



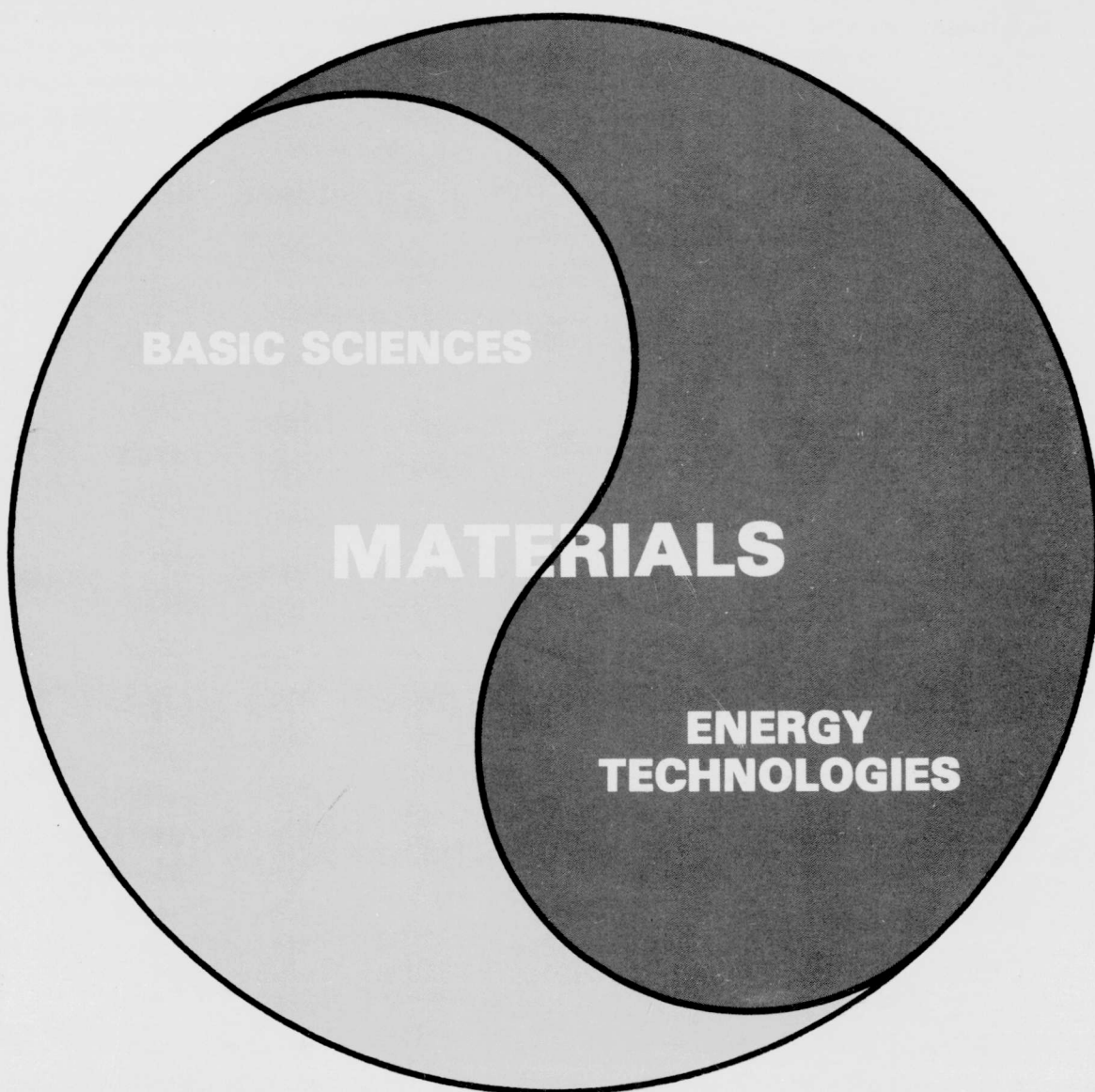
Materials Sciences Overview

A Series of Workshops Recommending Future
Directions in Energy-Related Basic Materials Research

II. Workshop Reports

Energy Research & Development Administration
Division of Basic Energy Sciences
Materials Sciences Program

AUGUST 1977



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Directions in Energy-Related Basic Materials Research

II. Workshop Reports

Organized by:

W.L. Clinton,* J.R. Cost & L.C. Ianniello**

Energy Research & Development Administration
Division of Basic Energy Sciences
Materials Sciences Office

August 1977

* On leave from Georgetown University

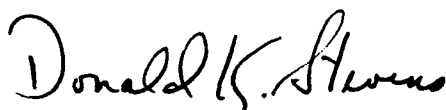
** On leave from Purdue University

Foreword

This volume is a compendium of the reports of nine workshops held in the Spring of 1977 to ascertain new directions and priorities for energy related basic research in the Materials Sciences Program. A summary conference was held June 13 and 14 which brought together workshop organizers and various administrative and management staff members in the materials community for the purpose of reviewing the conclusions in preparation for the final workshop reports.

