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December 1972

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Department of Materials and Metallurgical Engineering

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REPORT

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of

THE MATERIALS RESEARCH COUNCIL

December 1972

ARPA Order Number: 0236 Program Code Number: 1D10 Contractor: The Regents of The University of Michigan Effective Date of Contract: 1 May 72 Contract Expiration Date: 30 June 73 Amount of Contract: \$237,690 Contract Number: DAHC15-71-C-0253 Principal Investigator: Professor Edward E. Hucke Department of Materials & Metallurgical Engineering The University of Michigan Ann Arbor, Michigan 48104 (313) 764-3302

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## INTRODUCTION

This report provides a summary of the activities and output of the Materials Research Council for the year ending December, 1972, the fifth year of operation of the Council. Detailed technical papers and memoranda are in preparation for separate publication.

The idea of a Materials Research Council originated in 1966 when several individuals in materials and materials sciences including Dr. Robb Thomson, Director of the Materials Sciences Office of ARPA, discussed the possibility of bringing together 20-30 outstanding people in the materials field for an extended period each year to examine this area of study and relate their concerns and interests to those of DoD in these fields. The group was to be briefed on the current state of emerging problems and was to be challenged to develop solutions, or a consensus for approaches to the possible solutions of such problems.

Subsequent development of this idea led to the formation of the ARPA Materials Research Council and the bringing together of a group for an extended period of study during the summer of 1968 for the first summer conference. The concept proved to be so fruitful that the Council was continued through 1969, 1970, 1971, 1972 and plans are currently being projected through 1973.

-1-

The Council has indeed occasionally worked concurrent high priority problems and expects to do so in the future, but the real value of the Council lies in its long range and broad interdisciplinary vision of materials problems. A primary strength of the Council lies in its ability to recognize and work on future critical needs, rather than on current critical problems.

The initial concept that the members of the Council should be among the most able and highly qualified individuals in the country has proved to be a wise decision. The recognized abilities of the Council members in their respective fields has been such that the entire group, physicists, chemises, and engineers, have interacted in such a fashion that they are probably one of the most coherent, versatile and knowledgeable groups working in materials science and materials engineering in the country. It is noteworthy that the group has maintained a high degree of continuity chroughout its four-year history.

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Since the personnel of the Council is drawn largely from the academic community it was felt that exposure to longer range materials problems would have a beneficial influence on research undertakings of Council members and their students. This has indeed been the case. Follow-on work from problems encountered in the Council has emerged at most of the institutions represerted by the Council membership. Several graduate students and post doctoral fellows are actively pursuing problems first formulated by the Council. They include such topics as surface

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chemistry, the physics of surfaces, fracture analysis, stress corrosion, plasticity, high-temperature thermodynamics, composite materials, refractory materials, electronic properties, optical properties, carbon thermodynamics, etc. The interdisciplinary nature of the group is reflected in the wide range of researches that have been generated as a result of the problems discussed in the Council.

## PROJECT ORGANIZATION

The technical direction of the ARPA Materials Research Council is delegated to a nine-man Steering Committee, which is representative of the various disciplines embodied in the Council. Membership on the Steering Committee is normally for a period of three years with replacements occurring each year. The functions of the Steering Committee are:

- a) Work with ARPA and interested parties who contact ARPA, to select problem areas for consideration by the Council.
- b) Select Council members, specialists and consultants to work with the Council.
- c) Evaluate and direct project activities.
- d) Participate in project management.

The current Steering Committee is as follows:

Dr. George H. Vineyard Secretary of the Steering Committee Brookhaven National Laboratory Upton, Long Island, New York 11973

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Professor Willis H. Flygare Noyes Chemical Laboratory University of Illinois Urbana, Illinois 61801

Professor John P. Hirth Metallurgical Engineering Department Ohio State University Columbus, Ohio 43201

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Professor James A. Krumhansl Department of Physics Clark Hall of Science Cornell University Ithaca, New York 14850

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Professor Howard Reiss Department of Chemistry University of California Los Angeles, California 90024

Professor James Rice Division of Engineering Brown University Providence, Rhode Island 62912

Dr. Robb iI. Thomson National Eureau of Standards Institute of Applied Technology Washington, D.C. 20234

Professor Michael Tinkham Lepartment of Physics Harvard University Cambridge, Massachusetts 02138

To carry out the work of the Council, a contract has been arranged between ARPA and The University of Michigan. The Project Director is Edward E. Hucke, Professor of Materials and Metallurgical Engineering. The following functions are performed by the University:

- a) Coordinating planning, through the Steering Committee.
- b) Providing a central, responsive contact point and clearing house for all Council affairs.
- c) Negotiating consulting agreements with the project participants, and handling all administrative and financial affairs.
- d) Publishing the reports issued by the Council.

The current contract terminates June 30, 1973.

The members of the Council in addition to the members of

the Steering Committee are as follows:

Professor Michael B. Bever Department of Metallurgy & Materials Science Massachusetts Institute of Technology Cambridge, Massachusetts 02139

Professor A. Bienenstock Materials Science Department Stanford University Stanford, California 94305

Professor Nico Bloembergen Division of Engineering & Applied Physics Harvard University Cambridge, Massachusetts 02138

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Dr. John J. Gilman, Director Materials Research Center Allied Chemical Corporation Morristown, New Jersey 07960

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Professor Walter Kohn Department of Physics University of California La Jolla, California 92037

Professor L'astus II. Lee Department of Applied Mechanics Stanford University Stanford, California 94305

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Professor Paul L. Richards Department of Physics University of California Berkeley, California 94720

Professor Albert J. Sievers Laboratory of Atomic & Solid State Physics Cornell University Ithaca, New York 14850

### PROBLEM SELECTION - BACKGROUND

In 1968 the Steering Committee, working with the ARPA Materials Science Office, arranged a series of briefings with various DoD agencies to examine those areas which were believed most appropriate for consideration by the Council. As a result of these meetings and subsequent discussions with the entire Council, four general topics were chosen for detailed examination:

Composite Materials

Shock Propagation

Constitutive Relations at High Temperatures and Pressures

### Underground Sensing

At the 1968 summer conference, consultants and specialists worked with the Council to define more closely the problem areas, and to inform the Council members of related programs and progress. Individual members then worked either independently or in small

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subgroups on various segments of the problem areas and, after discussion and analysis, issued reports.

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The original concept of holding a summer conference where the entire Council could devote its concentrated efforts to a few selected issues proved to be fruitful, but it was evident that more detailed preparation prior to the summer conference was necessary in order to use the talents of the Council efficiently. Consequently, procedures were established for individuals or subgroups of the Council to undertake activities such as visits to DoD installations and DoD contractors or continuing investigations at home institutions in preparation for the following conference.

The technical report of the activities of the 1969 conference stimulated several meetings of the Council members with representatives of DoD laboratories. The results of this interaction were conveyed to the Steering Committee, enabling modification and addition of subject areas for the 1970 conference. Out of this meeting arose the following major areas of investigation:

 Shock - continuation of efforts were to examine studies of the Grüneisen constant; electrical effects; dispersion by periodic structures; and dislocation structures.

2) Fracture - continuation of efforts to define crack propagation criteria, particularly in multiphased materials; define strain conditions at moving cracks; formulation of dislocation models of fracturing materials undergoing plastic

-8-

deformation; and examination of surface energy considerations.

3) Composites - continuation of metal matrix composite investigation; examination of gradient composites; study of carbon composites; and analysis of wave propagation in composites.

Optics - continuation of analysis of laser glass
 materials problems; and optical properties of special composites.

5) New Materials - continued examination of materials and property measurements at extreme conditions of temperature; novel chemical combinations; and disordered carbon structures.

6) Stress Corrosion - continuation of survey of the field; examination of specific mechanisms.

7) Materials for Meeting Societal Needs - examination of superconductors for a magnetically suspended transportation system.

8) Bic Materials - examination of materials compatibility in human bodies; materials problems in artificial organs; blood clotting; biological polymers.

The Steering Committee recommended after the 1970 meeting that the Council conduct more small meetings during the year for the purpose of preparing a given subject area for the summer conference. In this way it would be possible to have the necessary outside consultants contacted early enough to allow them to plan to attend portions of the conference and to identify, secure, and screen the relevant literature. Preconference organizational meetings were held for planning in the subjects of Environmental Degradation of Materials, Amorphous Semiconductors, and Stable

-9-

Disordered Carbon Systems. It was proposed that aside from problem areas continuing or arising from previous Council activities, that a closer link be established between the Council and the ARPA Materials Science Director. In this way the talents of the Council could be brought to bear for the purposes of evaluation of future research directions in a particular problem area so as to serve as a long-range advisory group for the ARPA Materials Science Director. This objective was carried forward in the selection of problems for the 1971 summer conference. In line with the decision of the Steering Committee, several of the subject areas were organized into short meetings of one to three days duration. Considerable use was made of outside consultants with a structured program of presentations and a report of conclusions.

The 1971 activity in the remaining subject areas was carried out in the more traditional means by indivduals or two to five man discussion groups. The subject areas are listed below.

> Environmental Degradation of Materials Materials Factors in Design with Erittle Materials Gradient Materials Infra-red Transmitting Materials Amorphous Semiconductors Stable Disordered Carbon Systems Amorphous Metals Applications of Superconductivity Properties of Non-Biological Polymers Fracture Mechanics Materials at High Temperatures Stress Waves in Composite Solids Surface Thermodynamic Problems Irreversible Thermodynamics Solid Electrolytes

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### SUMMER CONFERENCE - 1972

The conference was held during the month of July, 1972, at the Centerville School in Centerville, Massachusetts. A list of the invited guests and consultants to the Council is appended. Pre-conference organizational meetings were held for planning in the case of the Environmental Degradation of Materials, Failure Prevention, and Design with Brittle Materials.

Several of the subject areas were organized into short meetings of one to three days duration, attended by outside experts. These meetings prompted considerable discussions and in most cases lead to the writing of technical memoranda or, in some cases, published papers. For these meetings a short summary is given in the appendix of this report as a technical memorandum, while a fuller account is to be published with the yearly report of the project.

The activity in the remaining subject areas was carried out in the more traditional means by individuals or two to five man groups. The 1972 subject areas are-listed-below.

