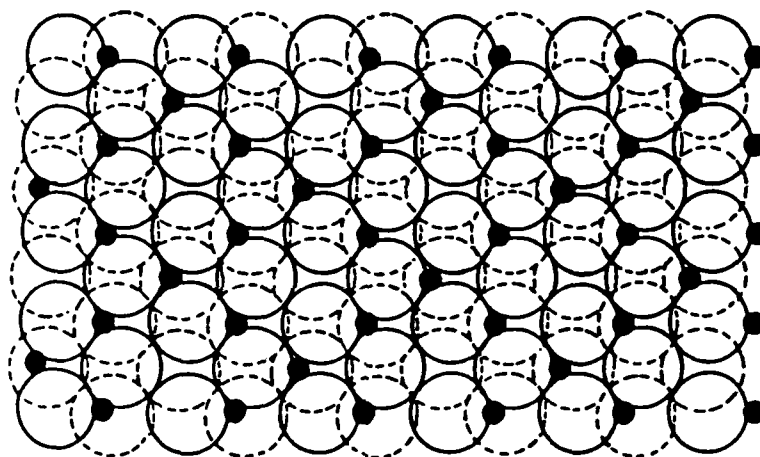
In chemisorption systems, a rich variety of surface structures has been found as a function of temperature and adsorbate coverage. In most cases the occurrence of different phases can be understood, at least qualitatively, with a lattice gas model in which the adsorption is site specific and the ordered phases are due to the lateral adsorbate-adsorbate interaction. However, recent experiments indicate that in the case of W(001) and Mo(001) even the clean surfaces undergo a reversible structural phase transition as the temperature is lowered. The role of the adsorbate at low coverage is to enhance or suppress the inherent instability of the surface towards reconstruction as well as to alter the relative stability of different structures which are close in energy. These phase transitions are of a different nature from those driven by adsorbate-adsorbate interactions. Our objective is to understand the nature of these new phases and propose new theoretical models for the study of these surface structural phase transitions. The theoretical approach uses both numerical Monte-Carlo simulation methods as well as analytical techniques such as renormalization group methods.

Research Achievements:

In the past few years, we have used a deformable lattice gas model to describe the surface structural phase transition on W(100) and Mo(100). This model allows us to understand many qualitative features of the phase diagram in the coverage temperature (θ, T) plane. In particular the theoretical understanding of the development of long range order just above the critical temperature allows us to unify many conflicting pictures of the phase transition. Recently we have shown that the commensurate-incommensurate transition on H/W(100) can be understood with the soliton picture. A microscopic soliton



Unreconstructed



Reconstructed

Publications:

J. W. Chung and P. J. Estrup, "Hydrogen-induced Reconstruction of W(110)," Forty-fourth Annual Conference on Physical Electronics (June 1984).

P. J. Estrup, "Reconstruction of Metal Surfaces," in Chemistry and Physics of Solid Surfaces V (Springer, 1984) 205.

Research Results

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 (through the use of Central
Facilities)

Objectives and Approaches:

Any detailed description of solid surface phenomena must include a model of the atomic geometry. In the case of transition metals the construction of such models is complicated by a tendency towards "surface reconstruction," a process in which the substrate atoms rearrange to give a new two-dimensional periodicity. On the (100) faces of molybdenum and tungsten, for example, the reconstruction can be induced either by lowering the temperature or by chemisorption of hydrogen. An improved understanding of the phenomenon appears to be essential for a microscopic description of chemisorption on transition metals and perhaps on other substrates as well.

Research Achievements:

The chemisorption of hydrogen on a tungsten(110) surface has been studied by means of Video LEED and related techniques. Simultaneous monitoring of many diffraction beams reveals that when the hydrogen coverage θ exceeds 0.5 monolayers, the symmetry of the surface is lowered due to the disappearance of one of the two mirror planes which exist at low θ . This effect is interpreted as being due to a hydrogen-induced reconstruction of the W(110) substrate, in which the top tungsten layer shifts laterally in the $\langle 110 \rangle$ direction, as illustrated in the figure (the black dots represent H atoms, the circles the top W layer, and the broken circles the second W layer). The proposed reconstruction has the effect of altering the long-bridge sites on which the adatoms are believed to be located. The model therefore offers an explanation of the coverage dependence seen in previous studies of the work function, the desorption rate, the photoelectron spectrum, and the diffusion coefficient.

Research Results

Conformational and Electronic Transitions in Macromolecular Systems

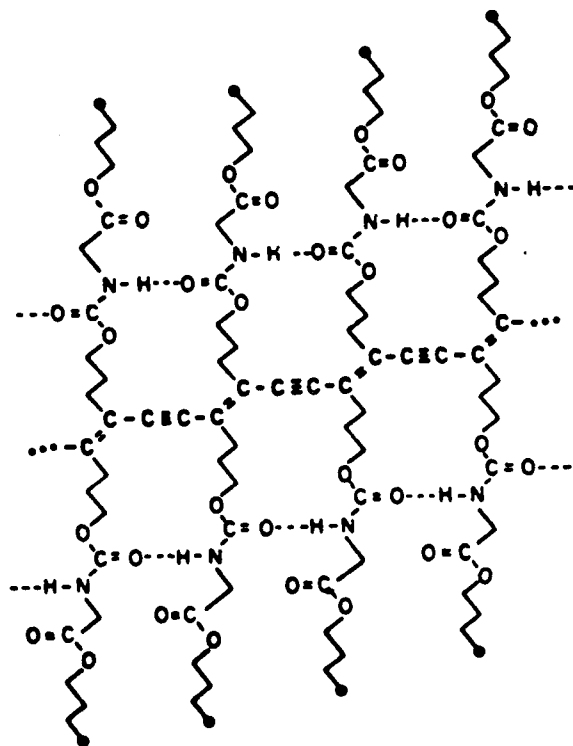
Principal Investigator: R. M. Stratt, Assistant Professor,
Chemistry Department

Personnel: S. Demoulini, Graduate Student, Chemistry Department

Sources of Support: NSF and MRL

Objectives and Approaches:

With the study of conjugated polymers such as polydiacetylene



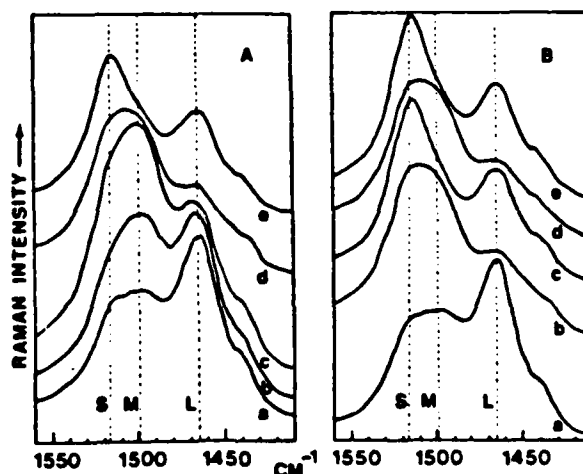
has come the realization that the physics of pseudo-one-dimensional, electron delocalized, materials involves far more than simply the conductivity. In the case of the actual polydiacetylene pictured, one also has to explain the dramatic sudden color changes that occur as the temperature is raised (or as the solvent composition changes in solutions). Spectroscopic evidence suggests that these polymers exist in a variety of conformations, which, in turn, suggests that the conjugation along the backbone is broken into more-or-less electronically independent regions by virtue of the rotations about

single bonds. Thus it is clear that the polymer conformation and the polymer electronic structure are intimately connected. What is not clear, however, is just what the appropriate conformations are.