The workshop series constitutes a study of the Materials Sciences Program of the Energy Research and Development Administration (ERDA), Division of Basic Energy Sciences (DBES). This is the first time such a comprehensive study has been undertaken. It should be noted that early in 1977 the Basic Energy Sciences Division was formed from portions of the former Division of Physical Research (DPR), which included the Materials Sciences Program. Also, at the time of writing this report, a new Department of Energy is being formed which will include ERDA.

Although there will be many different assessments of the study, a number of positive results can be stated already. The study has provided another opportunity for increased communication among scientists, both basic and applied. The involvement of the scientific community in planning has also had an important effect in making them aware of the problems and difficulties in setting priorities for the overall field of Materials Sciences. Their dedicated effort in establishing these priorities and pointing out the most exciting new areas in basic materials research for energy has brought forth this document. The task now for all of us is to carry through on the most important recommendations.



Donald K. Stevens
Assistant Director
(for Materials Sciences Program)
Division of Basic Energy Sciences

TABLE OF CONTENTS

	<u>Page</u>
Foreword	i
Introduction	v
Electronic, Magnetic, Optical and Thermal Properties	1-1
Surface Science	2-1
X-Ray, Neutron and Electron Scattering	3-1
Low Temperature Research and Superconductivity	4-1
Phase Transformations, Stability and Materials Interactions . .	5-1
Defects, Diffusion and Radiation Effects	6-1
Engineering Materials Science	7-1
Mechanical Properties	8-1
Thermodynamics and Electrochemistry	9-1

INTRODUCTION

In the two years since the multifaceted research and development activities of the Atomic Energy Commission (AEC) were merged into ERDA, the staff of the Materials Sciences office has worked very closely with its contractors at the National Laboratories and universities to encourage a responsiveness to the broadened responsibility for basic research in all areas of energy related materials science. The result of this broadening is evident in much of the research supported by the Materials Sciences Program. Specifically, new emphasis has been placed on the perceived needs of the fossil, solar and geothermal technologies as well as those of conservation, environment and safety.

As an additional response to the expanded mission of ERDA, the staff of the Materials Sciences Program inaugurated the current study. This study was designed to augment other planning mechanisms as well as give the basic scientists an opportunity to provide input to the overall planning process. Further, it was hoped that better communications between the basic science and energy technology communities would be a result, assuming a suitable methodology for the study - one encouraging basic and applied interactions. The primary charge to the scientists and engineers helping with the study was to ascertain the most promising and exciting new areas in energy-related basic research in the materials sciences and assign priorities to these areas. In considering this charge some important institutional questions concerning basic materials research supported by ERDA-DBES were discussed, including: optimal utilization of ERDA facilities; research mix among National Laboratories, universities, and industry; short-term and long-term impact of basic research; and technology transfer.

It was clear from the outset that a single conference of reasonable duration would not do justice to an endeavor of the magnitude under consideration. Therefore, it was decided that a workshop format was most appropriate in order to optimize communications. In addition to the workshops, which were the central and most important part of the study, three other major steps were envisioned. First, the materials sciences field had to be categorized or classified into subfields so that a cohesive workshop could be organized for each one. Then, after the workshops in the various subfields were held, the results had to be presented and discussed by a general audience consisting primarily of ERDA contractor managers, staff from the applied divisions of ERDA and personnel from other Federal agencies. Finally, a report would be needed which would be available to all interested persons.

The first phase of the process, division of the field of materials science into various subfields, presented a problem because it could be done in myriad ways. However, after many iterations, a classification based upon various materials-related phenomena (with one exception) was developed. This classification resulted in the nine workshop titles listed in Table I. It accomplished the two objectives of maximizing the compatibility of members of a given workshop and minimizing overlap between categories. Some overlap between workshops was inevitable; however, it was considered preferable to omission of a potentially important area. In addition, overlap was minimized by close coordination between the workshop organizers and the staff of this office.

The second major phase of the operation was to actually form a workshop in each of the nine areas. First, a major ERDA laboratory was chosen as the location for each workshop. The majority of the nine were held at the two largest Materials Sciences contractors, the Argonne and Oak Ridge National Laboratories. Next, co-organizers for each workshop were chosen. The criterion for their selection was individual scientific stature with appropriate representation from the university and industrial communities as well as from the National Laboratories. These principles were also used, in turn, by the organizers to choose the workshop participants. Additional guidelines used were that the majority of participants be from outside the National Laboratories and the energy technologies be represented. For all nine workshops, a total of 380 scientists and engineers participated, or an average of about 42 per workshop. The membership distribution included: National Laboratories (37%), Universities (33%), Industry (15%), ERDA (8%), Other, e.g., NBS (7%).

The format of each workshop was determined by its organizers; it was quite varied. Typically the workshops began with briefings or overviews from representatives of the major energy technologies who were charged with presenting the materials-related needs of their technology to the members. Also, at most of the workshops the highlights and status of particular scientific areas unique to the workshop were summarized by leaders in the field. In all but one of the workshops the members were divided into study groups of from 5 to 10 members. These study groups were the basic working unit of the workshops. Each one had the responsibility for studying and arriving at the workshop goals for a particular subcategory of the workshop subject area. It was emphasized to each study group leader that a several page draft of the report would be expected by the end of the workshop. The study group leaders were asked to present the group's recommendations when the full workshop membership met to establish priorities and make overall recommendations.