> Stress Corrosion Cracking, Surfaces of IR Laser Window Materials Gradient Materials Reliability of Brittle Materials, Prevention of Failures from Fracture, Materials Limitation in Advanced Energy Conversion Systems Structure of Stable Disordered Carbon Systems Strength Differential Effect Wave Propagation in Composites Materials Problems in Applications of Superconductivity Fracture Mechanics; Structure of Non-Biological Polymers Thermodynamic Properties of Materials at Very High Temperature Structure of Amorpho's Materials

-11-

Solid Electrolytes for Advanced Satteries, Recycling and Waste Disposal of Electricis,

As in the past, considerable use was made/of a computational system utilizing by telephone the University of Michigan Computing Center. Professors J. O. Wilkes and B. Carnahan were available to help formulate member's problems. ÷ -

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In addition; representatives of the various service laboratories were invited to the conference so as to provide a two-way communication between the Council and the respective laboratories. In this manner the results of the Council's efforts could be more directly communicated to DoD and other government groups working in the materials area. Also, the problem areas most deserving of consideration could be discussed with the Council so that they might be considered as topics at future conferences. The following governmental representatives attended portions of the conference:

- Alton F. Armington, U.S. Air Force Cambridge Research Laboratory
- Richard E. Balzhiser, Office of Science and Technology
- Francis I. Baratta, Army Materials & Mechnaics Research Center
- H. E. Bennett, Naval Weapons Center
- G. H. Bishop, Army Materials & Mechanics Research Center
- Rudolph A. Black, Advanced Research Projects Agency, Nuclear Monitoring Research Center
- Joseph I. Bluhm, Army Materials & Mechanics Research Center

-12-

B. F. Brown, formerly Naval Research Laboratory S. H. Bush, AEC Reactor Safeguards Sabri Ergun, U.S. Bureau of Mines, Interior Dept. John R. Fenter, Air Force Materials Laboratory Otto R. Gericke, Army Materials & Mechanics Research Center David Goldstein, U. S. Naval Ordnance Laboratory A. E. Gorum, Director, Army Materials & Mechanics Research Center Charles Grosskreutz, National Bureau of Standards D. Holmes, Air Force Weapons Laboratory R. Nathan Katz, Army Materials & Mechanics Research Center Jhan M. Knan, Lawrence Livermore Laboratory Jeroze Kruger, Hational Bureau of Standards E. H. Lence, Army Materials & Mechanics **Research** Center David R. Lide, National Bureau of Standards H. A. Lipsitt, Wright-Patterson Air Force Base Capt. John Loomis, Air Force Weapons Laboratory Elio Passaglia, National Bureau of Standards H. W. Paxton, National Science Foundation Janet S. Perkins, Army Materials & Mechanics Research Center James O. Porteus, Naval Weapons Center Harold Poser, USAF Cambridge Research Labs. G. D. Quinn, Army Materials & Mechanics Research Center

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Roy W. Rice, U.S. Maval Research Laboratory

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H. J. Sinnott, Director, Materials Sciences Office, Advanced Research Projects Agency

Marioz J. Soileau, Jr., Air Force Weapons Lab.

- C. Martin Stickley, Deputy Director, Haterials Sciences Office, Advanced Research Projects Agency
- Z. C. van Heuch, Naval Ship Research & Development Center

John I. Machtman, Jr., National Bureau of Standards

Richard Weiss, Army Materials & Mechanics Research Center

Sheldon miederhorn, Mational Eureau of Standards The interaction proved to be quite valuable to the Council.

As in prior years, the results of the Council's effort are divided into two broad categories; namely, 1) papers in a state ready for publiblication, and 2) reports and memoranda for limited distribution representing work in progress. The former category is available for general distribution and, in most cases, are in the process of publication in the appropriate technical journals. In many instances, the reports arising from the 1972 meeting were the completed forms of work started at earlier conferences. The restricted distribution reports and memoranda represent initial ideas, problem suggestions, position papers, and status reports and are aimed primarily to stimulate discussion within the Council. However, they are available by request to the Project Director subject to the author's release. The breadth of activity of the Council during the 1972 conference can be seen from the following list of papers produced. The abstracts are given in the Appendix. Titles marked with an asterisk are reports and memoranda for limited distribution; those marked with (f) are being published. Also included are notes and recommendations and summaries of the deliberations of some of the subgroups working within the Council.

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The Line Tension of a Crack Line, and Its Application to Kinks on Cracks R. M. Thouson

Randomness and Wave Propagation in Homogeneous Media J. A. Krumhansl

Threefold Coordinated Model Structure of Amorphous GeS, GeSe and GeTe A. Bienenstock

Plastic Relaxation Via Twist Disclination Motion in Polymers

J. J. Gilman

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Statistical Mechanics of Polymer Networks H. Reiss

Stress Averaging in the Dislocation Micromechanics Analysis of Deformation J. P. Hirth

AC Losses in Superconducting Magnet Suspensions for High-Speed Transportation M. Tinkham

Comments on the Prospects for Major Improvements in Rechargeable Batteries to Operate at Ambient Temperatures R. A. Huggins

Hardness of Pure Alkali Halides J. J. Gilman

Computer Experiments on Atomic Models of Cracks: Thoughts about Problems and Opportunities G. H. Vineyard

Simultaneous Determination of Long-Chain Branching and Helecular Weight Distribution in Polymers J. D. Ferry Current Fluctuations from Small Regions of Adsorbate Covered Field Emitters: A Wethod for Determining Diffusion Coefficients on Single Crystal Planes R. Gomer Crystallization Rate of Amorphous Alloys P. E. Dursez The Role of Cracks, Pores and Absorbing Inclusions on Laser Induced Damage Threshold at Surfaces of Transparent Dielectrics 1. Bloembergen Propagation of Low Frequency Elastic Disturbances in a Composite Material W. Kohn It's a Random World J. A. Arumhansl Theory of Ionic Transport in Crystallographic Tunnels W. H. Flygare and R. A. Huggins Theoretical Calculation of Thermodynamic Properties of Iron-Carbon Austenite S. K. Das and Z. E. Hucke Research Needs and Technical Opportunities for a Program on the Reliability of Brittle Materials A. G. Evans and R. L. Coble A Workshop on Fracture Data held at Centerville, Mass. C. Grosskreutz Conclusions and Recommendations Reached by the Stress-Corrosion Group M. Cohen Workshop on Materials for Energy Conversion A. L. Bement and R. Kaplow \*A Survey of Variational Methods for Elastic Wave Propagation Analysis in Composites with Periodic Structures E. H. Lee, (see "Dynamics of Composites", ASME, 1972)

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"Entanglement Networks Crosslinked in Strained States J. J. Perry, (see Proceedings of the National Academy of Sciences, 1972) TEnzyme Cascades and Their Control E. W. Montroll, (see Annual Review of Biophysics and Bigengineering Vol II) Theoretical Models and Experimental Properties of Liquid Metals at High Temperatures J. L. Margrave Exergetics of Strained Organic Molecules and of Various "Carbon" Samples by Combustion Calorimetry J. L. Hargrave Structural Studies and Chemical Syntheses in Low-Temperature Matrices J. L. Margrave Syntheses, Structures and Thermodynamic Properties of Perfluorocarbons J. L. Margrave Solar Energy, A Natural Resource for Everyone J. L. Margrave Hydrogen and Hydrides--Energy Carriers for the Future J. L. Margrave Polychromatic X-ray Diffraction; A Rapid and Versatile Technique for the Study of Solids under High Pressures and High Temperatures L. L. Margrave \*Discussion of Continuum Descriptions of Deformation E. H. Lee \*Gradient Materials R. L. Coble \*Biaxial Stress Relaxation in Glassy Polymers S. S. Sternstein \*Elastic Network Theory S. S. Sternstein Polymeric Entanglement Networks Cross-Linked in States of Strain J. D. Ferry and S. S. Sternstein

Recycling, the Supply of Materians, and the Disposal of Mastes: Models and Analysis H. J. Sever In the Horphology of Polymeric Alloys M. B. Bever and M. Shen Inclusion Patterns and Stress Criteria for Quasi-Static to Spall Fractures by Voic Coalescence D. C. Drucker Spali Fracture by Hole Growth in Incompressible Elastic Plastic Haterial F. A. HeClintock Estimating Prediction and Tolerance Limits for Extreme-Value Distributions F. 7. McClintock and J. O. Wilkes Fully Plastic Stress and Strain Distributions Around Moving Cracks F. A. McClintock and B. Budiansky Analysis of Ride Quality H. Tinkham and P. L. Richards A Perspective on the Strength-Differential Phenozenon J. P. Hirth and M. Cohen The Influence of Recovery on the Deformation Behavior of Highly-Strained Iron Titanium Alloys H. Cohen Conformation of the Mode and Wave Front Approach to the Analysis of Wave Propagation in Periodic Composites Z. H. Lee Influence of Properties Gradients on Stress Wave Propagation Applications E. H. Lee, E. Budiansky and D. C. Drucker Determination of Stress Profiles for Waves in Period\_c Composites L. Bevilacqua, J. A. Krumhansl and E. H. Lee

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## POST COMPERENCE ACTIVITIES

A briefing session for Dr. S. J. Lukasik, ARPA Director, was arranged in Washington to present the highlights of the accomplishments of the past five years. After this meeting the Steering Committee met with C. M. Stickley and E. C. van Reuth of the ARPA Materials Science Office to learn of new problem areas of importance to ARPA and to discuss plans for the 1972 Summer Conference. This meeting is planned for the month of July in the San Diego, California, area.

Selection of problem areas for next year will follow a letter communication with Council members asking for suggestions. APPENDIX

GUEST CONSULTANT LIST

### ARPA MATERIALS RESEARCH COUNCIL 1972 GUEST CONSULTANT LIST

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APPENDIX

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ABSTRACTS

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# THE LIVE TINSION OF A CRACK LIVE, AND ITS APPLICATEDE - J KINKS ON CRACKS

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R. A. Thomson

# Abstract

We investigate the definition of an effective line tension for a crack line similar to that used for dislocations. Although cracks have a distinct tendency to wipe out regions of higher curvature relative to straighter configurations, the effective line tension for a crack is not easy to separate from the crack extension force, which is area dependent. We are able to define a tension term, however, which must be used with discretion, and which is dependent on the size of the curved region.

-30-

# RANDOMNESS AND NAVE PROPAGATION IN INHOMOGENEOUS MEDIA

J. A. Brumbansl

# Abstract

The study of elastic wave propagation in composite media has led to the development and application of various methods of analysis appropriate to periodically inhomogeneous materials. In general these methods cannot be extended exactly to randomly inhomogeneous media. Nonetheless, some progress has been made during recent years in the analysis of electromagnetic waves in random media, and in solid state physics in the description of disordered materials. It appears that these methods can be used for disordered composites; this paper will survey the methods and indicate a few applications. TERLEPILE COORDENATEL MODEL STRUCTURE OF ANDRPHOUS GAS, Jese and JaTe

A. Bienenstock

### Abstract

The black P structure is presented as a model for the structures of amorphous GeS, GeSe and GeTe. It is shown that the short interatomic distances, low near neighbor mordinations and high covalencies of the amorphous materials, relative to the crystalline, can be rationalized with the model. When scaled to the near neighbor interatomic distances in the aporphous materials, the model yields satisfactory agreement with the observed position and area of the second neighbor X-ray radial distribution function peaks. The model predicts: (a) A first neighbor peak area for GeS which is significantly different from that predicted by the random covalent model, (p) phase separation in certain composition regions which, for the Ge-S system, should be observable by means of transmission electron microscopy and (c) differences between the valence band densities of states associated with this and the random covalent model which should be observable with photomission experiments.