In order to understand the conformational statistical mechanics, during 1983 my group started investigating simple models of the ways in which the long ranged influence of the electronic structure could lead to cooperativity among the torsional angles in a conjugated polymer. We were quickly led to predict the existence of "conformational defects" in such polymers: relatively well localized collections of backbone twists which were capable of interrupting the π -electron delocalization, but which were also capable of translating up and down the length of the chain. Frustratingly, the actual structure of the defects, though the subject of some study, had to be left unresolved. Still, we noted that it was very likely that there was some topological character to these defects in a condensed phase. That is, the shear bulk of the polymer was likely to restrict sharply those motions which could lead to easy removal (or creation) of these defects.

Research Achievements:

It turned out that the notion that the defects might have an interesting kinetics could be put to a severe experimental test. In collaboration with William M. Risen, Jr., the resonance Raman spectra of solutions of poly-3BCMU (the polymer pictured previously) was studied both as a function of temperature and of the history of the sample:



Resonance Raman spectrum of poly-3BCMU solution as a function of temperature and history showing the C = C stretching region. (A) The progression of (a) 25 °C → (b) 35 °C → (c) 45 °C → (d) 55 °C → (e) 25 °C. (B) The progression (a) 25 °C → (b) 55 °C → (c) 25 °C → (d) 55 °C → (e) 25 °C. The small peaks at 1445 and 1455 cm^{-1} are due to the hexane in the solvent mixture.

We found that the double bond stretching frequencies at room temperature (a sensitive indicator of the conjugation length(s) in the polymer) were different depending on whether or not the sample had ever been exposed to a higher temperature. When they were so exposed, the spectra revealed that short conjugation lengths were quenched almost permanently into the polymer. Indeed subsequent experiments showed that whatever relaxation there was occurred only on time scales of weeks or even months.

Aside from strongly supporting our ideas of there being conformational defects and of these defects being, in some way, metastable, these experimental results also forcefully suggested that we could consider each single polymer chain as if it were glass-like. By analogy with ordinary glasses, the original low temperature phase, with few conformational defects, plays the role of a crystalline solid; the high temperature phase, with its many defects, mirrors a liquid; which makes the low temperature phase resulting from cooling down the high temperature phase (and quenching in defects in the process) effectively a glass. Such an analogy clearly implies that some of the theoretical methods used for treating disordered systems may prove useful - an idea we are currently testing.

Publications:

R. M. Stratt and S. J. Smithline, "The Equilibrium Statistical Mechanics of Cooperative Intramolecular Behavior in Molecules with Coupled Conformational and Electronic Transitions," J. Chem. Phys. 79, 3928 (1983).

J.-M. Y. Ha, R. M. Stratt and W. M. Risen, Jr., "Observation of Glass-like Behavior in Conjugated Polymer Molecules," J. Chem. Phys. 81, 2855 (1984).

Surface Modification of Polymers

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

Personnel: L. Ytuarte, Graduate Student, Chemistry Department
C.-H. Jun, Graduate Student, Chemistry Department

Sources of Support: MRL, NSF, PRF and NIH

Objectives and Approaches:

The MRL funding has permitted us to extend our interest in hydrocarbon activation to the technologically and scientifically interesting problem of surface modification of organic polymers. It is often the case that a polyolefin such as polyethylene or polypropylene has desirable bulk properties, but the unreactive surface causes problems with undesirable adhesion, wettability, biocompatibility or electrostatic properties (see D. M. Brewis and D. Briggs, *Polymers*, 22, 7 (1981)). Thus, empirical treatments have been devised to modify the hydrocarbon polymer surface, including flame treatment, plasma processing, and the most common technique, chromate baths (P. V. Horton, U.S. Pat. 2,668,134). We are seeking to understand the chemistry, at the molecular level, of these surface treatments which introduce oxygenated groups and to develop better oxidants for hydrocarbon polymer surfaces, ones that avoid pitting of the surface and ones that avoid the use of carcinogenic materials. If one imagines what a polyethylene surface looks like at the molecular level, it resembles an unkept hedge, with individual polymer strands protruding above the bulk. In a sense, we are trying to invent molecular hedge clippers for these surfaces. A longer range goal is to correlate the surface oxidation state with bulk mechanical properties. I have been told that the fracture parameters of organic polymers change if one uses a N_2 atmosphere or O_2 , which implies that surface oxidation state may change mechanical properties.

Research Achievements:

We have been looking at very reactive molecular oxidants for the surface oxidation of hydrocarbon polymers in order to understand the basic mechanisms of surface functionalization. A molecule which turns out to be highly reactive is a variant on the species found in chromate baths - the molecule chromyl trifluoroacetate ($CrO_2(O_2CCF_3)_2$). We have found that this reacts at room temperature in organic solvents with hydrocarbon C-H bonds. It is selective for tertiary C-H bonds (as found in polypropylene), but will also attack secondary C-H bonds (as found in polyethylene). Both alcohol and ketone functional groups form, but selective conditions can be found to give only alcohols. Investigating this oxidant with the model hydrocarbon adamantane we have noticed that the oxidation is product inhibited, resulting in

inefficient utilization of the oxidant. We have found that the reason this occurs is because the $\text{CrO}_2(\text{O}_2\text{CCF}_3)_2$ reacts with the product alcohol to form chromate esters which do not react with hydrocarbon C-H bonds. The stoichiometry of these esters are being investigated as well as protocols which result in more efficient use of the molecular oxidant. We are now beginning spectroscopic studies of the functional groups formed on hydrocarbon polymers to compare these with the groups formed on our model hydrocarbons.

Publications:

J. W. Suggs and C.-H. Jun, "Directed Cleavage of Carbon-Carbon Bonds by Transition Metals: The Alpha-Bonds of Ketones," J. Am. Chem. Soc. 106, 3054, 1984.

J. W. Suggs, M. J. Wovkulich and S. D. Cox, "Synthesis, Structure and Ligand Promoted Reductive Elimination on an Acylrhodium Ethyl Complex," Organometallics, in press.

J. W. Suggs and C.-H. Jun, "Metal Catalyzed Alkyl Ketone to Ethyl Ketone Conversion in Chelating Ketones via Carbon-Carbon Bond Cleavage," J. Chem. Soc. Chem. Comm., 92, 1985.

Excluded Volume Effects in Rubber Elasticity

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

Personnel: J. Gao, Graduate Student, Physics Department

Sources of Support: MRL and Gas Research Institute

Objectives and Approaches:

The subject of rubber elasticity deals not only with natural and synthetic rubber, but with all polymeric materials which exhibit similar mechanical properties. The molecular nature of these materials is an amorphous network of highly flexible long-chain molecules which are cross-linked to each other through chemical bonds at widely separated random sites along their length.

It is now just fifty years since the recognition of the central role of entropy changes in the mechanical behavior of such network; these entropy changes are due to the high mobility of the chains and the way this mobility is decreased upon stretching. The theory which developed by the mid 1940's based on this concept has proved to be remarkably successful although some discrepancies between experiment and theory were noted at that time.

In spite of many years of effort, these discrepancies remain unresolved and they remain a subject for current research.

Research Achievements:

In addition to the strong covalent bonds which form the backbone of long-chain molecules, there are strong repulsive interactions which come into play when two atoms either from the same chain or from different chains attempt to occupy the same point in space. These are referred to as excluded volume interactions. In the theory of rubber elasticity it has been generally assumed that these interactions serve primarily to maintain the material at nearly constant volume, as in a liquid, and beyond that do not play a significant role.

We are currently re-examining this question by means of the computer simulation of idealized network models. These simulations, based upon the kinetic rather than the entropic viewpoint, provide new physical insights and suggest that intramolecular excluded volume effects contribute to the stress transmission in amorphous network in a manner which depends upon the state of strain. They also indicate the utility of new types of statistical mechanics formulation of rubber elasticity which we are now studying.