The third phase of the study was the workshop summary conference and the meeting of the workshop organizers. These meetings were scheduled on adjacent days, June 13 and 14. The conference on workshop summaries had the objective of presenting workshop results to a broad audience consisting of ERDA Headquarters representatives, workshop organizers, program managers from ERDA laboratories, staff of other agencies and some other key materials people. In each of the summary talks, one of the organizers from each workshop presented the priorities and new promising directions as viewed by the workshop membership. Ample time was allocated after each summary for discussion of the workshop results, including the technical priorities, by the attendees.

One of the recurring themes in the discussions both at the workshops and at the summary conference involved the following dilemma: "There is a need for basic research to be as undirected as possible to preserve its capacity to uncover the unexpected; on the other hand, the energy mission of the agency results in a need to direct the research (broadly speaking) to optimize the potential for pay-off." In this climate many basic scientists found themselves on the horns of the dilemma - the workshop goals of setting priorities brought this to the fore. One of the results of both the workshops and the meeting was to come to grips with this problem by recognizing that priorities did have to be set and that members of the scientific community as well as from the applied technologies could have important input to the process.

On the day following the workshop summary conference, the organizers held a half-day meeting at which the format of the report and the general question of "What has emerged from this Study?" were discussed. Three specific topics were considered: overall technical priorities; facility and equipment recommendations; and basic-applied interactions and followup suggestions. The results of these discussions are incorporated in the individual reports to the extent possible. Broad recommendations were provided for the Materials Sciences office. After the workshop reports are published and distributed a followup meeting will be considered.

The final phase of the workshop study of the Materials Sciences Program is the publication of two reports. The first (Vol. I) provides an executive summary of the study. The second (this publication) is a compendium of the workshop reports. In addition, several of the host laboratories will publish more detailed reports in order to include technology and basic science overviews and other ancillary information not included in the present volume.

Table I
Organization of Materials Sciences Program
Study Workshops

<u>Workshop Title</u>	<u>Location</u>	<u>Organizing Group</u>	<u>Dates</u>
1. Electronic, Magnetic, Optical and Thermal Properties*	ANL	D. Price (ANL) A. Freeman (Northwestern U.) M. Cohen (U. of Chicago) P. Seiden (IBM)	March 9-11
2. Surface Science*	LBL	G. Somorjai (LBL) J. Yates (NBS)	March 16-18
3. X-Ray, Neutron and Electron Scattering*	ORNL	M. Wilkinson (ORNL) A. Bienenstock (Stanford U.) J. Rush/J. Rowe (NBS) M. Blume (BNL)	April 13-15
4. Low Temperature Research and Superconductivity*	BNL	M. Strongin (BNL) J. Mercereau (Cal Tech) J. Wheatley (UC/San Diego)	April 18-20
5. Phase Transformations, Stability and Materials Interactions**	LBL	W. Morris (LBL) L. Brewer (LBL) P. Shewmon (Ohio State U.)	April 18-20
6. Defects, Diffusion and Radiation Effects**	ORNL	F. Young (ORNL) J. Stiegler (ORNL) A. Nowick (Columbia U)	April 27-29
7. Engineering Materials Science**	ORNL	C. McHargue (ORNL) C. Wert (U. of Illinois)	May 2-4
8. Mechanical Properties**	ANL	F. Kocks (ANL) A. Evans (Rockwell Int.)	May 5-7
9. Thermodynamics and Electrochemistry**	ANL	F. Cafasso (ANL) N. Nachtrieb (U. of Chicago) L. Darken (Penn State U.)	May 18-20

Bill Clinton (*) and Jim Cost (**) on leave to the Materials Sciences Program from Georgetown University and Purdue University respectively, were members of the designated workshop Organizing Group.

MATERIALS SCIENCES WORKSHOP ON

ELECTRONIC, OPTICAL, MAGNETIC AND THERMAL PROPERTIES

Held March 9 - 11, 1977 at Argonne National Laboratory

Organizers

D. L. Price, Argonne National Laboratory
W. L. Clinton, ERDA, Division of Physical Research
M. H. Cohen, University of Chicago
A. J. Freeman, Northwestern University
P. E. Seiden, IBM, Yorktown Heights