53

-32-

# PLASTIC RELAXATION VIA TWIST DISCLINATION MOTION IN POLYMERS

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J. J. Gilman

### Abstract

Measurements of the internal friction in polymers exhibit a spectrum of peaks at low temperatures that are related to the plastic behavior at higher temperatures. This manuscript deals with a particular supramolecular defect that rehaves in a manner consistent with the observations. The defect is a twist disclination consisting of two molecules that cross over one another.

The energies of formation and motion for the twist disclination are calculated in terms of the width of the twisted region, the displacement that is produced by the twist, the molecular radius, and the elastic stiffnesses of the molecules. The total energy is minimized to find the optimum width and the formation energy.

For motion to occur dilatations caused by contour modulations of the molecules must be overcome. This effect yields expressions for the motion activation energy, and the stress for non-activated motion.
# STATESTICAL MECHANICS OF POLYMER METMORKS

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H. Reiss

# Abstracy.

The conventional theory of rubber elasticity is reviewed critically and discussed in terms of a simple gaussian network. An approximate theory, based on a variation principle, is then introduced and compared with the conventional theory. It is shown that this theory leads to the standard results of rubber elasticity when the restrictive assumptions, inherent in the conventional theory, are imposed on it. However, the new theory can be more simply extended to nongaussian networks, and several methods for achieving this extension are derived and discussed. In future work, specific applications of the new method to nongaussian networks will be attempted.

# STRESS AVERAGING IN THE DISLOCATION MICROMECHANICS ANALYSIS OF DEFORMATION

J. P. Hirth

# Abstract

The strain-rate of a deforming crystal is related to a sum over dislocation segments of isolated thermally activated and viscously damped motions. Appropriate averaging methods are suggested to yield a relation between strain rate and the macroscopic variables of stress and temperature. Several specific examples are analyzed in detail.

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# AC LOSSES IN SUPERCONDUCTING MAGNET SUSPENSIONS FOR HIGH-SPEED TRANSPORTATION

M. Tinkham

# Abstract

A rather general relation is derived between vertical accelerations of the train and cryogenic power dissipation due to AC currents induced in the superconducting suspension magnets. Our theoretical results give a good account of the rather large losses observed in the Fuji Electric test vehicle, which used less than state-of-the-art conductors. Even with parameters estimated to represent the best currently available materials, however, it appears that these losses will be comparable with the total heat leak due to all other causes if the accelerations are as large as permitted by subjective human ride quality considerations. Empirical data on losses under appropriate conditions of B, B, and  $I/I_c$  may be needed to ascertain whether improved materials will be required to avoid serious design constraints by cryogenic heating.

-36-

# COMMENTS ON THE PROSPECTS FOR MAJOR IMPROVEMENTS IN RECHARGEABLE BATTERIES TO OPERATE AT AMBIENT TEMPERATURES

R. A. Huggins

## Abstract

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The important parameters relating to high performance batteries are described. The factors controlling the specific energy are pointed out, and it is shown that, in view of recent progress on solid electrolytes, there are no fundamental limitations to the development of high specific energy cells to operate at ambient temperatures. The achievement of high values of specific power at such temperatures will be a much more difficult problem, and the important factors are described. The primary limitations will be in the cathode system, and several different approaches to circumventing them are described.

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J. J. Gilman

# Abstract

An explicit expression is derived for the indentation hardness numbers of alkali halide crystals in terms of ionic binding, combined with the theory of plastic identation. The resistance to indentation is caused by the electrostatic faults that exist at the cores of  $\{100\} < \overline{110} >$  dislocations.

The theoretical hardness is given by (c.g.s. units):

$$H_0 = 0.096 \frac{e^2}{\epsilon b^4} = 1.2 \times 10^{-2} C_{44}$$

where e = electron charge;  $\varepsilon = static$  dielectric constant; b = Burgers displacement; and  $C_{4,4}$  = elastic shear stiffness. The theoretical hardness for NaCl is 17 kg/mm<sup>2</sup> compared with the observed value of 16.7 kg/mm<sup>2</sup>.

# COMPUTER EXPERIMENTS ON ATOMIC MODELS OF CRACKS: THOUGHTS ABOUT PROBLEMS AND OPPORTUNITIES

G. H. Vineyard

## Abstract

Although the process of the formation and propagation of cracks in brittle fracture has been under investigation for a long time, new opportunities for improved understanding are foreseen in computer experiments on atomic models of the crack tip and its surrounding region. Exploratory work has been reported recently by Gehlen, Kanninen, Chang, and others. Possible atomic models for extensions of this work are considered, and a number of problems inherent in such computations are discussed. The atomistic calculations are divided into two classes, static and dynamic. A point of view is recommended which goes beyond the usual description of crack fronts and related energies by dealing with extremal points of the potential energy in configuration space. This viewpoint provides a unified and more nearly rigorous framework for discussion and is naturally related to the results of static computer experiments. Problems that may be illuminated if not completely solved by computer experiments are discussed. In particular, the role of jogs and kinks in crack propagation and the question of the formation of dislocations by advancing cracks are seen as suitable for more concentrated attack.

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# SIMULTANEOUS DETERMINATION OF LONG-CHAIN BRANCHING AND MOLECULAR WEIGHT DISTRIBUTION IN POLYMERS

J. D. Ferry

# Abstract

A proposed procedure is outlined to combine gel permeation chromatography data with linear viscoelastic properties measured in dilute solution and extrapolated to infinite dilution, in order to derive simultaneously the molecular weight distribution and branching index of an unfractionated polymer sample with long-chain branching. CURRENT FLUCTUATIONS FROM SMALL REGIONS OF ADSORBATE COVERED FIELD EMITTERS. A METHOD FOR DETERMINING DIFFUSION COEFFICIENTS ON SINGLE CRYSTAL PLANES.

Robert Gomer

#### Abstract

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A novel method is presented for determining surface diffusion coefficients of adsorbates on single crystal planes of field · mitters in terms of the time correlation function of current fluctuations. The method is based on the fact that current fluctuations are related to adsorbate density fluctuations, whose time correlation is governed by relaxation times simply related to diffusion coefficients. A general formalism is presented, some idealized cases are worked out analytically, and the case of a circular aperture is treated in detail numerically. Switching between different adsorption states, in addition to but not affected by diffusion, is also included. The forms of the correlation function are shown to be complicated, with a l/t tail at large t, and cannot be represented by simple exponential decay.

-41-

#### CRYSTALLIZATION RATE OF AMORPHOUS ALLOYS

P. E. Duwez

### Abstract

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A summary is given cf the various modes of crystallization of amorphous alloys. All transformations reported so far depend on both temperature and time, and hence there is no unique way of defining a crystallization temperature. In some cases the transformation takes place in one step, that is, directly from the amorphous structure to the equilibrium crystalline structure. In most cases, however, and depending on both time and temperature, intermediate metastable crystalline phases with apparently complex crystal structures are found before final equilibrium is reached. The various methods used to study the transformation kinetics are reviewed.

# THE ROLE OF CRACKS, PORES AND ABSORBING INCLUSIONS ON LASER INDUCED DAMAGE THRESHOLD AT SURFACES OF TRANSPARENT DIELECTRICS

N. Bloembergen

#### Abstract

The concentration of the electric field strength in the neighborhood of micropores and cracks may lower the nominal external intensity for electric avalanche breakdown by a factor two to one hundred depending on the geometry of the crack and the dielectric constant.

The presence of absorbing inclusions at the edge of microcracks will often be the dominant mechanism giving the lowest surface damage threshold. Inclusions and cracks with characteristic dimensions less than about  $10^{-6}$  cm will not lower the breakdown threshold appreciably.

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## PROPAGATION OF LOW FREQUENCY ELASTIC DISTURBANCES IN A COMPOSITE MATERIAL

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W. Kohn

### Abstrace

In the limit of low frequencies the displacement u(x,t)in a one-dimensional composite can be written in the form of an operator acting on a slowly varying envelope function, U(x,t):  $u(x,t) = (1 + v_1(x) \frac{\partial}{\partial x} + ...) U(x,t)$ . U(x,t) itself describes the overall long wavelength displacement field. It satisfies a wave equation with constant, i.e., x-independent, coefficients, obtainable from the dispersion relation  $\omega = \omega(k)$  of the lowest band of eigenmodes:  $(\partial^2/\partial t^2 - \bar{c}^2\partial^2/\partial x^2 - \partial^2/\partial x^4 + ...)U(x,t) = 0$ . Information about the local strain, on the micro-scale of the composite laminae, is contained in the function  $v_1(x)$ , explicitly expressible in terms of the periodic stiffness function, u(x), of the composite. Appropriate Green's functions are constructed in terms of Airy functions. Among applications of this method is the structure of the so-called head of a propagating pulse.

## IT'S A RANDOM WORLD

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J. A. Krumhansi

#### Abstract

Random semiconductors, alloys, and magnetic materials have recently received considerable attention by solid state physicists, and a variety of theoretical approaches have been developed. However, these developments are only part of an extensive history of randomness in physical situations. This paper is a report on some of the related history in other fields where randomness has been an ingredient; a basic bibliography is provided.

## THEORY OF IONIC TRANSPORT IN CRYSTALLOGRAPHIC TURNELS

W. H. Flygare and R. A. Huggins

#### Abstract

A model has been developed for the treatment of the motion of ions through crystallographic tunnels, as are found in materials that are interesting solid electrolytes. Consideration of both point charge and higher order attractive terms as well as overlap repulsion effects allows the calculation of the minimum energy positions of mobile ions and the activation energy barrier that they must surmount to move through the tunnel in the lattice. Calculations have been made for ions of different sizes in the AgI lattice which show that there is a set of minimum energy paths which do not follow the centerline of the tunnel, but deviate periodically, with both direction and magnitude depending upon the cationic size. Also, in accordance with experimental observations, the activation energy for motion is smallest for cations of intermediate size, where the Coulombic, polarization, and repulsive contributions to the total energy are best balanced.

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-46-

# THEORETICAL CALCULATION OF THERMODYNAMIC PROPERTIES OF IRON-CARBON AUSTENITES

S. K. Das and E. E. Hucke

### Abstract

A calculation of all the partial and integral thermodynamic properties of iron-carbon austenite is presented. The configurational entropy has been calculated using Boltzman's relation. The partial vibrational entropy of iron has been calculated using Einstein's model for the specific heat of a crystalline solid, together with available lattice parameter data of austenite as a function of temperature and composition. The resulting total entropy has been integrated over temperature to obtain the partial Gibb's free energy of iron; and then partial properties of carbon have been obtained by Gibb's-Duhem integrations. The integration constants have been evaluated using the available thermodynamic data for the phases in equilibrium with the austenite phase. The results obtained in the present model are in remarkable agreement with the available experimental data.