Publications:

J. Gao and J. H. Weiner, "Excluded Volume Effects on Stress Transmission in Rubber Elasticity," J. Chem. Phys., 81, 6176 (1984).

Bond Forces in Long-Chain Molecules

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

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

Sources of Support: MRL and Gas Research Institute

Objectives and Approaches:

There has been extensive research over the years on the force-length relation for long-chain molecules. Here what is desired is the force, referred to as the axial force, which must be applied to the end atoms of the molecule in order to maintain a given end-to-end displacement. Knowledge of this force-length relation is important for understanding the elastic behavior of a large amorphous cross-linked network of such chains, as in the subject of rubber elasticity.

Research Achievements:

When we turn to the question of crack initiation in such materials by the process of bond breaking, it is not the axial force which is of direct relevance, but rather the bond force, that force which acts on a particular covalent bond of the backbone chain.

By the use of equilibrium statistical mechanics, we have developed theoretical formulae for the bond forces in a freely-jointed long-chain molecule of arbitrary length with arbitrary end-to-end displacement. An unexpected aspect of these results is that the mean bond force is large and tensile even when the end-to-end displacement is zero and, in the absence of excluded volume effects, the axial force vanishes. This tensile bond force is due to the large-scale thermal motion and accompanying centrifugal forces.

We have also found theoretical expressions for the fluctuations in the bond forces. These fluctuations turn out to be quite large.

Computer simulation of the model confirmed the theoretical results and also provided a kinetic view of the process.

Publications:

J. H. Weiner and D. H. Berman, "Thermomechanical Behavior of Interacting Tie Molecules in Semicrystalline Polymers," *Macromolecules* 17, 2015 (1984).

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

Physical and Electronic Properties of the Ge_3N_4 -Ge Interface

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

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

Sources of Support: MRL, Lansdale Transistor & Electronics Corp.

Objectives and Approaches:

The rapid increase in the number of transistors which can be successfully fabricated on one integrated circuit is making power dissipation a critical issue. One popular approach to this problem is the use of a circuit technology known as CMOS, in which the two types of metal-insulator-semiconductor field-effect transistors (MISFETs) -- those which use electrons as their conduction carrier and those which use holes as their conduction carrier -- are combined on one integrated circuit in a configuration which permits a substantial savings in power. Silicon, out of which all CMOS circuits are currently made, is not optimum since the mobility of its electrons and holes (and therefore the speed of silicon MISFETs) is not very high. Germanium is a logical candidate for high speed CMOS since it is the only semiconductor with high mobility for both electrons and holes. In addition germanium has very useful optoelectronic properties in optical fiber communication applications.

The major obstacle to the development of germanium CMOS is the absence of a suitable insulator for the MISFETs. Our approach to this problem is to examine the physical and electronic properties of the Ge_3N_4 system (Ge_3N_4 is an insulator) which is formed by thermal nitridation of germanium. We plan to demonstrate that this system has both the physical and electronic properties necessary for a viable MISFET based technology. Currently planned electrical studies include current-voltage and capacitance voltage measurements on MIS capacitors as well as various electrical measurements of MISFETs (which will be fabricated with the aid of the Microelectronics facility). Short range plans for physical measurements center around optical and electron microscopy. Longer range plans include microprobe and ESCA measurements of the films.

Research Achievements:

In the first four months of this project our major objective was to build up our nitridation facility and reproduce the previous work on thermal nitridation of germanium. This goal has largely been met. We have produced germanium nitride films using a wide range of growth conditions and compared the resulting film morphologies with morphologies of films produced under the same conditions in previous work done elsewhere. We have been able to essentially identically reproduce the previously obtained morphologies.

Additionally, we have made some preliminary electrical measurements on MIS capacitors. We have an ongoing problem with leakage in some of our large area capacitors, which we believe is related to wafer preparation prior to film growth. Solving this problem is currently the main focus of our work. In addition to current-voltage measurements, we have made some capacitance voltage measurements on some of the less leaky capacitors. Capacitance-voltage data shows the interface to be of reasonably high quality, and more sophisticated measurements aimed at quantifying these statements are planned.

SECTION 5 CENTRAL FACILITIES

Introduction

The MRL Central Facilities provide services for the MRL program as a whole, but in addition, most of them pursue research in areas of expertise of their directors who make use of the availability of advanced experimental equipment. We quote here the scientific accomplishments of A. Wold, Director of the Materials Preparation Facility, and his collaborators in cooperative programs with the National Magnetic Laboratory on Semimagnetic Semiconductors, with GTE Laboratories on new semiconducting chalcogenides and with the University of Wisconsin on photoluminescent and electroluminescent properties of manganese doped CdSe electrodes, and also the scientific accomplishments of W. M. Risen, Jr., Co-director of the Facility for Fourier Transform Spectroscopy, and his collaborators on new approaches to catalysis and on optically induced transformations in metal-charge transfer organometallic complexes.

Research Results

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
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. 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. Wolff, Director, M.I.T./Francis Bitter National
Magnet Lab

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

Objectives and Approaches:

Semimagnetic semiconductors are solid solutions of conventional semiconductors with transition metal compounds that crystallize in the covalently bonded structures of the parent semiconductor. The largest family of semimagnetics studied to date is based on the manganese chalcogenides which include $\text{Cd}_{1-x}\text{Mn}_x\text{S}$, $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$, $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$, and $\text{Hg}_{1-x}\text{Mn}_x\text{Te}$. These solid solutions form zincblende or wurtzite lattices over a wide range of x -values.

The program with M.I.T. has concentrated on some of these materials, i.e., $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$. The most remarkable properties of these compounds and the main interest in these materials stem from the large coupling between the magnetic and semiconducting subsystems. This is the s - d exchange coupling between the spin of an electron (or hole) near the band edge and the spins of the Mn^{2+} ions. The s - d interaction is usually assumed to be local, and of the Heisenberg-exchange type. Because of this interaction, the optical and transport properties of the semiconductor reflect the magnetic order in the Mn^{2+} subsystem, which can be modified by changing the temperature, the Mn^{2+} concentration, or by the application of an external magnetic field. In addition to effects due to the s - d interaction, the magnetic order in the Mn^{2+} subsystem is itself of great interest. At low Mn^{2+} concentrations, the magnetic properties are governed by the probabilities of finding isolated Mn^{2+} spins, pairs of coupled spins, triplets, etc., and by the exchange constants. For moderate x , spin-

glass behavior is observed. At high x , large antiferromagnetically ordered spin clusters occur at low temperatures. The rich variety of magnetic and semiconductor properties, and their interdependence, make the semimagnetics the ideal meeting ground of magnetism and semiconductor physics.

The crystal chemistry of the semimagnetics is also unusual. Most transition metal compounds do not form solid solutions with semiconductors. The special stability of the Mn^{2+} ion in covalently bonded structures is presumably a result of the localized nature of the $3d^5$ configuration.

In this collaboration, the crystal growth and preliminary characterization are carried out at Brown by D. H. Ridgley, R. Kershaw, K. Dwight and A. Wold. The physics experiments and theory are performed at the Francis Bitter National Magnet Laboratory at M.I.T. by R. L. Aggarwal, D. E. Heiman, Y. Shapira and P. A. Wolff. The two groups meet at three-week intervals at M.I.T. and the topics discussed include sample characterizations, crystal chemistry issues, and the results of physics measurements.