Participants

B. Abeles, RCA	L. C. Ianniello, ERDA, Physical Research
D. Adler, MIT	I. S. Jacobs, General Electric
R. H. Baughman, Allied Chem.	G. Jones, Boston Univ.
H. Birnbaum, Univ. of Illinois	E. S. Kirkpatrick, IBM
A. N. Block, Johns Hopkins Univ.	G. G. Libowitz, Allied Chem.
H. K. Bowen, MIT	A. A. Maradudin, UC-Irvine
M. B. Brodsky, Argonne Nat'l Lab.	P. J. Melz, IBM
F. C. Brown, Univ. of Illinois	D. W. Murphy, Bell Labs.
J. I. Budnick, Univ. of Connecticut	S. R. Nagel, Univ. of Chicago
F. A. Cafasso, Argonne Nat'l Lab.	R. L. Orbach, UCLA
R. S. Claassen, Sandia	D. L. Price, Argonne Nat'l Lab.
W. L. Clinton, ERDA, Physical Research	D. W. Readey, ERDA, Physical Research
M. H. Cohen, Univ. of Chicago	W. L. Roth, General Electric
H. L. Davis, Oak Ridge Nat'l Lab.	G. Seidel, Brown Univ.
J. P. DeNeufville, Exxon	P. E. Seiden, IBM
C. B. Duke, Xerox	B. O. Seraphin, Univ. of Arizona
V. J. Emery, Brookhaven Nat'l Lab.	R. W. Staehle, Ohio State Univ.
H. F. Franzen, Ames Laboratory	M. B. Stearns, Ford Motor Co.
A. J. Freeman, Northwestern Univ.	M. C. Smith, Los Alamos Sci. Lab.
S. Foner, MIT	R. W. Vest, Purdue Univ.
A. F. Garito, Univ. of Pennsylvania	J. B. Wagner, Arizona State Univ.
T. Geballe, Stanford	A. R. Williams, IBM
K. A. Gschneidner, Ames Laboratory	R. K. Williams, Oak Ridge Nat'l Lab.
B. K. Halperin, Harvard	M. Wolf, Univ. of Pennsylvania
S. D. Harkness, Argonne Nat'l Lab.	C. R. Wronski, RCA
J. Hulm, Westinghouse	

WORKSHOP PRIORITIES

This broadly based Workshop, covering the fundamental properties of condensed matter and their measurement, identified a large number of high priority areas of research important to basic materials science problems in the energy technologies. These are discussed in detail in the individual Study Group Reports and summarized in the body of this Workshop Report. Major priorities, representing large scale areas common to many study groups, or specifically emphasized by individual groups, are given here.

Priority I: Exciting Scientific Area with High Probability for New Findings.

- There is a critical need for the preparation and investigation of new materials, since it is in this way that radical improvements in materials properties will be made. In general, efforts directed towards systems where the structure or chemical bonding already suggests the existence of unusual properties should be encouraged. Examples include ternary compounds (providing, for example, the opportunity to dramatically change material properties by a change in stoichiometry), intercalation compounds (e.g., super-acids in graphite, which are claimed to have conductivities comparable to copper), amorphous materials (discussed by many study groups for their enhanced chemical resistance, high strength combined with ductility, possible use as selective absorbers for photothermal conversion, etc.), biological materials (e.g. synthetic enzyme catalysts), unusual oxidation states, anisotropic materials, organics and polymers, composites, aggregates, inhomogeneous phases and granular materials. The development of new materials will require novel methods of synthesis. In some cases (e.g., amorphous and ceramic materials), it seems that understanding of fundamental properties will not be achieved without better preparative procedures.
- Theoretical activities need to be increased substantially. Important areas for energy research are: unification of existing empirical correlations of properties (e.g., the structure and stability of alloy phases), the calculation of properties for which capabilities are presently available, but which may be expensive (e.g., electronic properties of ternary superconductors) and the extension of present capabilities to the more complex systems needed in energy technologies (e.g., electronic and thermal properties of ceramics).

It was repeatedly stressed that there is a need for closer cooperation between theorists and experimentalists.

Priority I: Basic Research Critically Important to Energy Technology.

- Increased funding is vital in both materials preparation and materials characterization. Many attractive materials (organics, polymers, solid electrolytes,...) cannot now be prepared in the desired quantity and quality. New preparative techniques are needed in many areas (a prime example being solar materials) to improve reliability and reduce costs for commercial purposes.

There was widespread concern about the sparsity of first-rate efforts on materials characterization. In many cases it seems that sophisticated characterization techniques exist, but are not generally available to many persons who need them.

- Although not generally pursued by materials science researchers, ceramics will play an important role in many energy technologies. Fundamental understanding of the properties of these materials is at an early stage. Electrical properties of ceramics have the greatest potential influence.

Priority I: Research Utilizing Unique ERDA Facilities and/or Capabilities.

- There is an increased demand and reliance on centralized facilities of a specialized nature where users may obtain results which would otherwise be prohibitively expensive or time-consuming. These include synchrotron radiation sources, intense neutron sources, computational facilities, magnetic fields in the range of 200-300 kG, and ion-implantation facilities.

Priority II: New Areas of Research Important for Energy Technology Base.

- Systematic studies of the optical properties of a wide variety of materials over the wavelength range 0.3 - 30 μm and the temperature range 300 - 1000 K have the potential for high impact on the solar energy program. Materials studied should include metals, semiconductors, insulators, cermets, smokes and paints.
- A number of problems in electrochemical storage involve the need for a better understanding of the electrical properties of solid ionic conductors.
- Properties of metal hydrides are important for energy storage and transfer. This area is also noteworthy because of the anticipation that particularly significant progress can be realized through the interaction of theory and experiment.