# RESEARCH NEEDS AND TECHNICAL OPPORTUNITIES FOR A PROGRAM ON THE RELIABILITY OF BRITTLE MATERIALS

A. G. Evans\* and R. L. Coble

### Abstract

A Symposium on Mechanical Properties of Brittle Materials was held on July 17, 18, 19, 1972 at Centerville, Massachusetts. The Symposium reviewed the progress in the ARPA Brittle Materials Program with additional papers by others from industry and universities, thus in toto, constituting a review of the present technical situation relative to the reliability of brittle materials. Mechanical and fracture properties, materials development, statistical variation, and non-destructive testing in brittle materials were all reviewed. Recommendations for further work involve:

- Work in critical stress intensities factor for small inherent flaws
- 2. Work on second phase materials
- 3. Slow crack growth at elevated temperatures
- Work on the investigation of the effects of multiaxial stress
- 5. Work on statistical strength variations
- 6. Additional work on flaw detection procedures.

\*Materials Department, School of Engineering and Applied Science, University of California, Los Angeles.

# A WORKSHOP ON FRACTURE DATA HELD AT CENTERVILLE, MASSACHUSETTS July 20, 21, 1972

Report Prepared by Charles Grosskreutz National Bureau of Standards

### Abstract

A workshop organized by the National Bureau of Standards was held under the auspices of the Materials Research Council to review needs for compilations of fracture data. The recommendations will be used to design an appropriate activity in Fracture Data at the Bureau of Standards. Participants from three basic industries were invited: automobile and construction equipment, railroad, and pressure vessel and electrical generating equipment. In addition, professionals from the academic community and the National Bureau of Standards attended. Recommendations for the development of two types of fracture data compilations were made, one for a simplified introductory compilation for day-to-day design purposes. This handbook is intended to alleviate the paucity of modern design handbooks oriented to fracture design control. A second, more complete fracture data compilation again directed at the design community is also needed, and the specific subjects are outlined in the report.

-49-

## A SURVEY OF VARIATIONAL METHODS FOR ELASTIC WAVE PROPAGATION ANALYSIS IN COMPOSITES WITH PERIODIC STRUCTURES\*

E. H. Lee

# Abstract

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The propagation of harmonic waves through composite media with periodic structures is analyzed using Floquet or Bloch theory common in crystal lattice studies. Variational principles in the form of integrals over a single cell of the composite are developed, and provide a means of determining phase velocities and stress distributions in Floquet waves which travel through the composite unchanged in form from cell to cell. The variational principles apply to three-dimensional lattices, but applications to onedimensional lattices are emphasized since, for this case, the exact solution is available to assess the accuracy of Rayleigh-Ritz variational procedures with the objective of suggestion techniques for application to higher dimensional lattices. Both strain energy and complementary energy principles are utilized. Because of the sharp change in elastic constants from the stiff reinforcing filaments to the softer matrix, the analysis must accommodate discontinuities in strain across the interfaces. The Floquet wave solutions form a complete set of functions over the while of space and thus provide a means of expressing general transient motions. The motion caused by an impulsive pressure variation on the surface of a half space is obtained in this way.

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\*See "Dynamics of Composites", ASME, 1972.

-50-

## ENTANGLEMENT NETWORKS CROSSLINKED IN STRAINED STATES\*

J. D. Ferry

### Abstract

Linear 1,2-polybutadience is cross-linked to  $0^{\circ}$ C by  $\gamma$ irradiation while strained in simple extension with extension ratios from 1.3 to 2.0. During irradiation times up to several hours, entanglement slippage is slight, since the temperature is only slightly above the glass transition. Subsequently, samples are released and reach their equilibrium states of ease at room temperature. From the extension ratio at state of ease, the ratio of  $\nu_{\hat{\mathbf{x}}}$  (effective network strands terminated by cross-links introduced) to  $\nu_{\hat{N}}$  (effective network strands terminated by entanglements) is calculated by composite network theories of Flory and others; and from the extension ratios together with the modulus, measured at small extensions,  $\nu_{\hat{N}}$  is calculated explicitly. It appears that  $v_{\hat{\mathbf{x}}}$  increases approximately independent of irradiation, and it corresponds to a molecular weight between effective entanglement loci of about 13,000. This figure, however, which is larger than that deduced from rheological properties of the uncross-linked polymer, is subject to future downward correction for partial entrapment of the entanglements and other refinements. \*See Proceedings of the National Academy of Sciences, 1972.

## ENZYME CASCADES AND THEIR CONTROL IN BLOOD PLASMA\*

E. W. Montroll

# Abstract

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Provide Statements

Since the uninterrupted, well regulated flow of blood is vital to the life of higher animals it is essential that mechanisms exist to respond to fluctuations induced by accidents and external agents. In the course of the evolution of those species which have survived, no outside expert was available to make quick repairs when fluctuations became too large. Hence the appearance of an assortment of molecules capable of inducing the chemical reactions and participating in the physical mechanisms basic to the spontaneous repair processes had to be concurrent with the development of the complex animals.

Any leaks which appear in the blood conducting tubes have to be plugged before too much of the valuable fluid is lost. Invading organisms which penetrate into the blood stream must be destroyed before their population multiplies to a level which endangers the life of the host. The blood pressure must be controlled and the system should be capable of adjusting to the variations in the elasticity and of the cross section of the tubes of the circulatory system which result from aging.

The response mechanisms should be well tuned so that they are not activated by false signals. Spontaneous blood coagulation

-52-

in arteries without leaks is as dangerous as no coagulation to seal lesions. It seems likely that the large numbers of steps which precede the activation of the final repair process in enzyme cascades has evolved to distinguish signal from noise. If each of the preliminary steps follows some clue from the agent which demands the completion of the cascade, their large number would require a precise characterization of the agent. Then the probability that the normal harmless fluctuations in the system would mimic the agent in more than a small number of ways at a given time would be very small. The development strategy of such a control system would be analogous to the design strategy of a sophisticated sea mine which is constructed to explode under a special kind of ship such as an aircraft carrier and which is also supposed to be difficult for the enemy to sweep. A mine sweeper with a noise maker which simulates the noise of the carrier would only activate one component of the response system; a long electrical conductor towed by the sweeper might mimic the magnetic field of the hull of the carrier and activate the next component. However, unless the sweeper could also generate the special pressure field developed by such a long streamlined object in rapid motion in the water the mine would eventually return to its inactive state without exploding.

The volume of clinical and biochemical literature of enzyme cascades, especially blood coagulation probably exceeds that of almost any other specialized technical subject. Some of the important basic ideas have resulted from curious old obser-

-53-

vations which one would hardly have expected to have the same status as those from carefully planned experiments. Clever mechanisms which are still of interest were proposed long before one had any idea of the structure of the molecules involved. There is even a certain charm to a subject of such great activity which can still have important process factors named after patients who lacked them - Christmas, Hageman, Stuart - rather than after the physicians who discovered them. When the Mendelian laws of heredity became generally known at the turn of the century one of the first applications to human genetics was the analyses of the inheritance of hemophilia. This was, of course, facilitated by known records of victims of the disease in royal families whose geneologies were documented.

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The process of hemostasis and the formation of the hemostatic plug involves (i) highly specialized cells of the blood stream, the platelets, which have an afinity for sites in the blood vessel where damage has occured, (ii) blood coagulation, the phase transition of monomer fibrinogen into a polymeric fibrin network in and around the aggregated platelets, stabilizing the plug, and (iii) the dynamics of the blood vessel which leads to these processes and which finally must perform the healing process.

An important part of the extensive literature on hemostasis is to be found in the proceedings of many conferences on the subject. Some of the conferences such as the Hamburger Symposium Über Blutgerinnung and the Wayne State Conferences are held at regular intervals as are those of various international

-54-

committees on blood such as the Committee on Blood Clotting Pactors and the Committee on Haemostasis and Thrombosis. One of the main journals on the subject, Thrombosis et Diathesis Haemorrhagica has a supplement which contains the proceeds of many of the important conferences. The proceedings of the conference of the British Royal Society (organized by R. G. MacFarlane) on triggered enzyme systems in blood plasma (1 July 1969 issue of Proc. Roy. Soc. B) has been very valuable to the author in preparing this review.

Since the main intent of the review is to present a guide to the literature to physicists and engineers who wish to learn something of biological control mechanisms, it will be made more self contained by starting with a few remarks on nature of proteins and classical enzyme kinetics. An attempt has been made to use a minimum of medical terminology. If some has crept in with insufficient definition the uninitiated can find good explanations in one of the standard books such as Best and Taylor, Physiological Basis of Medical Practice (Williams and Wilkins). Two excellent books have recently appeared on blood clotting, one edited by W. H. Seegers and entitled Blood Clotting Enzymology (Acad. Press 1967) and the other, edited by K. Laki, entitled Fibrinogen (Dekker 1968).

<sup>\*</sup>To appear in Annual Reviews of Biophysics and Bioengineering Vol. II

### THEORETICAL MODELS AND EXPERIMENTAL PROPERTIES OF LIQUID METALS

J. L. Margrave

## Abstract

There are now available a great many measurements of various properties of liquid metals over wide ranges of temperature and pressure and it is informative to examine these properties in the light of the various available theories as proposed by Mott, MacDonald, Bernal, Ziman, Faber, Edwards, Knight, Heine and others. Of special interest in this report are the structures deduced for liquid metals as well as the absolute values, and perhaps more crucially, the temperature coefficients of these values for electrical conductivity, thermal conductivity, Hall coefficients, Knight shifts, specific heats and optical properties.

The studies of high melting metals by the technique of levitation calorimetry are being continued and new data for Ni and Ta are evaluated.<sup>1</sup> The general problems of correction for heat losses due to radiation and thermal conduction to the gaseous atmosphere have been resolved and all data adjusted appropriately.<sup>2</sup> Favorable intercomparisons have been made between our work and Russian studies of liquid vanadium<sup>3</sup> and between our work and studies at Sandia (Albuquerque) or liquid copper.<sup>4</sup> ]]

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<sup>1.</sup> D. W. Bonnell, A. J. Valerga and J. L. Margrave, to be published. 2. D. W. Bonnell, A. J. Valerga and J. L. Margrave, to be published.

D. W. Bonnell, A. J. Valerga and J. L. Margrav
L. Gurvich, private communication, 1972.

<sup>4.</sup> H. P. Stephens, presented at the 27th Calorimetry Conference, Park City, Utah, July 22, 1972.