Research Achievements:

Brown's Contribution to the Cooperative Program with the National Magnet Laboratory at M.I.T.: As-grown crystals of $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ possessed a relatively high range of inhomogeneity with respect to manganese distribution from top to bottom of the boules. An equilibrium state could, however, be attained by a subsequent five-day annealing of the growth tube in the constant temperature zone of a wound-core transport furnace at 600°C to yield samples with high resistivity. The crystals thus formed were cut into discs and subjected to various treatments and measurements. The addition of excess cadmium and trace quantities of gallium or indium to slices of the crystal, and annealing in evacuated silica tubes at various temperatures, increased the conductivity as well as the number of carriers. The maximum number of carriers obtained was $2 \times 10^{19} \text{ cm}^{-3}$.

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

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

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

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

References

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

Publications:

R. L. Aggarwal, S. N. Jasperson, J. Stankiewicz, Y Shapira, S. Foner, B. Khazai and A. Wold, "Magnetorelectance at the Band Edge in $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$," Phys. Rev. B 28 (12), 6907 (1983).

Y. Shapira, S. Foner, D. H. Ridgley, K. Dwight and A. Wold, "Technical Saturation and Magnetization Steps in Diluted Magnetic Semiconductors: Predictions and Observations," Phys. Rev. B 30, 4021 (1984).

D. Heiman, Y. Shapira, S. Foner, B. Khazai, R. Kershaw, K. Dwight and A. Wold, "Exchange Energy, Magnetization and Raman Scattering of $(\text{Cd,Mn})\text{Se}$," Phys. Rev. B 29, 5634 (1984).

J. Warnock, D. Heiman, P. A. Wolff, R. Kershaw, D. H. Ridgley, K. Dwight, A. Wold and R. Galazka, "Determination of the Antiferromagnetic Exchange Constant Between Nearest-Neighbor Mn^{++} Ions in $\text{Cd}_{0.95}\text{Mn}_{0.05}\text{Se}$," Proc. XVII Intl. Conf. Physics Semiconductors, San Francisco, 1984 (to be published).

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 Commu. (in press).

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

Principal Investigator: A. Wold, Vernon 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. Baglio, Research Chemist, GTE Laboratories

Sources of Support: NSF, GTE, MRL and ONR

Objectives and Approaches:

Hydrodesulfurization Catalysts

The transition metal dichalcogenides MoS_2 and WS_2 have important applications as hydrodesulfurization catalysts (compounds capable of removing sulfur from fossil fuels). These compounds are made more efficient by the addition of a promotor such as cobalt or nickel. We have been engaged in a joint program with GTE to understand the role of cobalt in the improvement of the catalytic activity of MoS_2 .

Last year we reproduced the work of Bahl, et al. (1, 2) which showed that when MoS_2 is heated in an oxidizing atmosphere above 400°C , oxidation takes place preferentially at edge planes or dislocation steps. It has also been shown by Topsøe (3) that in the hydrodesulfurization catalyst $\text{Co-Mo-S}/\gamma\text{-Al}_2\text{O}_3$, the cobalt is present at vacant molybdenum edge sites forming a surface CoMoS phase. We have been studying the nature of this phase using SEM and Hall measurement techniques. Our results to date fail to confirm the existence of a true CoMoS phase. Instead, all of the cobalt appears to occupy surface edge sites. With our new chromatographic equipment we should be able to show the relationship between the nature of this surface phase and the activity of the HDS catalyst.

References

- (1) O. P. Bahl, E. L. Evans and J. M. Thomas, Surface Science 8, 473 (1967).
- (2) O. P. Bahl, E. L. Evans and J. M. Thomas, Proc. Roy. Soc. A 306, 53 (1968).
- (3) H. Topsøe, B. S. Clausen, R. Candia, C. Wivel and S. Mrup, J. Catal. 68, 433 (1981).

March 22, 1984

Condensed Matter Seminar: Professor Nabil Lawandy, Division of Engineering, Brown University, TWO FIELDS INTERACTING WITH A THREE LEVEL SYSTEM; OPTICAL BISTABILITY AND LASER INSTABILITY

Energy Seminar: Dr. Yoshihiro Hamakawa, Osaka University, RECENT ADVANCES IN AMORPHOUS SILICON SOLAR-CELL TECHNOLOGY AND JAPAN'S SUNSHINE PROJECT

Solid Mechanics Seminar: Mr. Gregory Fenves, University of California, Berkeley, EARTHQUAKE RESPONSE OF CONCRETE GRAVITY DAMS

March 23, 1984

Materials Science Seminar: Dr. Leontios Christodoulou, Martin Marietta Laboratories, EFFECT OF COBALT CONTENT ON THE SCC BEHAVIOR OF POWER METALLURGY ALUMINUM ALLOYS

March 27, 1984

Engineering/Applied Math Seminar: Dr. Tony Warnock, CRAY Research Corp., WHAT A SUPERCOMPUTER CAN DO

March 28, 1984

Materials Science Seminar: Dr. William J. Clegg, Oxford University, INTERFACE CONTROLLER DIFFUSIONAL CREEP

April 4, 1984

Materials Science Seminar: Dr. Nack Joon Kim, University of Wyoming, STRUCTURE AND PROPERTIES OF DUAL-PHASE STEELS

Condensed Matter Physics Discussion Group: Dr. Julia M. Phillips, AT&T Bell Labs, GROWTH AND CHARACTERIZATION OF EPITAXIAL FLUORIDES ON SEMICONDUCTORS

April 5, 1984

Condensed Matter Seminar: Dr. Helen H. Farrell, Bell Communications Research, ENERGY LOSS SPECTROSCOPY STUDIES OF SEMICONDUCTOR SURFACES

Solid Mechanics Seminar: Dr. Ramesh Talreja, Department of Solid Mechanics, The Technical University of Denmark, Lyngby, Denmark, ON INTERNAL VARIABLE REPRESENTATIONS OF DAMAGE STATES IN COMPOSITES

April 6, 1984

Solid Mechanics Seminar: Dr. Laurence S. Costin, Sandia National Laboratories, MICROFRACTURE DAMAGE IN BRITTLE MATERIALS UNDER STATIC AND DYNAMIC LOADING

February 27, 1984

Physics Colloquium: Dr. Dan Stein, Princeton University, THE KAPITZA PROBLEM AT ULTRALOW TEMPERATURES

Solid Mechanics Seminar: Dr. T. X. Yu, Cambridge University Engineering Department, Currently Visiting Research Associate, Brown University, SPRINGBACK AND WRINKLING OF PLATES STAMPED INTO CURVED DIES

February 28, 1984

Inorganic Glasses Seminar: Professor H. Maris, Department of Physics, Brown University, PHONONS IN GLASSES

February 29, 1984

Condensed Matter Physics Discussion Group: Nicholas Read, Imperial College, THE MIXED VALENCE PROBLEM

March 1, 1984

Condensed Matter Seminar: Professor M. Pollak, University of California at Riverside, TRANSPORT IN DISORDERED SYSTEMS

March 5, 1984

Solid Mechanics Seminar: Dr. Renator Perucchio, Lecturer/Research Associate, Department of Structural Engineering, Cornell University, COMPUTER GRAPHICS MOSELLING AND BOUNDARY ELEMENT ANALYSIS FOR THREE DIMENSIONAL ELASTIC FRACTURE MECHANICS

March 8, 1984

Condensed Matter Seminar: Mr. George K. K. Wong, Department of Civil Engineering, Stanford University, A DISLOCATION METHOD FOR SOLVING 3-D CRACK PROBLEMS IN LINEAR ELASTIC SOLIDS

March 13, 1984

Inorganic Glasses Seminar: Professor C. Elbaum, Department of Physics, Brown University, LOW TEMPERATURE PROPERTIES OF METALLIC GLASSES