In addition to the above there were some areas repeatedly mentioned which were considered in detail by other workshops. Because of their importance one should note the concern of this workshop for continued work on problems of

- Corrosion mechanisms and the development of corrosion resistant materials.
- Surface properties, the relationship of surface to bulk properties, and interfacial phenomena.
- Phase relationships, crystal chemistry and the collection of thermodynamic data.

I. INTRODUCTION

This broadly based workshop dealt with the electric, magnetic, optical, and thermal properties of solids, and as such was concerned with fundamental properties of condensed matter and their measurement. Although the workshop emphasized energy needs, such properties are basic to any area of study, and the techniques for their measurement are essential for both materials characterization and research. The organization of the workshop reflected this awareness and was aimed at identifying and ordering the importance of basic materials problems in the various energy technologies and, within these, the importance of specific and unique basic research techniques for determining electric, magnetic, optical and thermal properties. Seven study groups were organized to focus on certain fundamental research areas: metals and alloys, ceramics, disordered materials, organics and polymers, storage materials, solar materials and new materials. The broad scope of the workshop led naturally to consideration of both specific research problems and general questions relevant to materials research.

In the first day and a half, seven prominent scientists addressed the question of "Materials Needs in Energy Technology" and an equal number reported on the "Status of Energy-Related Materials Research." During the remainder of the Workshop, all participants were assigned to the seven active study groups [Metals & Alloys, Ceramics, Disordered Materials, Organics and Polymers, Storage Materials, Solar Materials and New Materials] to focus on specific challenging and promising basic research areas. A key element was the two night sessions, the first for the Organizers and Study Group Chairmen and the second devoted to the work of the Study Groups. Their major conclusions and recommendations were presented to the entire Workshop at a Plenary Session late morning of the third day for criticism and review before completion of the reports.

Section II presents summaries of the Study Group Reports; common themes which emerged from these are given in Sec. III together with the associated conclusions and recommendations. Appended to this Report are the Program and List of Participants by Study Group. Detailed reports of the Study Groups will be published separately as an Argonne National Laboratory report.

II. SUMMARIES OF STUDY GROUP REPORTS

A. METALS AND ALLOYS

Basic research on metals and alloys is of great importance to all energy technologies. We have defined eight critical basic research needs in electric, optical, magnetic, and thermal properties which are relevant to the long-range goals of ERDA. These follow, in order of probable greatest impact:

(i) The principal basic research needs lie in the area of new materials for (a) the preparation of particular desired characteristics or properties, e.g., improved superconducting characteristics, mechanical properties, corrosion resistance, or magnetic behavior; and (b) testing or advancing our knowledge of alloy theory, crystal chemistry, empirical methods or other theoretical calculations. Particularly important examples are anisotropic systems, complex structures and aggregates.

(ii) Transition metals and alloys, the backbone of our modern technological society, will continue to play a central "role" in energy technologies. Of importance will be high temperature materials, where experimental studies are incomplete and theoretical studies are known to be sometimes in serious error (e.g., for the high temperature conductivity of refractory metals). A combined experimental and theoretical effort is essential in studies of d- and f-electron materials, which are important as catalysts, superconductors, magnetic materials, etc. Realistic theoretical calculations are difficult to perform with the highly precise methods now available; implementation requires large computational facilities and support. Refined studies of anisotropy, magnetostriction, strain and fabrication techniques for soft magnetic materials are needed, as well as improvements of hard magnetic materials. Because of their widespread use, fractional decreases in energy losses in the latter materials give rise to large integrated savings in energy.

(iii) The development of corrosion-resistant materials is needed. While information is available on the general parameters determining the rate of attack of many materials, the detailed interrelationships are not well known.

(iv) There is continuing need for theoretical models which will allow, for example, the prediction of basic properties of more complex materials, or the behavior of more complex properties of simple materials, with emphasis on predicting properties of new materials. Specific areas include band structure calculations, empirical alloying theory and crystal chemistry, and thermodynamical theories.

(v) Trace impurities and defects can have profound effects on the properties of materials. For example, there still exist "pure" metals for which the intrinsic properties have not yet been established because of the presence of small concentrations of impurities, notably the magnetic transition metals (Cr, Mn, Fe, Co, and Ni) and the interstitial elements (H, C, N, and O). Vacancies, dislocations, voids, and interstitials, etc., have a pronounced effect on the microstructure of the matrix materials and thus on many properties. In some cases, knowledge about impurities and defects, has been used to improve specific properties of metals and alloys. In many instances we do not understand the role that impurities and/or defects play in determining the behavior of materials under certain conditions of pressure, temperature or chemical environment, e.g., stress corrosion cracking. More widespread utilization of implantation techniques in both the analysis and the preparation of specific alloy systems is desirable, and positron annihilation studies on defects are to be encouraged.

(vi) Accurate phase diagrams and phase relationships provide information essential, e.g., for the understanding of materials preparation; these can be used to develop or evaluate alloy theories. Combined theoretical and experimental studies on the stability of materials subjected to radiation are required. Particularly important is the time dependence of phase transitions in alloys subjected to high stress levels. Reliable thermodynamic data (heats of formation, heat capacities, etc.) are also essential. While many empirical correlations are observed in studying phase transitions, theoretical understanding on a first principle basis is still inadequate. (Of particular importance are structural and mixed valence instabilities.)