## ENERGETICS OF STRAINED ORGANIC MOLECULES AND OF VARIOUS "CARBON" SAMPLES BY COMBUSTION CALORIMETRY

J. L. Margrave

## Abstract

High-precision combustion calorimetry for pure organic compounds can lead to important energetic information about bond energies and strain energies in unusual configurations. For example, various propellanes (synthesized by Prof. P. Eaton, University of Chicago) have been burned and strain energies evaluated.<sup>1</sup> Also, a series of diazo-organic compounds has been burned to provide a reliable value for the energy contribution of the group  $\{N=N\}$ .<sup>2</sup>

Studies of the heats of combustion of various "carbon" samples, including some of the materials prepared by polymer pyrolyses by Prof. E. Hucke, are in progress in an effort to establish quantitative enthalpy differences and to link these to structural characteristics.

<sup>1.</sup> J. L. Wood and J. L. Margrave, to be published.

<sup>2.</sup> J. L. Wood, P. S. Engel and J. L. Margrave, presented at 27th Calorimetry Conference, Park City, Utah, July 20, 1972.

## STRUCTURAL STUDIES AND CHEMICAL SYNTHESES IN LOW-TEMPERATURE MATRICES

J. L. Margrave

### Abstract

New techniques for structural studies and for synthetic chemistry are explored in which potentially reactive (unstable) species generated either in arcs, discharges or furnaces, or by pyrolysis are co-condensed in either inert or reactive matrices at low temperatures and then allowed to warm up and react.

Structural studies of current interest include:

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(1) the establishment of the structure LiNC as the preferred formula for indicating the proper order in "lithium cyanide". NaCN and KCN are normal cyanides.<sup>1</sup>

(2) the determination of bond angles for the species  $Li_2S$ ,  $Al_2S$ ,  $Ga_2S$ ,  $In_2S$ ,  $Tl_2S$  and for  $SiCl_2$  and  $SiBr_2$ .<sup>2</sup>

(3) the determination of the symmetry  $(C_{3v})$  and other parameters for matrix-isolated CCl<sub>3</sub>-radicals by esr spectroscopy.<sup>3</sup>

In the synthetic area, interest is directed to the reaction of atoms and molecules at low concentrations in inert matrices, " e.g.,

(a)  $(Cr + 2 C_6 H_6)_{Ar \text{ or } Ne} = Cr (C_6 H_6)_{Matrix}$ 

(b)  $(\text{Li} + O_2)_{\text{Ar or Ne}} = \text{Li}O_2$ Matrix

-58-

(c) 
$$(SiF_2 + BF_3)_{Ar}$$
, Ne or N<sub>2</sub> = SiF<sub>3</sub>- $(SiF_2)_n$ -BF<sub>2</sub>  
Matrix

and also to the reactions of atoms and molecules directly with reactive matrices,<sup>5</sup> e.g.,

- (d)  $(CH_4 + F/P_2)_{P_2-Matrix} = CP_4, CP_3H, CP_2H_2, CPH_3$
- (e)  $(BF + BF_3)_{BF_3-Matrix} = B_2F_4$ ,  $B(BF_2)_3$ , etc.
- (f)  $(C + C_2 H_4)_{C_2 H_4}$ -Matrix =  $H_2 C_{H_2}$ , etc.  $H_2 C_{H_2}$
- (g)  $(U + CC)_{CO-Matrix} = U(CO)_x$  where x = 1, 2, 3, 4; etc.

One of the major ..dvances in this field has been the development of low-temperature devices and techniques which allow synthesis on the multi-gram scale and thus bring this approach to synthetic chemistry into direct competition with traditional laboratory methods.

- 1. Z. K. Ismail, R. H. Hauge and J. L. Margrave, to be published.
- 2. R. H. Hauge and J. L. Margrave, to be published.
- 3. G. Maass, R. H. Hauge and J. L. Margrave, Z. anorg. u. allgem. Chemie, 1972, in press.
- 4. See for example the work of P. L. Timms, Bristol; Lester Andrews, Univ. of Virginia; D. Milligan, National Bureau of Standards; and J. L. Margrave, Rice University.
- See for example the work of P. L. Timms, Bristol; P. Skell, Penn. State University; W. Weltner, Univ. of Florida; A. Streitweiser, Univ. of California, Berkeley; and J. L. Margrave, Rice University.

~59-

### SYNTHESES, STRUCTURES AND THERMODYNAMIC PROPERTIES OF PERPLUOROCARBONS

J. L. Margrave

### Abstract

The increasing interest in solid perfluorocarbons as practical lubricants, as battery constituents, as chemical reactants in diamond syntheses and for other applications makes it especially important to have workable syntheses and reliable structural and thermodynamic properties. Our patent covering both certain compositions of matter as well as broad synthetic approaches for the syntheses of super-stoichiometric CFX<sup>R</sup> has recently been issued.<sup>1</sup> Other preparative approaches to pure fluorocarbons and to the preparation of "gradient polymers" in which perfluorocarbon surfaces are formed on hydrocarbon substrates are described in other patent applications. Thermal stabilities, gas permeabilities, chemical corrosion resistance and other properties are under investigation.

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Among the structural studies in progress are (1) nmr studies of solid CFX which gives information on the number and types of groups in the solid ( -CF ; CF ; -CF ).

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R. J. Lagow, R. B. Badachhape, J. L. Wood and J. L. Margrave, U.S. Patent No. 3,674,432, issued July 4, 1972.

(2) ESCA studies on CFX to identify characteristic energy levels for various groups.

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(3) low-temperature  $C_p$ -measurements to provide the absolute entropy at 298°K for use in electrochemical calculations for the Li/CFX cell.

(4) heats of formation of  $C_*F$ ,  $CF_{0.7}$ ,  $CF_{0.9}$  and  $CF_{1.2}$  to establish the enthalpies as a function of composition.

(5) studies similar to the preceding for compounds like  $C_{10}F_{18}$ ,  $C_{14}F_{24}$ ,  $C_{18}F_{30}$ , etc.

# SOLAR ENERGY, A NATUKAL RESOURCE FOR EVERYONE

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J. L. Margrave

#### Abstract

Three new factors now on the scene in the United States and throughout the world may finally make the exploitation of solar energy, which has long been practical in a scientific and engineering sense, economically feasible and olitically desirable: The factors are

(1) the tremendous surge of interest in non-polluting energy sources.

(2) the growing recognition that fossil fuel resources are really finite and the realization that this dire prediction for the future is not so far away as shortages of natural gas, fuel oil and electric power lead to "brown-outs", "black-outs", and to price increases and restrictions on usage.

(3) the societal concern about better living standards for all people which creates an impetus for better housing and new construction with minimal operating costs. Here is an opportunity to develop and install on an extended basis solar water heaters and house heating units which are efficient and attractive both to the resident from the viewpoint of economics and to society as a whole from the two viewpoints outlined above.

-62-

Scientists, engineers and architects can work together with governmental agencies to facilitate the development and use for the people of the world this free, non-polluting energy resource.

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# HYDROGEN AND HYDRIDES--CHEMICAL ENERGY CARRIERS

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J. L. Margrave

# Abstract

As a part of the solution to the long-range energy problem, one must devise a way to store and transport--probably in chemical form--the energy produced by burning fossil fuels or by nuclear fission or fusion reactors.<sup>1</sup> From an economic point of view, some of the most attractive energy carriers are elemental hydrogen and the various simple hydrides. Gaseous hydrogen can be distributed under pressure through the same systems now being used for natural gas, and the binary hydrides are liquids or solids, often with reasonable properties of the same sort as gasoline.

Among the sources of hydrogen currently available are the pyrolysis of hydrocarbons, and of coal and oil shales. On a longrange basis, the production of hydrogen will probably be electrolytic--from water, or  $KHF_2$  or molten metal hydrides. One must consider the economics and the scientific needs in choosing an electrolysis process and produce both hydrogen (a reducing agent) and probably either fluorine or oxygen (oxidizing agents). There

-64-

See series of articles, "Hydrogen, Likely Fuel of the Future", Chemical and Engineering News, p. 14, June 26; p. 16, July 3 p. 27, July 10, 1972.

is some advantage in choosing to produce fluorine because of its greater chemical versatility.

The metal hydrides themselves are interesting solid energy carriers, capable of yielding hydrogen either on heating or on hydrolysis. Light-element hydrides are especially attractive on an energy/gram basis.

# POLYCHROMATIC X-RAY DIFFRACTION. A RAPID AND VERSATILE TECHNIQUE FOR THE STUDY OF SOLIDS UNDER HIGH PRESSURES AND HIGH TEMPERATURES

L. M. Albritton and J. L. Margrave

# Abstract

The use of polychromatic X-ray diffraction with multichannel energy analysis offers a rapid and versatile new approach to the problem of X-ray diffraction of solids, especially under conditions of high temperatures and high pressures.<sup>1</sup> Phase transitions at pressures up to 50,000 atm. and temperatures up to  $500^{\circ}$ C have been observed for alkali halides, PbF<sub>2</sub> and other systems. 1

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<sup>1.</sup> L. M. Albritton and J. L. Margrave, High Temperatures-High Pressures, 1972, in press.

## POLYMERIC ENTANGLEMENT NETWORKS CROSS-LINKED IN STATES OF STRAIN

J. D. Ferry and S. S. Sternstein

#### Abstract

The results of recent experiments on states of ease of amorphous highly entangled polymers which have been cross-linked while strained in simple extension are reviewed, and deviations from the predictions of an earlier report on this subject are examined. In particular, the approach to the state of ease following release of stress after cross-linking is unexpectedly slow, and therefore the kinetics of this process have been treated. Wich the approximation of linear viscoelasticity, it is found that the sum of the relaxation moduli of the engantlement and crosslink networks can be calculated from observations of sample dimensions as a function of time during approach to equilibrium. For neo-Hookean viscoelasticity, the relaxation moduli of the individual networks can in principle be calculated. Further experiments designed to clarify the phenomenon are outlined.

-67-

# RECYCLING, THE SUPPLY OF MATERIALS AND THE DISPOSAL OF WASTES: MODELS AND ANALYSIS

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A STATEMENT

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M. B. Bever

## Abstract

This memorandum presents a survey of models and analyses of the recycling of materials. The emphasis is primarily on a systematic and analitically sound arrangement but some critical evaluation will also be included.

It should be mentioned at the outset that not all the analysis were intended to be cumulative, or total, several are partial and cumulative.