March 14, 1984

Condensed Matter Physics Discussion Group: Dr. G. Giuliani and Professor J. J. Quinn, Department of Physics, Brown University, SOME THOUGHTS ON THE FRACTIONAL QUANTUM HALL EFFECT

March 15, 1984

Solid Mechanics Seminar: Mr. Aik-Siong Koh, University of Texas at Austin, ROCKING OF A RIGID BLOCK ON A MOVING FOUNDATION, ALLOWING UPLIFT

January 23, 1984

Solid Mechanics Seminar: Dr. S. Tanimura, Visiting Associate Professor of Engineering (Research) University of Osaka Prefecture, Osaka, Japan, RECENT EXPERIMENTAL AND THEORETICAL RESULTS ON DYNAMIC PLASTICITY IN JAPAN

January 26, 1984

Condensed Matter Seminar: Dr. Alex Baratoff, IBM Research Lab, Zurich, THEORY OF SCANNING, TUNNELING MICROSCOPY: A NEW SURFACE PROBE WITH ATOMIC RESOLUTION

January 31, 1984

Inorganic Glasses Seminar: Professor W. M. Risen, Jr., Chemistry Department, Brown University, SPECTRAL STUDIES OF IONIC OXIDE GLASSES

February 2, 1984

Condensed Matter Seminar: Professor Peter Nightingale, University of Rhode Island, WETTING AND GROWTH BEHAVIORS IN ADSORBED SYSTEMS WITH LONG-RANGE FORCES

February 9, 1984

Condensed Matter Seminar: Dr. Ian K. Robinson, Bell Labs, X-RAY DIFFRACTION ANALYSIS OF RECONSTRUCTED SURFACES

February 13, 1984

Special Solid State Seminar: Dr. W. P. Su, University of Illinois, SOLITON EXCITATIONS IN A MIXED PEIERLS SYSTEM

Solid Mechanics Seminar: Professor S. Nemat-Nasser, Department of Civil Engineering, The Technological Institute, Northwestern University, MICROMECHANICS OF BRITTLE FAILURE IN COMPRESSION: THEORY AND EXPERIMENT

February 14, 1984

Inorganic Glasses Seminar: Professor P. J. Bray, Department of Physics, Brown University, MRL STUDIES OF GLASS STRUCTURE

February 20, 1984

Solid Mechanics Seminar: Dr. C. R. Calladine, Reader in Structural Mechanics, Cambridge University, Cambridge, England, THE STRENGTH OF THIN PLATES IN COMPRESSION

February 23, 1984

Condensed Matter Seminar: Dr. Aron Pinczuk, Bell Laboratories, FREE CARRIERS, PHONONS, AND EXCITONS IN SEMICONDUCTOR SUPERLATTICES

November 3, 1983

Joint Condensed Matter and Inorganic Glasses Seminar: Professor Gary Grest, Exxon Labs, RELAXATION PHENOMENA IN GLASSES

November 9, 1983

Solid Mechanics Seminar: Dr. X. R. Wu, Royal Institute of Technology, Sweden, SURFACE CRACKS IN RESIDUAL STRESS FIELDS IN WELDED PLATES

November 10, 1983

Condensed Matter Seminar: Dr. V. J. Emery, Brookhaven National Lab, FRACTIONAL QUANTIZATION OF THE HALL EFFECT

November 17, 1983

Joint Condensed Matter, Surfaces/Interfaces and Physical Chemistry Seminar: Dr. Galen B. Fisher, General Motors Research Labs, ELECTRON SPECTROSCOPY OF SURFACES SPECIES: MOLECULAR CLUSTER ANALOGY

November 21, 1983

Joint Mechanics of Solids and Materials Science Seminar: Professor Harold Margolin, Department of Physical and Engineering Metallurgy, Polytechnic Institute of New York, STRAIN DISTRIBUTION EFFECTS IN TWO-PHASE α/β TITANIUM ALLOYS

December 5, 1983

Solid Mechanics Seminar: Dr. P.-S. Lam, Research Associate, Brown University, NUMERICAL ANALYSIS OF STEADY CRACK GROWTH IN SMALL-SCALE YIELDING

December 8, 1983

Condensed Matter Seminar: Dr. W. D. Draeft, Rostock University, East Germany, NON-IDEAL GASEOUS AND SOLID STATE PLASMAS

December 16, 1983

Joint Condensed Matter and Inorganic Glasses Seminar: Professor J. Hertz, Nordita, SPIN GLASS DYNAMICS

January 6, 1984

Seminar in Solid Mechanics and Structures: Dr. Miguel Ortiz, Head of Computational Hydrodynamic Program, Department of Coasts and Harbors, Ministry of Public Works, Madrid, ELEMENT BY ELEMENT PROCEDURES IN COMPUTATIONAL MECHANICS

October 11, 1983

Solid Mechanics Seminar: Professor Herman Riedel, Max-Planck Institute, RECENT THEORETICAL AND EXPERIMENTAL RESULTS ON CREEP CRACK GROWTH

October 12, 1983

Condensed Matter Physics Discussion Group: Dr. G. Giuliani, Brown University INELASTIC LIFETIME OF QUASI-PARTICLES IN TWO-DIMENSIONAL SYSTEMS

October 13, 1983

Theoretical Seminar: Dr. S. B. Libby, Brown University, THEORY OF THE QUANTIZED HALL EFFECT

October 20, 1983

Condensed Matter Seminar: Dr. John Toner, IBM, DISLOCATION LOOP THEORY OF THE LIQUID CRYSTAL NAC POINT

October 24, 1983

Physics Colloquium: Professor P. Lee, MIT, DISORDERED ELECTRONIC SYSTEMS

October 26, 1983

Condensed Matter Physics Discussion Group: Mr. David Hintenlang, Brown University, NMR STUDIES OF FIC GLASSES.

October 27, 1983

Joint Condensed Matter and Inorganic Glasses Seminar: Professor Eric Cotts, University of Virginia, THE INFLUENCE OF STRUCTURAL RELAXATION UPON THE LOW TEMPERATURE PROPERTIES OF METALLIC GLASSES

October 28, 1983

Chemistry Colloquium: Professor H. Maris, Brown University, HEROIC ATTEMPTS TO PREPARE SUPERFLUID LIQUID HYDROGEN

October 31, 1983

Solid Mechanics Seminar: Professor Erhard Krempl, Rensselaer Polytechnic Institute, VISCOPLASTICITY. THE INTERACTION OF HARDENING AND RATE-DEPENDENCE

Physics Colloquium: Professor E. Tosatti, International School for Advanced Studies/Trieste, Italy, RELAXATION, RECONSTRUCTION AND MELTING OF CRYSTAL SURFACES

LECTURES IN THE MATERIALS RESEARCH LABORATORY PROGRAM, 1983-84

July 19, 1983

Solid State Discussion Group: Professor P. Stiles, Physics Department, Brown University, QUANTIZED RESISTANCE IN TWO-DIMENSIONAL SYSTEMS.

July 26, 1983

Solid State Discussion Group: Mr. Peter Smith, Physics Department, Brown University, THERMOELECTRIC EFFECTS.

Solid State Discussion Group: Mr. Dale Syphers, Physics Department, Brown University, MULTIPLY-CONNECTED QUANTIZED RESISTANCE REGIONS.