(vii) Composite materials have many potential applications. Of particular importance to energy technologies is an understanding of their thermal properties because thermal stress and heat transport properties limit the usefulness of the existing materials, e.g., in fusion (first wall limiters and superconducting magnets) and energy storage (flywheels). Interface phenomena are also of particular importance.

(viii) Research on the interrelationship between bulk and surface properties will require the most advanced techniques to specify surface properties. Attention should be given to the role of trace elements, surface history, and specific gaseous environments in determining surface composition, as well as the parameters responsible for surface segregation.

B. CERAMICS IN ENERGY SYSTEMS

The development of new, and improvement of existing energy systems, require the development of new and understanding of old materials, many of which must be ceramic. There are several recurring needs in considering the theory and properties of ceramics and their application to energy systems which include the effects of the environment (contamination, radiation and gradients of temperature, voltage and stress), the effects of surfaces and interfaces (multiphase or composite structures); general requirements in energy conversion systems for materials which act as sensors and detectors; and the need to "tailor" properties to the system needs (e.g., use of solid solutions to vary the band gap of electrodes in photoelectrolysis systems). It is extremely important that the relationship between the properties, the microstructure and the phase equilibria be established.

There is a special need for well-characterized ceramic materials, both as dense polycrystalline ceramics and in single crystal form. Sample to sample variation of basic properties is often very large, resulting in a lack of reliable experimental data which can be compared with theoretical models. The growth and characterization of these materials will frequently require expensive special facilities. Special techniques such as CO₂-laser-driven zone refining and crystal growth in any ambient atmosphere should be considered. Specific examples of materials preparation worthy of special effort are (i) zone refining and subsequent controlled doping of Al₂O₃ and MgO crystals, (ii) preparation of crystals of LaCrO₃-ZrCO₃ solid solutions for high temperature conductivity studies, (iii) doped titanates for use in photoelectrolysis and (iv) preparation of forged single crystals to study "intrinsic" grain-boundary effects.

The elegant theories and calculations of electronic structure and bonding available for metals and compounds need to be extended to ceramic systems. Very basic, but critical, parameters are missing in ceramic systems: e.g., does Al₂O₃ form Frenkel or Schottky defects, and what are the formation energies? There is a clear need for a much stronger coupling of the condensed state theorist with the careful experimentalist than has occurred in the past. Theorists need to present models not only for fundamental properties, but also for "mixing rules" which allow one to predict the properties of mixed materials present either as homogeneous or inhomogeneous phases.

We consider an understanding of electrical properties to have the greatest potential influence. In broad terms, priority should be assigned to theoretical calculations, studies of defects, ionic and superionic conductors, interfacial phenomena and mixed conductors. There are some general electrical properties such as the mobility, concentration and trapping effects of electronic and ionic carriers in ceramics, including the effects of grain boundaries and interfaces, which should be studied. For example, the intrinsic properties of insulators (Al_2O_3 , MgO) are not measurable and thus doped materials must be studied. However, intrinsic quantities such as defect formation energies should be calculated and compared with experimental data. As another example we note that theory and experiments to develop electrolytes with cooperative ionic motion having greater net current transfer could advance battery and fuel cell development.

The basic understanding of optical properties is closely coupled to the electronic properties. There are few ceramic materials for which the optical properties over a wide range of frequencies and temperatures have been measured. There are few data on the transition metals in tetrahedral or octahedral sites. The most significant advances to ceramics will come when techniques such as ESCA, XPS, UPS, etc. have been applied to surfaces, interfaces and grain boundaries of ceramic materials. This will establish the near-surface chemistry and structure which often determine the physical properties. Another extremely important, but less elegant, area is the theory and measurement of the emissivity of materials, especially in the reactive environments of energy systems.

There are still many areas in the study of thermal properties where important advances can be made. That we don't understand and can't model the heat transfer from oxide fuel pellets (and so lose several percent in the energy conversion efficiency) is an indication of some of the basic misunderstandings in an oft-studied ceramic, UO_2 . In particular, creative new techniques for high temperature measurements of thermal expansion, conduction (radiative and lattice vibration modes) and heat capacity are needed. The classical experiments for subtracting the measured lattice parameter from the thermal expansion to yield vacancy concentrations has never been done on ceramics. Experimental data and theories for multiphase and composite structures are needed for those who must eventually design systems using real materials. Mixing laws for tailoring the thermal expansion to match other materials must also be derived. Intimately connected to the thermal properties are the stresses which result in ceramics because of gradients and transients. These stresses are the most important single effect which limits the use of ceramics in high temperature systems. Special attention should be given to non-linear temperature profiles; both calculations and new measurement techniques must be done.

The magnetic characteristics of ceramic materials are probably the most advanced because of the extensive commercial interest in the past of ferrites and garnets. The use of magnetic spectroscopic techniques (Mössbauer, EPR, NMR, etc.) will continue to provide the basic data about the state of ions in ceramics. There are also reports that the understanding or improvement of catalytic characteristics may be advanced through studies in magnetic fields.