# INCLUSION PATTERNS AND STRESS CRITERIA FOR QUASI-STATIC TO SPALL FRACTURES BY VOID COALESCENCE

D. C. Drucker

#### Abstract

A crude model is offered for the predictive calculation, as well as qualitative understanding, of the process of fracture through microscopic void coalescence in metallic alloys. Problems discussed include plane-strain crack initiation and dynamic propagation ( $K_{T_{C}}$  values), fracture of smooth and notched round tensile specimens, and spall caused by high velocity impact. The voids of diameter d and effective spacing D are assumed to be generated by the cracking of inclusions of diameter d and the failure of their bond to the ductile matrix. The effective initial D for the connected fracture surface is taken to be about 1/2 the average spacing in this highly simplified picture which is quasistatic on the microscale. The matrix is approximated as perfectly plastic with a yield stress  $\sigma_{_{\rm O}}$  appropriate for the level of strain rate and work hardening in each problem considered. A lower bound  $2\sigma_0 \ln (D/d)$  and an upper bound  $\frac{4\sigma_0}{3} \left[ \ln \frac{D}{d} + \frac{D}{3d} + \frac{1}{4} \right]$  for full lateral constraint, although not close, then provide a reasonable estimate of the void coalescence stress on the microscale for comparison with the macroscopic stress levels in cracks or necks and the time history of stress in spall.

-69-
# SPALL FRACTURE BY HOLE GROWTH IN INCOMPRESSIBLE ELASTIC PLASTIC MATERIAL

F. A. McClintock

#### Abstract

Calculations are presented for spall fracture by hole growth as approximated by the spherical growth of holes in incompressible, elastic-plastic material. An order of magnitude estimate indicates that inertia effect, are more important than rate effect. Comparisons are made with the empirical fracture criterion of Tiller and Butcher, and with the more detailed numerical calculations by Wilkens. 1

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# CONFORMATION OF THE MODE AND WAVE FRONT APPROACH TO THE ANALYSIS OF WAVE PROPAGATION IN PERIODIC COMPOSITES

E. H. Lee

# Abstract

The limiting phase velocity of Floquet waves at high frequencies should be consistent with the geometrical optics limit of a wave front travelling through each component at the appropriate wave speed. The resulting average wave speed should be in accordance with the phase velocity for high order bands of the frequency spectrum. By studying the structure of the mode shapes with increasing band number, a pattern becomes apparent, which permits determination of the relationship between band order and frequency. This is shown to be in agreement with the geometrical optics limit.

# INFLUENCE OF PROPERTIES GRADIENTS ON STRESS WAVE PROPAGATION APPLICATIONS

E. H. Lee, B. Budiansky and D. C. Drucker

# Abstract

Variation of elastic properties through a plate has been considered in order to increase its resistance to penetration. The relative merit of properties changes in a series of steps graded material - or continuous variation - gradient material is investigated.

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It is found that for an elastic slab with elastic modulus increasing with depth, the stress wave front associated with an applied discontinuous surface pressure increases in proportion to  $\sqrt{\rho(\mathbf{x})\tau(\mathbf{x})}$ , where  $\rho$  is the density and  $\tau$  the elastic wave speed for dilatational waves. This grows indefinitely with increasing  $\tau(\mathbf{x})$ . However, for a sudden change of properties at an interface, it is known that in the limit of change to a rigid body  $(\tau \leftrightarrow \infty)$ , the stress magnitude only doubles. This paradox is explained by noting a singular approach to the limit in the continuously varying case. A boundary layer of high stress peak occurs for sharp changes of properties; which narrows in time towards zero duration as the gradient material approaches a graded one. The significance of this result to material damage under dynamic loading is assessed.

-72-

# DETERMINATION OF STRESS PROFILES FOR WAVES IN PERIODIC COMPOSITES

L. Bevilacqua, J. A. Krumhansl and E. H. Lee

#### Abstract

Floquet or Bloch wave theory provides a convenient basic set of functions for representation of the propagation of transient elastic stress waves in periodic composites (Krumhansl, ARPA Mat. Res. Council Report, p. 175, 1970). Variational principles for computing dispersion relations and hence phase velocities generate a band structure of pass and no-pass frequency bands (Kohn, Krumhansl and Lee, ARPA Mat. Res. Council Report, Vol. I, Paper No. 2, 1969 and ASME Preprint 71-APMW-21, to appear in Jour. Appl. Mech.). Dispersion curves (frequency versus wave number) were accurately evaluated for laminar composites by using smooth Fourier series test functions for displacement in a Rayleigh-Ritz approximation procedure, but the corresponding stress profiles were unsatisfactory since the required continuity of stress at the inclusion-matrix inferface was ruled out by the use of the smooth test functions for displacement and corresponding continuous strain profiles.

In this paper exact stress profiles are calculated for waves propagated normally to the laminae, and satisfactory

-73-

approximations to these are generated with the extended variational principle which permits independent test functions to be used in the matrix and inclusions. An augmented plane wave approach in the Rayleigh-Ritz procedure was adopted in which exact solutions of the wave equation were used as component test functions in the filament. It was found that with this procedure, accuracy was essentially independent of the ratio of elastic moduli of the inclusion and matrix. The variational approach is applicable to two and three-dimensional composite configurations, which are not amenable to exact evaluation.

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# APPENDIX

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# MEETING SUMMARIES

# FUTURE DIRECTIONS IN OPTICAL SURFACE AND COATING RESEARCH FOR IR LASER WINDOWS

Summary of Meeting Held in Centerville, Mass.

The meeting which was held July 5-7, 1972 in Centerville was organized by C. M. Stickley with assistance from N. Bloembergen to bring together workers in the field of surface preparation and surface analysis of widely different background. The main purpose was to find out how their expertise could be brought to bear on the problem of the absorption and damage to surfaces and coatings on windows traversed by high intensity infrared laser beams. Such windows need antireflection coatings and, in many cases, also protective coatings against atmospheric deterioration. The requirements are for 0.1% antireflection and protective coatings at 10.6  $\mu$ m on alkali halides such as KCl and KB, with the absorption losses being less than  $10^{-4}$  per surface. Antireflection coatings on ZnSe and CdTe are also needed with an absorption less than  $10^{-4}$  per surface. For higher absorption, phase distortion of the optical beam degrades the quality of the beam. Coatings should be uniform to  $\lambda/40$  ( $\lambda$  = 10.6 or 3-5 µm) with the ccated window uniform to  $\lambda/20$ . With respect to mechanical properties coatings must be moisture resistant, cleanable, and make good thermal contact to the substrate.

-76-

In addition, there is a requirement for a damage threshold of the coatings and surfaces to approximate as closely as possible the damage threshold of the bulk material. As the laser pulse deviation is shortened and the peak power densities rise, the low damage threshold of presently available coatings present a serious bottleneck. There are similar requirements for coatings on window materials transmitting in the 2-5  $\mu$ m wavelength region. Finally, with respect to laser characteristics, pulsed laser powers are expected to be 10<sup>6</sup> W/cm<sup>2</sup> or greater with pulse durations of 10-50  $\mu$  seconds. CW and average power densities are expected to be 10<sup>4</sup> W/cm<sup>2</sup>.

With these background problems in mind, the meeting was organized with the following program:

Introduction	C. M. Stickley Materials Sciences Office ARPA
Anticipated Coating Requirements	D. Holmes and M. J. Soileau Air Force Weapons Lab.

#### LASER INTERACTION EFFECTS

Evidence for Avalanche Breakdown	M. Bass
on Uncoated Dielectric Surfaces	Raytheon Research Div.
Increased Surface Damage Threshold	C. Giuliano
by Ion Polishing	Hughes Research Lab.
Surface Damage Studies in Glass	N. Boling Owens-Illinois
$CO_2$ Laser Induced Damage to Mirrors	M. Braunstein Hughes Research Lab.

# CURRENT OPTICAL COATING RESEARCH & TECHNOLOGY; SURFACE FUNDAMENTALS

Surface and Coating Research at Perkin-Elmer	F. Zernike Perkin-Elmer
Dielectric Coatings for Windows and Mirrors	M. Braunstein Hughes Research Lab.
Surface and Coating Research at ITEK Corporation	R. Hills, Jr. ITEK Corporation
Polymeric Films and Other Techniques from Integrated Optics for Low Loss Coatings	G. Smolinsky Bell Telephone Lab.
Crystallization of Vitreous Coatings	D. Dove University of Florida
Surface Science and Surface Damage	J. Khan Lawrence Livermore Lab.
SURFACE PREPARATION AND FILM	DEPOSITION
Surface Preparation Techniques	E. Mendel IBM, Fishkill
Silicon Surface Control	L. von Ohlsen Bell Telephone Lab.

Physical Methods of Film Deposition and Applications to Optics

Film Growth by CVD and Applications Applications to Optics

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J. Vossen RCA, Princeton

H. M. Manasevit North American Rockwell Electronics Group

# SURFACE ANALYSIS AND CHARACTERIZATION

Electron Beam Methods for Optical	J. Porteus
Surface Evaluation	Naval Weapons Center
Ellipsometry as a Technique Yor	H, Bennett
Evaluating Optical Surfaces	Naval Weapons Center
Alkali Halide Surface Absorption	T. Deutsch Raytheon Research Div.

Surface Adsorption and Diffusion	G. Haller	
Studies by IR spectroscopy	Yale University	
Elemental Analysis of Thin Surface	J. W. Coburn	
Layers of Solids	IBM, San Jose	
Mechanical Properties of Films	R. W. Hoffman Case Western	

The meeting provided a forum for the exchange of information in surface technology. The interaction between experts with optical and semiconductor background respectively proved to be very useful. Workers in the high-power laser field became better acquainted with the problems of surface analysis and characterization. Conversely, experts in the fabrication of coatings were exposed to the problems of laser induced damage. At the end of the meeting the participants were invited to write down comments and and suggestions for future work.

The first session, <u>Laser Interaction Effects</u>, was meant to be an elaboration on the problem as we know it, in particular, the problem of surface breakdown at high pulsed laser powers. Bass gave impressive evidence for surface breakdown of nonlinear optical materials being an avalanche effect. Bass also reported that sleeks in the surface did not change the damage threshold. Giuliano showed that ion polishing of sapphire can raise the damage threshold by some 2 to 6 times, approaching to within a factor of 4 to 5 of the bulk breakdown threshold (where selffocusing is avoided).

A satisfactory explanation now exists as to why the exit

-79-

and entrance surface damage thresholds on optical materials are different. This seemed to be well explained by N. Boling, Owems-Illinois, by considering what the actual electric fields are in the glass at the exit and entrance surface. One needs a higher incident intensity to produce an acting field of threshold breakdown at the front surface than to produce the same field strength at the exit surface. Strong support for the argument seems to be given by the results of their experiment in which a piece of glass was cut at brewsters angle and then irradiated with a laser beam. For this case the exit and entrance surface damage thresholds were the same.