September 12, 1983

Applied Mathematics Colloquium and Solid Mechanics Seminar: Professor M. Sayir, Institute of Mechanics, ETH Zurich, Switzerland, SOME APPLICATIONS OF PERTURBATION METHODS TO PROBLEMS OF SOLID MECHANICS

September 15, 1983

Condensed Matter Seminar: Dr. Harvey Scher, Xerox, THEORY OF GEMINATE RECOMBINATION ON A DISCRETE LATTICE

September 22, 1983

Condensed Matter Seminar: Professor Robert A. Pelcovits, Brown University, CHARGE DENSITY WAVES AND THE DEVIL'S STAIRCASE IN ONE-DIMENSION

September 26, 1983

Physics Colloquium: Dr. Horst Störner, Bell Laboratories, FRACTIONAL QUANTIZATION OF THE HALL EFFECT

September 28, 1983

Condensed Matter Physics Discussion Group: Professor J. J. Quinn, Brown University, SOME THOUGHTS ON THE QUANTUM HALL EFFECT

September 29, 1983

Condensed Matter Seminar: Dr. Robert Laughlin, Lawrence Livermore Laboratory, THE ANOMALOUS QUANTUM HALL EFFECT

September 30, 1983

Chemistry Colloquium: Dr. Richard Hall, Exxon Research Laboratories, LASER INDUCED SURFACE EXCITATION AS A REAL TIME PROBE OF SURFACE CHEMISTRY

Publications:

E. I. Kamitsos and W. M. Risen, Jr., "Raman Spectroscopic Study of Molecular Orientation in AgTCNQ Thin Films," J. Chem. Phys. 79, 477 (1983).

E. I. Kamitsos and W. M. Risen, Jr., "Raman Studies in CuTCNQ: Resonance Raman Spectral Observations and Calculations for TCNQ Ion Radicals," J. Chem. Phys., 79, 5808 (1983).

E. I. Kamitsos and W. M. Risen, Jr., "Optically Induced Transformations of Metal TCNQ Materials," Solid State Communications, 45, 165 (1983).

Optically Induced Transformations in Organometallic Complexes

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

Personnel: E. I. Kamitsos, Research Associate, Chemistry Department

Sources of Support: MRL/NSF and ONR

Objectives and Approaches:

The metal-charge transfer organometallic complexes of the type MTCNQ exhibit interesting electrooptical properties, including electric field-induced switching and optically induced transformations. In this work the mechanism of these transformations, the relationship between spectral properties and both structure and charge-transfer, and the role of the preparation methods were investigated. The goals of the studies are to discover transformation phenomena and determine the conditions under which optically induced transformations occur. The potential application for thin films of these and related materials is optically addressable switching and information storage media.

Research Achievements:

The work on this project in the previous period led to an understanding of the mechanism of electrical switching in CuTCNQ films. In this period optically induced transformations were reported. Both partial and complete transformations to the component metal and TCNQ were achieved with visible light, laser writing on thin films was achieved, and the conditions for spontaneous, thermal reversal of the process of optical transformation were determined.

The next stage of the research involved determination of the structures of the thin film materials and the relationship of their resonance Raman behavior to the electronic excitations of the TCNQ ion radicals. The structural studies were carried out by measuring the polarization and angle dependences of Raman scattered light. The key result is that the TCNQ radicals in AgTCNQ have a preferred orientation relative to the substrate and occur in relatively small domains in the region sampled in ca 2000 angstrom films. The spectral dependence of the resonance Raman spectra and the power dependence of the optical transformations, together with approximate quantum mechanical calculations on the TCNQ ion radicals, showed that the optical transformations are photochemical, and occur at lower electric field thresholds than those achieved by application of static electric fields.

ionomer domains was achieved in the cases of Ag, Rh, Pt, Ru and Pd ionomers. In some cases, such as Rh in PSSA, the particles were less than 10 angstroms in diameter, while in others, such as Pt, Ph and Ru in Nafions the ca 40 angstrom ionic domain structure apparently forced a very narrow metal particle size distribution peaked at ca 30 angstroms in diameter. Third, the small particles formed in these ionomers were shown to carry out reactions ranging from carbonyl formation and particle oxidation to catalyze CO oxidation and Fischer-Tropsch reactions. Fourth, the rates of several reactions were measured and compared with analogous reactions at exposed heterogeneous catalytic sites. The results included observation of Ag oxidation, the key to ethylene epoxidation catalysis, which exhibits the same kinetic form as known catalysts. The rates of CO oxidation over Rh, Ru and Pt-containing ionomers also were determined. The range of kinetic constants, in the form of standard turnover numbers, showed that the matrix was acting as a diffusion limiter in the cases of very fast reactions but not in the cases of such slower ones as the Pt-catalyzed CO oxidation. Thus, the metal ionomer systems have been shown to form small, well distributed metal particles in efficient molecular scale reactors, to catalyze important reactions and to retain their gas diffusion selectivity. Given that these materials are formable as films, the prospect for practical systems is significant. Further studies of the range of reactions that can be effected by this approach are planned.

Publications:

V. D. Mattera, Jr., P. J. Squattrito and W. M. Risen, Jr., "The Chemistry of Metals in Ionomers: Reactions of Rh-PSSA," *Inorganic Chemistry* 23, 22 (1984).

I. W. Shim, V. D. Mattera, Jr. and W. M. Risen, Jr., "The Chemistry of Ruthenium in PSSA Ionomers," *Journal of Catalysis*, in press.

G. Chryssikos, V. D. Mattera, Jr., A. T. Tsatsas and W. M. Risen, Jr., "Oxygen Adsorption on Silver in PFSA Films," *Journal of Catalysis*, in press.

D. M. Barnes, G. D. Chryssikos, V. D. Mattera, S. L. Peluso, I. W. Shim and W. M. Risen, Jr., "Chemistry in Ionomers," Chapter in *Ionic Polymers*, A.C.S. Symposium Series Book, American Chemical Society, in press.

V. D. Mattera, Jr., R. D. Gonzales, S. N. Chaudhuri and W. M. Risen, Jr., "Reactions of Platinum Ionomers," *Journal of Catalysis*, in submission.

Chemistry in Ionomers - New Approaches to Catalysis and Separation

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

Personnel: G. Chryssidos, I. W. Shim, V. D. Mattera, Jr.,
Graduate Students, Chemistry Department

Sources of Support: MRL/NSF Central Facilities, ONR

Objectives and Approaches:

There are a number of important considerations in carrying out chemical reactions that are catalyzed at metal-containing centers. They include obtaining the desired product in good yield, of course, but achieving favorable kinetics requires control of such variables as particle size and material flux. In addition, favorable process economics require lowering the work needed to obtain both good physical (PV) reaction kinetics and product separation. An ideal catalytic system would be one in which the product distribution and chemical kinetics as well as product separation and purification are attained at the lowest possible expenditure.

As a practical matter these requirements mean that for heterogeneously catalyzed reactions between gaseous species, the reaction pressures and temperatures should be low, the surface areas containing the catalytic sites must be high (particle sizes low), and the substrate must have high but selective gas flow characteristics. On the basis of our studies of ionic interactions in ionic oxide glasses and metal ionomers as models for them, we concluded that it was possible to approach such a system by using transition metal ionomers. The basic idea is that the metal ions in ionic domains could be reduced to yield small metal particles in a polymer matrix of high but selective gas flow characteristics. Once formed, such domains containing trapped metal particles would act as small reactors in which gas molecules admitted at low pressure would have a residence time at the catalytic sites equivalent to gases interacting with exposed catalytic sites at much higher pressure.