The potential use of high gradient magnetic fields to clean fuels of iron-sulfur compounds, and the use of spectroscopic techniques to classify the state of the compound (FeS , FeS_2 , etc.) suggests that basic research would be fruitful on coals. This is a real extension of the definition of materials (or ceramics), but is one where important advances are needed.

Recommended areas for magnetic studies are: (i) coal studies, such as the use of high-gradient magnetic fields to clean fuels of iron-sulfur compounds; (ii) theory (iii) use of spectroscopic techniques (Mössbauer, EPR, NMR, etc.) to characterize the state of ions in ceramics; (iv) magnetic field assisted surface reactions.

C. DISORDERED MATERIALS

The field of disordered materials is presently very active. Although it has already provided a number of theoretical insights and new classes of materials with novel physical properties, the field is still at an early stage of development and promises much more in the way of new materials, fundamental understanding of condensed matter, and technological opportunities.

The applications of amorphous metals are numerous due to properties such as low magnetic hysteresis losses, high strength combined with ductility, resistance to hostile environments, etc. The central research need is an understanding of the glass transition itself. Microscopic factors which enhance glass formation (e.g. the relative importance of electronic structure vs. size effects) need to be isolated and analyzed. A theory of d-bands in amorphous transition metals is needed in this connection, since d-electrons have been implicated in glass formation and stability. Further theoretical effort is needed on viscosity in liquid metals, the effects of the amorphous structure on the constituent electronic states, electronic and thermal transport in these materials, and the sources of magnetic anisotropy in magnetic glasses.

Differences caused by the preparation of glasses in different ways are of fundamental interest, as is the role of defects on anisotropies and irreversible mechanical properties, and the resistance of metallic glasses to radiation damage.

Amorphous semiconductors are characterized by intrinsic conductivity mechanisms such as variable range hopping and non-ohmic conductivity at low temperatures and/or high electric fields. No unified theoretical framework is available which defines the limits of performance of these materials. An understanding of cohesion is needed, both in an idealized random network structure as well as on experimentally achievable materials. Diverse techniques will be required to identify and characterize intrinsic structure and extrinsic defects. For example, recent interest has focused on the prediction of a variety of charged, spin-paired defects which may control the a.c. conductivity, infrared transparency and diamagnetism. The large dependence of acoustic attenuation on glass composition for the chalcogenides is not adequately understood. The extent to which localized vibrational and electronic states can be attributed to or neutralized by defects is not known. Understanding the role of chemical components (e.g. H in α -Si appears to neutralize defects and enhance carrier lifetimes) is important.

In insulating glasses, localized excitations have a profound effect on the low temperature specific heat, low frequency propagation losses and optical line widths. Their precise nature and their apparent long range interaction remain a major unsolved problem. It is known that the efficiency of fluorescence in glasses having rare-earth impurities depends on energy transfer between rare-earth sites and traps in the glass host. The concurrent development of new fluorescent techniques and improvements in energy transfer theory suggests that the time is ripe for an extensive investigation of optical energy transport in these disordered systems, including the transition from spatially localized to delocalized optical excitations. High power glass lasers are inhibited by the nonlinear index of refraction; however, substitution of atoms having small atomic number (and hence low polarizability) in the glass site could lead to smaller non-linear indices. A major recent development of glass technology has been optical fibers with low absorption, creating experimental opportunities for characterizing intrinsic and extrinsic loss mechanisms with increasingly lower cross sections.

The bulk properties of composite materials (substances in composite, aggregated or textured form) may be varied over extremely wide ranges, but the preparation and analysis of these materials is still primitive. Characterization tools which go beyond microscopic examination of two-dimensional sections are particularly needed. An elegant theory of the bulk properties of composites is available, but has not been integrated with experimental results. Little is known about what details of a texture must be specified to designate its macroscopic properties. For example, it is known that not only porosity, but also distribution of pore size is important in obtaining desired mechanical properties of sintered materials such as UO_2 fuel. In depth studies of the simpler anisotropic textured materials (e.g. fiber/plastic composites) seems timely. This could lead to the discovery of new physical phenomena as well as provide needed data for design work. The high interface to volume ratio and extreme anisotropies present in composites also present unique conditions from which new discoveries may be anticipated. Examples are granular materials which have caused significant improvements in videcon tubes, and superconductor-normal metal composites which have given high critical currents but have also been used for studies of fluctuations in superconductors, electronic localization and hopping conduction.

Studies of phase transitions in disordered magnetic materials raise new questions: For example, can a sharp magnetic transition exist, and if so how do the critical properties compare with ordered materials? There is also great interest in systems having magnetic ions randomly substituted in a nonmagnetic host, particularly for concentrations near the percolation threshold. For low concentrations in a nonmagnetic metal, the strong disorder in the magnetic coupling leads to a new phase, the "spin-glass", where the magnetic moments on each site are frozen into a random orientation. The role of disorder on metal-insulator transitions in various materials is of interest.