Braunstein reported on pulsed  $CO_2$  laser induced damage to mirror surfaces. Damage thresholds as high as 140 J/cm<sup>2</sup> in pulsed lengths of 10 microseconds were reported. They were for metal films on metal reflectors. For dielectric enhancement layers on metal reflectors much lower breakdown energies, 10 to 20 J/cm<sup>2</sup>, were observed. Braunstein felt the reason for this difference was due to the high absorption which appears in the films. Other factors which he felt to be of importance were high thermal conductivity of the coating layers as well as purity of starting materials for making the coatings.

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In the session on <u>Current Optical Coating Research and</u> <u>Technology</u>, Zernike reported being able to achieve more adherent, thicker coatings using sputtering. He attributed this to the lower temperature of the sputtering deposition process relative

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to thermal vacuum evaporation. He also pointed out that by propagating the beam along the surface of the coated substrate, one can evaluate not only the losses within the coating but also the losses caused by the substrate. This could be a new approach to measuring low losses in coatings as well as substrate roughness. In the second talk Braunstein reported achieving mirror reflectivities in excess of 99.8%. However, he still has difficulty in predicting the refractive index of the films which are deposited, and finds that it is necessary to monitor this with a stable CO<sub>2</sub> laser. Again, absorption is dominant in the CdTe and ThF, films. It is 10 to 100 times higher than at the same wave length in the bulk material. He feels that higher purity starting materials, better deposition techniques, and identification of impurities are needed. Further, an explanation for the discrepancy between theory and experiment in thin film thickness is needed.

Hills of ITEK reported that the bowl feed polishing process produced dramatic reduction in surface scatter which continues earlier research results. Thermal cycling tests performed on gold coated mirrors indicated failure of the gold coatings. With respect to windows, ITEK has applied protective coating: to KCL windows which can withstand power densities in excess 10<sup>4</sup> watts/cm<sup>2</sup> continuously for minutes and which are also impervicus to environmental attack. The nature of these coatings was described as being proprietary.

-61-

Smolinsky of the Bell Telephone Laboratories reported on the study of the use of polymeric films for optical wave-guides. Potential advantages for their use as coatings for IR laser windows are that the indices can be low (in the 1.3 range), the refractive index could be graded if necessary, and they are pinhole-free. It is necessary to deposit coatings using oxygen free techniques, and the transmission of such coatings in the 10 micron range may be questionable.

Work reported by Dove indicated that although vitreous coatings such as  $As_2S_3$  are attractive for coating alkali halide materials one must be aware that they may not be that stable and may become crystalline. This could lead to cracking of the coatings and subsequent attack by moisture on windows.

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Khan reviewed some nine different techniques for studying surfaces and urged that they be employed between the various steps in polishing surfaces as well as in depositing coatings.

In the session of <u>Surface Preparation and Pilm Deposition</u>, Eric Mendel of IBM described three chemical-mechanical techniques which have been developed for polishing silicon. Two of these he feels could be modified for achieving defect free surfaces on glass and perhaps some other materials. He also pointed out that corfam is a superior polishing cloth as a result of its porosity. Von Ohlsen of the Bell Labs described the very elaborate surface preparation procedure which has evolved there for cleaning silicon for use in picture phone applications.

-82-

Vossen of RCA reviewed the various film deposition techniques (vacuum evaporation, electron beam evaporation, laser evaporation, glow discharge evaporation and sputtering) with greatest emphasis on sputtering. He felt that sputtering has good potential for use with optical coatings but one has to be careful and develop it specifically for the application for which it was intended. Manasevit of North American Rockwell reviewed the growth of III-V and II-VI films using chemical vapor deposition. Although they have not done characterization of them for optical applications, he recommends CVD as a technique to be used because of the flexability one has in the process and the purity that can be maintained.

In the session of <u>Surface Analysis and Characterization</u>, Porteus of the Naval Weapon Center reviewed the pros and cons of the various electron beam methods for surface evaluation. Bennett reviewed ellipsometry as a technique for evaluating optical surfaces. The technique is extremely sensitive (100th of a monolayer or less) but at the same time can lead one to extremely precise wrong answers if the operator does not have a great depth of experience in the use of this technique.

Deutsch of Raytheon reviewed the measurement of surface absorption by both calorimetry and by attenuated total reflection. Experimental data obtained by the two techniques were within a factor of 2 of agreem nt. He felt that the limit of surface absorption measurement by either of these techniques is on the

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order of 10<sup>-4</sup> per surface. Straightforward calculations indicate that for the case where a surface absorbs a tenth percent of a one joule per square centimeter beam in a depth of 10 microns a temperature rise between 1 and 10 degrees will result. Clearly, if the equivalent surface thickness is less than this, the temperature rise will increase proportionately. He reviewed the results of measurements of KCl crystals from various sources as well as barium fluoride and zinc selenide. Numbers for fractional surface absorption in various samples of these materials ranged from 3 to 12 times  $10^{-4}$  per sample. On the other hand bulk absorptions range from 3 to 28 times  $10^{-4}$ /cm. These numbers indicate the extreme difference in surface absorption from bulk absorption since an equal amount of surface absorption is occurring over a path length some 10<sup>4</sup> times shorter. Deutsch reported measuring the surface absorption with a cleaved halide crystal from Cornell and found that the surfaces of this crystal has a high loss. Haller of Yale University described other experiments on surface adsorption and diffusion studies using techniques similar to those by Deutsch. He observed the same absorption bands on the alkali halides as Deutsch reported. Heating in a vacuum tended to drive off the  $1000 \text{ cm}^{-1}$  adsorption. He feels that the carbon-carbon stretching frequencies are primarily responsible for this; he also emphasized that oxygen double bonds with heavy metals absorb in the vicinity of 10 microns.

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Coburn of IBM described a technique combining sputtering and ion mass spectroscopy for determining the impurity content of

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layers of materials near surfaces. The technique is destructive and has no spatial resolution but has the potential for a quantitative standardless surface analysis technique which is independent of the host or matrix material. The sensitivity is currently 10<sup>11</sup> atoms per second leaving the surface but he feels that this could be improved upon considerably. He also reviewed other methods for obtaining composition as a function of depth in materials; he felt that the nuclear back scattering technique was important since it is the only nondestructive one that is available.

Finally Hoffman of Case Western reviewed present knowledge of the mechanical properties of films. Film characteristics which are important in achieving low stress are that the thermal expansions of the film and the substrate be the same. Additionally, the lattice constant should be small in order to prevent dislocation development in films. He also pointed out how little was known about adhesion. Specifically, there are no techniques for yielding quantitative numbers for it. Various comments were made about what approaches one takes for increasing adhesion. There were differences of opinion as to whether or not it was more important to have a clean surface than to have a clean one with some specific impurities present. What these impurities might be are not known.

The conference may be summarized in the following conclusions:

I. Uncoated Surfaces

1. The ideal intrinsic surface, free from grooves, incipient

-85-

cracks and impurities, should have absorption and damage characteristics comparable to the bulk. It is true that specific surface states, surface vibrations and other excitations, as well as the breakdown of symmetry at the surface may cause variations in the absorption characteristics. If one stays sufficiently far away from bulk absorption edges, however, such intrinsic surface absorption mechanisms appear to be negligible. 1

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2. Extrinsic surface characteristics such as scratches, inclusions from abrasive dust, chemical impurities, etc., play an important role in lowering the surface damage threshold, as discussed in more detail in a separate research note by Bloembergen.

3. The extrinsic properties of the surface are a sensitive function of the polishing techniques used. Much effort should be directed towards avoiding surface irregularities, such as pits and grooves on a scale larger than 0.01  $\mu$ m. Polishing techniques which avoid the use of any solid materials which absorb at 10.6  $\mu$ m and are liable to be deposited as damaging inclusions, should be developed for IR window materials, cleaning mechanisms to remove all absorbing materials and fluids should be included in the study of polishing techniques.

4. The surface of the window materials, before depositing coatings, should be characterized by

a. Optical scattering and flatness.

b. Scanning electron microscopy to determine geometry density and size of deviations from a shooth geometry.

-96-

c. Surface absorption calorimetry.

d. Damage threshold for high power density laser pulses.

It is believed that electron beam diffraction and other spectroscopic techniques are less useful in the development of acceptable IR window surfaces. In this connection it should be noted that a sizeable coverage of the first surface layer by -0 or -OH bonds is acceptable for operation at 10.6  $\mu$ m.

II. Coatings

5. Film deposition techniques should be studied with the goal of minimizing the density and size of pores, absorbing inclusions, and achieving good film adherence with uniform thickness.

6. The films should be characterized by the same techniques as mentioned under (4) for surfaces.

7. In choosing film materials attention should be given to the following characteristics:

a. Low intrinsic bulk absorption.

b. Matched thermal expansion with that of the substrate.

c. Adhesion and interfaces.

d. The possibility of epilaxial growth on single crystal substrates to avoid pores and cracks.

e. The influence of the structure of the film and substrate (i.e., single crystal, state of surface polish, absorbed surface layers, grain boundaries, amorphous or polycrystalline structure) should be investigated.

f. Spec al attention should be given to the development of organic polymer coatings both for protective and antireflective purposes because of their promise to avoid cracks, pores and inclusions, their low optical index of refraction and mechanical strength.

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8. The presence of pores and microcracks is detrimental to both the electrical and mechanical breakdown strength of the film. The problem becomes progressively more severe in thicker films. The antireflection coatings of the required properties will be much more difficult to produce than protective coatings. The presence of pores and microcracks is relatively more detrimental in materials with a high index.

#### PROGRESS REPORT OF STRESS-CORROSION GROUP

# ARPA Materials Research Council Centerville, Massachusetts 10-12 July 1972

#### Members

B. F. Brown, Naval Research Laboratory (formerly)
M. Cohen, Massachusetts Institute of Technology
J. P. Hirth, Ohio State University
H. H. Johnson, Cornell University
J. Kruger, National Bureau of Standards
F. A. McClintock, Massachusetts Institute of Technology
H. W. Paxton, National Science Foundation
E. N. Pugh, University of Illinois
H. H. Uhlig, Massachusetts Institute of Technology

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The above group met for the three-day period of 10-12 July 1972 in order to:

(1) assess the Materials Research Council Report of July 1971 on the "Environmental Degradation of Stressed Materials," in preparation for drawing up a set of conclusions and recommendations relative to important problem areas in stress corrosion; and

(2) examine the feasibility of preparing a Handbook on Stress Corrosion, and to suggest ways of implementing such a project.

These objectives have been reached, and a detailed report is now being written by M. Cohen and H. H. Johnson. A draft of the report will be mailed to the participants for further refinement before it is submitted to the Council.