Research Achievements:

To explore this approach several transition metal ionomer systems have been investigated. While the results of the studies are too extensive to detail here, they can be summarized as follows. First, the feasibility and limits of this type of reaction system were explored using facile reactions, such as that of Cu^{+2} in Nafion and PSSA ionomers with NH_3 , and reactions, such as that of CO with Ag^+ in these ionomers, which are difficult to achieve without forcing conditions. Second, reduction to produce small metal particles in

ADDITIONAL PROGRAMS

Electrochemical Reduction of Benzene
Electronic Properties of Transition Metal Oxides
Reduction of Carbon Monoxide
Gasification of Carbon

Additional Personnel: M. Gray, Graduate Student, Chemistry Department
D. Pasquariello, Graduate Student,
Chemistry Department
J. Foise, Graduate Student,
Chemistry Department
L. Carreiro, Graduate Student,
Chemistry Department
J. Fournier, Graduate Student,
Chemistry Department
Y. Qian, Research Associate,
Chemistry Department

Additional Support: U.S. Army Research Office, Exxon Research
Laboratories

Additional Publications:

J. V. Marzik, R. Kershaw, K. Dwight, A. Wold, "Photoelectronic Properties of ReS_2 and ReSe_2 Single Crystals," J. Sol. St. Chem. 51, 170 (1984).

M. Tellefsen, L. Carreiro, R. Kershaw, K. Dwight and A. Wold, "Homogeneity and Magnetic Susceptibility in Some Substituted Cadmium Spinel," J. Phys. Chem. 88, 754 (1984).

D. Pasquariello, R. Kershaw, J. Passaretti, K. Dwight and A. Wold, "Low-Temperature Synthesis and Properties of Co_9S_8 , Ni_3S_2 and Fe_7S_8 ," Inorganic Chem. 23, 872 (1984).

Y-T Qian, R. Kershaw, S. Soled, K. Dwight and A. Wold, "Stability of Several Substituted Ferrites in a Reducing Atmosphere," J. Sol. St. Chem. 52, 211 (1984).

H. C. zur Loye, R. Kershaw, K. Dwight, J. K. Pabst, R. J. Lang and A. Wold, "Gasification of Carbon Using Calcium Oxide," Mat. Res. Bull. 19, 459 (1984).

M. Gray, W. Croft, K. Dwight and A. Wold, "The Effect of High Pressure on the Electronic Properties of VO_2 ," J. Sol. St. Chem 54 (3), 421 (1984).

The intensity of PL from the electrodes can be quenched by the electric field present in the semiconductor during PEC operation, although the spectral distribution is unaffected. The extent of PL quenching has been studied as a function of carrier concentration ($n \sim 1 \times 10^{16} - 4 \times 10^{18} \text{ cm}^{-3}$), excitation wavelength (457.9, 514.5 and 607nm), and applied potential (-0.7 V to open circuit, $\sim -1.4 \pm 0.1 \text{ V}$ vs. SCE).

The data are analyzed in terms of a dead-layer model previously used to describe PL quenching in semiconductor/metal (3) and PEC (4,5) Schottky barrier systems: electron-hole pairs formed within a distance on the order of the depletion width do not contribute to PL. Since the model relates PL intensity to the electric field in the semiconductor, it may possibly serve to map the field and thus to probe how applied potential is partitioned across the semiconductor-electrolyte interface.

When used as a dark cathode in aqueous, alkaline peroxydisulfate electrolyte, samples of $n\text{-Cd}_{0.95}\text{Mn}_{0.05}\text{Se}$ exhibit red electroluminescence (EL). The EL spectrum at low resolution is similar to the PL spectrum. Measured EL efficiencies, $\sim 10^{-5}$ to 10^{-6} , are comparable to PL efficiencies and suggest that population of the emissive excited state can be very efficient in EL experiments. The influence of etching, including photoelectrochemical etching, on PL and EL properties will be discussed.

References

- (1) B. Khazai, R. Kershaw, K. Dwight, and A. Wold, *Mat. Res. Bull.* 18, 217 (1983).
- (2) H. Wiedemeier and A. G. Sigai, *J. Electrochem. Soc.* 117, 551 (1970).
- (3) R. E. Hollingsworth and J. R. Sites, *J. Appl. Phys.* 53, 5357 (1982) and references therein.
- (4) W. S. Hobson and A. B. Ellis, *J. Appl. Phys.* 54, 5956 (1983).
- (5) R. Garuthara, M. Tomkiewicz and R. B. Silberstein, *J. Appl. Phys.* 54, 6787 (1983).

Publications:

A. A. Burk, Jr., A. B. Ellis, D. H. Ridgley, and A. Wold, "Photoluminescent and Electroluminescent Properties of $\text{Cd}_{0.95}\text{Mn}_{0.05}\text{Se}$ Electrodes," submitted to *Journal of Photoluminescence*.

Photoluminescent and Electroluminescent Properties of Mn Doped CdSe Electrodes

(Cooperative Program with the Department of Physics,
University of Wisconsin)

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

Personnel: D. H. Ridgley, Research Associate, Chemistry Department
A. B. Ellis, Professor, Chemistry Department,
University of Wisconsin
A. A. Burk, Graduate Student, Chemistry Department,
University of Wisconsin

Sources of Support: MRL and University of Wisconsin

Objectives and Approaches:

Photoluminescence (PL) and electroluminescence (EL) can be used to characterize electric fields in semiconductor electrodes through their influence on electron-hole (e^-h^+) pair recombination (1). Solid solutions of II-VI compounds such as n-CdS and n-CdSe have provided a useful family of tunable band gap materials for such studies (2). We have extended these studies to emissive electrodes derived from a solid solution of MnSe and CdSe. In this program we have found that PL from n-Cd_{0.95}Mn_{0.05}Se electrodes used in photoelectrochemical cells (PEC's) can be used to map the electric field in these solids, and that EL obtained from the electrodes originates, on average, nearer the semiconductor-electrolyte interface than PL.

Quenching of photoluminescence and initiation of electroluminescence from n-Cd_{0.95}Mn_{0.05}Se electrodes is used to map the electric field in these solids, grown by a modified Bridgman method.

Single-crystal samples of n-type Cd_{0.95}Mn_{0.05}Se, grown by a modified Bridgman method (1), have been used as electrodes in photoelectrochemical cells (PEC's) employing aqueous diselenide electrolyte. After etching with HCl/HNO₃ (1:1 v/v), the samples exhibit photoluminescence (PL) when excited with ultraband gap excitation ($E_g \sim 1.75$ eV) (2); the maximum of the PL band, ~ 690 nm, is near the band gap energy and appears to follow E_g , blue-shifting to ~ 680 nm at 77K. In some samples, subband gap PL is observed (uncorrected $\lambda_{max} \sim 890$ nm). The radiative efficiency, ϕ_r , of the edge emission can be as large as $\sim 10^{-4}$ at 295K and $\sim 10^{-2}$ at 77K.

Insulating Al_2O_3 Films on InP

The second part of our joint program with GTE has been to produce a dielectric film on InP (later on InGaAsP) which eliminates the unstable electrical properties associated with both multiphase and overlayer type structures. It is believed that, by forming a single phase of Al_2O_3 by chemical reaction of indium phosphate alcoholate solutions with derivatized InP (InGaAsP) surfaces, one can obtain a structure which exhibits the preferred dielectric properties while maintaining chemical and structural compatibility with the InP substrate. There are no known published results using this approach.

Films of Al_2O_3 on InP were prepared by spinning a colloidal solution of aluminum oxide on an etched crystal of InP. The colloidal solution was obtained by the hydrolysis of aluminum isopropoxide with aqueous acetic acid. A slice of InP (100) was etched with hydrogen peroxide and mounted on a photoresist spinner. The solution containing Al_2O_3 was added dropwise (total added 1 ml) rapidly and the spinning rate was maintained at 3000 rpm for 5 minutes.

The film was then heated in vacuum at 200°C for 2 hours and appeared to be uniform and homogeneous. The measured thickness of the films was approximately 6000Å as characterized by SEM. Measurements of the I-V characteristics indicated that 20 volts can be applied to the film without breakdown. Further work will be carried out in order to determine the number of surface states present compared to uncoated III-V samples.