-89-

With respect to item (2) above, we are in complete agreement that a "handbook program" should be implemented in order to transmit quickly what is known about the hazards and prevention of stress corrosion to design and operating engineers. The plan that we recommend for this purpose involves three parts: ------

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Part I:	Case Histories of Stress Corrosion
Part II:	Compilation of Qualitative Engineering Information on Stress Corrosion
Part III:	Compilation of Quantitative Engineering Data on Stress Corrosion

# Part I

It now seems quite feasible to select up to about 50 well-documented case histories encompassing all the main alloy/ environment systems in which conspicuous stress-corrosion failures have occurred, and for which remedies are now available. Each such case history can be introduced with a preview of the essential phenomena and dangers being illuminated by the account, and can also be concluded with statements concerning the range of applicability of the lessons being portrayed. It is essential that good photographs and micrographs be incorporated wherever possible, and a detailed index will be necessary for leading the reader to those histories which have points of interest to him.

We estimated that this project would take about one year for completion.

#### Part II

We also propose that the engineering information on stress-corrosion, gathered in Part I and from other sources,

-90-

should be tabulated in qualitative form, as a companion piece to Part I. Conceivably, the two sections could be bound into the same book, but that decision does not have to be made until the program is underway.

There will be two types of compilation displays in Part II: (a) arranged according to the alloy system, (b) arranged according to the environmental system.

In (a), the key alloys will be approximately 30 in number: steels, including maraging steels and stainless steels, aluminum alloys, titanium alloys, copper alloys, monel, and magnesium alloys. Under each such heading, there will be (i) a list of known stresscorrosion hazards (e.g., this material will crack in the presence of...), (ii) a list of relevant stress-corrosion control methods (e.g., galvanic protection, deaeration, inhibiting ions, etc.), and (iii) special remarks pertaining to fabrication, residual stresses, references to case histories in Part I, etc. Key papers will be referenced where appropriate throughout this tabulation.

In (b), the display will be categorized by type of environment, perhaps 25 in number. Among these to be considered are: pure water, tap water, sea water, atmosphere, caustic solutions, acid solutions, chlorides, nitrates, ammonium salts, sulphates, sulphites, sulphides, cyanides, and several liquid metals and salts. Under each such heading, the following qualitative information on stress corrosion will be given for each material that can be reported on: A. No failures in laboratory or in the field; B. Failures in the laboratory, but not in the

-91-

field; C. Failures in the laboratory and in the field. When possible, these A, B and C designations will be used to show trends with respect to pH, temperature, ion concentration, deaeration, circulation, etc.

We estimate that Part II can be completed within one year after Part I.

# Part III

It should be evident that Part I, as proposed here has a missionary objective in transmitting the acquired experience in stress-corrosion failures to the engineering community, while Part II will present systematized back-up information in readily accessible (but qualitative) format. In contrast, Part III will be a handbook compilation of more quantitative data which will be of particular value in design and failure analysis. Clearly, this is a more difficult and longer-range assignment than in the case of Parts I and II. Its exact nature and feasibility will require more careful study, but we have evolved some specific ideas on the matter which make the task look achievable.

M. Cohen

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#### GRADIENT MATERIALS

# Summary of Meeting Held in Centerville, Mass.

A one-day meeting of gradient materials was held on July 12, 1972. This was an extension of a similar meeting held last year.

Five prepared talks were given by invited lecturers, one by a consultant and one by a Council member. The subjects were: an introduction to the structure and properties of gradient materials (Bever), the topological and percolation criteria for phase connectivity as applied to gradient structures (Quinn and Bishop), gradient polymers (Shen), impact-resistant gradient steels (Goldstein) and three talks on armor materials involving ceramics (Clougherty, Stiglich and Gazza, respectively).

The meeting produced a great deal of discussion. Subjects of special interest were (i) several fundamental problems, especially concerning connectivity, (ii) materials preparation, (iii) penetration mechanics of armor and (iv) general applications of gradient materials. Subsequently, two memoranda on subjects suggested by the meeting were written by Coble and by Lee, Budiansky and Drucker.

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-93-

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-93-

#### REPORT OF STRENGTH-DIFFERENTIAL GROUP

# ARPA Materials Research Council Centerville, Massachusetts July 1972

From an experimental standpoint, the strength-differential effect shows up most simply as a positive difference between the flow stress in uniaxial compression and that in uniaxial tension. Most of the available data on this phenomenon have been obtained on martensitic steels and certain polymers.

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Several informal meetings were held during the Centerville sessions in an effort to elucidate the origin of the strengthdifferential effect. Those participating from time-to-time were:

B. Budiansky, Harvard University
R. Coble, Massachusetts Institute of Technology
M. Cohen, Massachusetts Institute of Technology
D. C. Drucker, University of Illinois
J. J. Gilman, Allied Chemical Corporation
J. P. Hirth, Ohio State University
H. H. Johnson, Cornell University
E. H. Lee, Stanford University
F. A. McClintock, Massachusetts Institute of Technology
S. V. Radcliffe, Case Western Reserve University
S. Sternstein, Rensselaer Polytechnic Institute

It now appears that the strength-differential arises primarily in the intercept flow stress (i.e., the flow stress extrapolated back to zero plastic strain) rather than in the strain-hardening characteristics. In addition, there are both athermal and thermal components in the strength-differential phenomenon which seem to require different models. Evidently, the existence of a strength-differential signifies that the resolved shear stress does not uniquely control the flow process, but the other stress components (such as hydrostatic pressure or the resolved normal stress across the glide plane) have an effect on the flow strength. Attention was given to various hypotheses for explaining the strength-differential phenomenon, particularly in comparing the concepts of continuum plasticity and activated flow. Much depends here on whether a macroscopic volume expansion occurs during plastic deformation or whether there is a local (and transient) dilatation associated with an activation step in the elementary flow process. Several experimental approaches for resolving such questions were proposed.

In the light of the different viewpoints held by the Council members, a comprehensive outline on the strengthdifferential was prepared, covering the main theoretical ideas on the subject and pointing up the remaining critical issues. This will form the basis for a definitive group paper next summer, tentatively entitled "A Perspective on the Strength-Differential Phenomenon."

M. Cohen

-95-

# SYMPOSIUM ON MECHANICAL PROPERTIES OF BRITTLE MATERIALS

On July 17, 18, 19, a symposium on the mechanical properties of brittle materials was held with special reference to  $Si_3N_4$  and SiC. The purposes of the meeting were to:

(1) Review the general materials situation for these materials in connection with the ARPA Ford-Westinghouse contract, in the millieu of the MRC with a carefully picked group of other university and industrial experts.

(2) Review the special situation of flaw detection and the reliability of brittle materials.

Meetings were held on the general topics of slow crack growth, relation of microstructure to mechanical strength, and flaw detection techniques. The technical discussion was unusually free of constraints from industrial proprietary barriers because of the format of the meeting, and provided a clear picture of the state of the art at the present time. Several participants attended from Ford, Westinghouse, AMMRC, and NBS, with about a dozen other specialists. A detailed summary of the meeting has been prepared by A. G. Evans and R. L. Coble for use as a background document for the development of a program in the reliability of hrittle materials at NBS. The full paper is included in the annual project report with an abstract included in this report (see abstracts appendix).

#### R. Thomson

-96-

#### A WORKSHOP ON FRACTURE DATA

Held at Centerville, Massachusetts July 20, 21, 1972

A workshop organized by the National Bureau of Standards was held under the auspices of the Materials Research Council to review needs for compilations of fracture data. The recommendations will be used to design an appropriate activity in Fracture Data at the Bureau of Standards. Participants from three basic industries were invited: automobile and construction equipment, railroad, and pressure vessel and electrical generating equipment. In addition, professionals from the academic community and the National Bureau of Standards attended. Recommendations for the development of two types of fracture data compilations were made, one for a simplified introductory compilation for day-to-day design purposes. This handbook is intended to alleviate the paucity of modern design handbooks oriented to fracture design control. A second, more complete fracture data compilation again directed at the design community is also needed, and the specific subjects are outlined in the report. The full paper is included in the annual project report.

R. Thomson

-97-

#### REPORT OF ENERGY GROUP

# ARPA Materials Research Council Centerville, Massachusetts 20-21 July 1972

The Materials Research Council hosted a two-day workshop on energy-materials, organized by Professors A. L. Bement and R. Kaplow of MIT. Other active participants were S. H. Bush, P. L. Farnsworth, R. Fitzgerald, M. C. Flemings and C. T. Sims. Several members of the Council also attended these sessions.

Overviews of the following energy-conversion subjects were presented:

1. Enumeration of Proposed New Energy Schemes

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- 2. Solar Energy
- 3. Fast Breeder Reactors
- 4. Fission Reactors
- 5. Fusion Reactors
- 6. Magnetohydrodynamics
- 7. Steam and Gas Turbines
- 8. Review of Current Materials Processing Issues

Two of the above energy-conversion technologies were

then selected for detailed examination: Gas Turbines and Fusion Reactors. Consideration was given to the needed R and D areas, the timing for effective impact, and the cost of such material programs. A comprehensive report on the proceedings has been prepared by Professors Bement and Kaplow. It can be found in the annual project report. It is likely that the Materials Research Council will elect to continue with these energymaterial studies.

M. Cohen

# STRUCTURE OF DISORDERED CARBONS

# Summary of Meeting Held in Centerville, Mass. July 25, 1972

The meeting brought together several active investigators with interested members of the Materials Research Council for a review of recent findings and a discussion of future direction for the ARPA disordered carbon programs currently underway at four laboratories.

Mechanical, physical, and thermodynamic properties of porous glassy carbons were discussed by E. Hucke. Particular attention was given to the wide range of structures obtainable through processing variations. Structural differences as deduced from X-ray, electron diffraction, electron microscopy, porosimetry, and surface area measurements were shown to be present on size levels from 10 angstroms to the micron level.

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G. Tingey reported on measurements of thermal shock, oxidation kinetics, specific heat, thermal diffusivity, and fracture toughness.

The effects of pyrolysis under high pressure were reviewed by F. Dachille. R. Kammereck reported on the interesting possibilities of "alloying" carbons by way of controlled additions of Fe and other materials to the precursor polymers.

-100-

Disordered carbons produced by gas pyrolysis and possibilities of controlled additions of Si, Ti and B were discussed by J. Bokros.

The short range structure of carbons was given considerable attention by the group. J. Carpenter reviewed his recent measurements of neutron diffraction and scattering. E. Hucke discussed a thermodynamic method for characterizing disorder in terms of the configurational entropy.

S. Ergun reported on the results of his very detailed X-ray analysis of pyrolytic graphite and glassy carbon. His results, which are to be published, lead him to conclude that atoms in the graphite structure are not in a hexagonal array, but rather correspond to a slightly distorted "Quinoidal" arrangement.

A lively discussion ensued on many of the points raised. It was concluded that little can be stated with certainty about the short range bonding in disordered carbons, except that they are disordered layered structures.