Publications:

R. Brusasco, J. Gnassi, C. Tatian, J. Baglio, K. Dwight and A. Wold, "Preparation and Characterization of Fibrillar Boehmite and Gamma Al_2O_3 ," Materials Research Bulletin (in press).

D. M. D'Ambra, J. Marzik, J. Baglio, R. Kershaw, A. Wold, "Preparation and Properties of MoS_2 and WS_2 Single Crystals Grown in the Presence of Cobalt," to be published in Journal of Solid State Chemistry.

April 9, 1984

Physics Colloquium: Professor Janor Kirz, SUNY at Stony Brook, SYNCHROTRON RADIATION AND IT APPLICATIONS IN X-RAY MICROSCOPY

Joint Mechanics of Solids and Materials Science Seminar: Professor Harold Margolin, Department of Physical and Engineering Metallurgy, Polytechnic Institute of New York, STRAIN DISTRIBUTION EFFECTS IN TWO-PHASE α/β TITANIUM ALLOYS

April 11, 1984

Materials Science Seminar: Dr. James E. Krzanowski, Army Materials & Mechanics Research Center, Watertown, Massachusetts, MECHANISMS OF TEMPERED MARTENSITE EMBRITTLEMENT IN AN EXPERIMENTAL Mo-Cr STEEL

April 12, 1984

Condensed Matter Seminar: Professor C. Jayaprakash, Ohio State University, REGULAR ARRAYS OF JOSEPHSON JUNCTIONS

April 17, 1984

Seminar Series on the Physics and Chemistry of Inorganic Glasses: Professor Robert Cole, Chemistry Department, Brown University, STUDIES OF FAST CHARGE TRANSPORT PROCESSES

April 19, 1984

Condensed Matter Seminar: Professor Roger Bowley, Department of Physics, Brown University (University of Nottingham), KAPITZA CONDUCTANCES BETWEEN SOLID HELIUM AND HELIUM 3, HELIUM 4, MIXTURES

April 26, 1984

Condensed Matter Seminar: Professor A. A. Maradudin, University of California at Irvine, DIFFRACTION OF LIGHT BY A RANDOMLY ROUGH METAL SURFACE

May 1, 1984

Seminar Series on the Physics and Chemistry of Inorganic Glasses: Professor J. Tauc, Department of Physics and the Division of Engineering, Brown University, OPTICAL STUDIES OF ULTRAFAST PROCESSES IN GLASSES

May 3, 1984

Condensed Matter Seminar: Professor John Reppy, Cornell University, SUPERFLUIDITY IN A DILUTE BOSE GAS

May 7, 1984

Physics Colloquium: Professor David Edwards, Ohio State University, SURFACE OF SOLID HELIUM

May 14, 1984

Physics Colloquium: Dr. R. C. Dynes, Bell Laboratories, ELECTRON
LOCALIZATION AND METAL-INSULATOR TRANSITION

May 25, 1984

Joint Seminar - Materials - Fluids - Chemical - Combustion: Dr.
Stephen C. Danforth, Department of Ceramics, Rutgers University,
SYNTHESIS AND PROCESSING OF UNIFORM FINE CERAMIC POWDERS

LIST OF STAFF IN THE MATERIALS RESEARCH LABORATORY PROGRAM

APPLIED MATHEMATICS

Professors C. Elbaum (Physics) and A. Hikata (Research)

CHEMISTRY

Professors R. H. Cole, K. Dwight (Research), P. J. Estrup (Physics), E. F. Greene, W. M. Risen, Jr., A. Wold; Associate Professor G. J. Diebold; Assistant Professors R. M. Stratt, J. Suggs; Research Associates E. I. Kamitsos, Y. Qian, D. H. Ridgley, P. Winsor IV; Graduate Students D. M. D'Ambra, R. Brusasco, L. Carreiro, G. Chriyssikos, S. Demoulini, J. Erickson, J. Foise, J. Fournier, M. Gray, J.-M.Y. Ha, C.-H Jun, V. D. Mattera, Jr., P. R. Muessig, D. Pasquariello, J. Prybyla, I. W. Shim, D. Stewart, D. Turcotte, L. Ytuarte

ENGINEERING

Professors R. J. Asaro, R. J. Clifton, J. Duffy, L. B. Freund, J. Guralnd, G. S. Heller, A. Needleman, M. H. Richman, J. Tauc (Physics) J. H. Weiner (Physics); Associate Professor C. F. Shih; Assistant Professors R. D. James, J. Rosenberg, S. Suresh; Visiting Research Associate A. Marchand; Research Associates P. S. Lam, M. Toullos, Graduate Students R. Beck, R. Becker, D. Berman, K. M. Cho, H. I. Chung, D. Deve, A. A. Douglas, B. Glicksman, R. J. Godse, K. A. Hartley, D. Hymes, S. Harren, R. W. Klopp, S. Lee, J. LeMonds, F.-Z. Li, C. C. Ma, G. Meir, B. Moran, T. Nakamura, G. Ravichandran, A. J. Rosakis, T. Shawki, D. Steigmann, Y. L. Su, F. H. Wu; Former Graduate Students Y. W. Chang, L. L. Lisiecki, T. Goto, D. Q. Nelson; Undergraduate Student T. Christman; Senior Research Engineers E. E. Crisman, R. H. Hawley, R. J. Kershaw; Technical Assistants G. J. LaBonte, P. Rush, H. J. Stanton

MATERIALS RESEARCH LABORATORY

Research Associates J. R. Beamish and A. Khurana

PHYSICS

Professors P. J. Bray, C. Elbaum (Applied Mathematics), P. J. Estrup (Chemistry), A. Houghton, J. M. Kosterlitz, H. J. Maris, P. J. Stiles, J. Tauc (Engineering), S. C. Ying; Assistant Professor R. A. Pelcovits; Visiting Associate Professor W. Myung; Graduate Students M. Altman, S. J. Chung, J. W. Chung, G. Cibuzar, P. De, J. Gao, S. J. Gravina, J. S. Ha, M. Han, S. Heinekamp, E. Holupka, G. Y. Hu, K. F. Lau, J.-I Lee, A. LeGrand, B. Minchau, R. Mulkern, B. Parker, F. Seco, P. E. Stallworth, J. Strait, S.-P. Szu, C. Thomsen, S. Tiersten, M. L. Williams, J. Zhong; Undergraduate Student J. Smith; Senior Research Engineer E. E. Crisman.

PRINCIPAL INVESTIGATORS

Asaro, R.J.	54, 59, 69, 71
Bray, P.J.	86, 87, 95, 96, 97, 99, 100, 103, 104
Clifton, R.J.	43, 45, 46, 49
Cole, R.H.	84
Diebold, G.J.	117
Duffy, J.	4, 9, 15
Elbaum, C.	52, 53, 92
Estrup, P.J.	106, 113
Freund, L.B.	22, 25, 33
Greene, E.F.	110
Gurland, J.	27, 29, 30
Houghton, A.	80
James, R.D.	41
Maris, H.J.	76, 78
Needleman, A.	30, 31, 39, 71
Pelcovits, R.A.	82
Risen, Jr., W.M.	84, 88, 90, 138, 140
Rosenberg, J.	127
Shih, C.F.	31, 33
Suresh, S.	35
Stiles, P.J.	115
Stratt, R.M.	120
Suggs, J.	123
Tauc, J.	76
Weiner, J.H.	37, 125, 126
Wold, A.	130, 133, 135
Ying, S.C.	108, 112

END

FILMED

8-85

DTIC