Detailed understanding of disordered materials will require better preparation and characterization techniques than are currently employed. The following special facilities are needed: molecular-beam deposition and ion-

implantation equipment, access to a synchrotron radiation source, and high resolution scanning transmission electron microscopy coupled with energy loss spectroscopy and elastic electron scattering.

D. ORGANICS AND POLYMERS

The major thrust of this report is the indication of the great vitality of research and development in organics and polymers. The field is characterized by novel materials, extended characterization capability and a rich array of theoretical concepts. Not only has it already provided considerable technological advances, but it also promises truly expansive horizons in the emulation of plant and animal metabolism, such as synthetic enzyme catalysts which are already being prepared.

In the past few years, a dramatic transition has taken place in this field, formerly the concern primarily of the chemist. Solid state physicists are now deeply interested in electronic properties. Organic crystals have received broad attention primarily due to the variety of phenomena exhibited by charge-transfer salts. Current areas of investigation include electrical conductivity, magnetism, charge density waves, disorder and phase transitions. These developments have also demonstrated the potential for electronic applications of organic and polymeric materials.

In addition, enzyme metabolic systems offer examples of high efficiency energy conversion and storage. Better understanding of these mechanisms should bring about new materials for catalysts, and possibly for components in energy conversion storage devices.

Efforts to understand the properties of organic materials (primarily charge-transfer complexes) have led to the development of a number of new concepts and theoretical techniques. Similarly studies of organic and polymeric solids have led to the development of several new measurement capabilities, as well as novel adaptations of existing techniques. At the computational level, molecular orbital calculations have been applied to a number of types of spectroscopic data and advances in modeling energy calculations have aided the understanding of the cohesive binding of organic and polymeric solids. Analogies of helix-coil transitions and the extension of polymers with critical phenomena and particle motion on disordered materials can be exploited. There are opportunities for new chemistry, e.g. solid-state reaction kinetics. Progress on organics and polymers requires a continued combined experimental-theoretical effort.

Because materials purification is an expensive and lengthy task, the concept of an ERDA national purification and characterization center should be considered. The facility would include, in addition to standard analytical techniques, instruments and techniques such as the following: small angle neutron and x-ray scattering; x-ray, neutron, and electron topography; high resolution mass spectrometers; atomic emission and absorption spectrometers; optical fluorescence spectrometers; high resolution electron microscopes; gas and liquid chromatographs; differential scanning calorimeter; zone refiners; zone and gradient sublimators.

E. ENERGY STORAGE

The general area of energy storage has been reviewed and the relative importance of a number of topics considered on the basis of (1) relevance, (2) scientific promise and (3) technological payoff. The most promising areas for research, categorized by technologies in order of priority, are electrochemical, fuel storage (primarily metal hydrides), thermochemical, photochemical and mechanical.

Of these various approaches, electrochemical storage with batteries appears to be the most promising for a broad range of applications. Recently, novel advanced battery systems have evolved which require material properties which cannot be provided by current technology. Among the pervasive problems encountered are those related to interfacial phenomena and to corrosion. In any system having solid-liquid interfaces (e.g. with molten salt electrolytes, or with fuel cell electrodes having a liquid-gas interface with a porous structure), the ability of the liquid phase to wet the other components is of great importance. Little systematic data is available on interfacial tensions or contact angles in solid-liquid melt-molten salt systems, and the theories which are available for such parameters may not be applicable to these systems. Corrosion of components in high temperature electrochemical systems is one of the most common causes of failure. While some definition of the types of corrosion and of the important parameters has been established, an understanding of the mechanisms or even which mechanisms are dominant for particular systems is not available.

A number of research problems are related to solid ionic conductors. Studies of the role of domains and extended defects in the conduction properties coupled with theoretical calculations of the activation energy of migration could lead to improved electrolytes that would operate at lower temperatures. Studies of the crystal-chemical factors limiting oxygen conduction are important in the development of electrodes for the direct conversion of chemical to electrical energy. Theoretical studies of the factors controlling ion transport in superionic conductors are needed as well as studies of cooperative phenomena at high temperature and high electrical stress. Studies of structure, electron-ion interactions and charge transport in solid solution electrodes are needed. New experimental and analytical techniques are needed to help distinguish between short-range and long-range ion motion in solids, and between intra- and inter-granular resistance in polycrystalline materials.

Other fruitful areas of research in electrochemical storage are related to problems of electro-catalysis, inorganics with unusual electrical properties, photoelectrolysis and photogalvanic cells. Several of the above areas are also directly related to fuel cells.

The use of metal hydrides in energy storage is associated with the high density of hydrogen per unit volume possible, and the use of the heat of formation of the hydride. These may find use in peak-shaving and load levelling applications at primary electric power plants, storage and transport of tritium for fusion reactors, thermochemical storage, etc. Research areas of primary importance to energy storage are: (1) The development of new metal hydrides, requiring an experimental effort to study electronic, magnetic and thermodynamic properties, as well as theoretical approaches to provide a rationale

for new material design. (2) Thermodynamics and kinetics of hydrogen transport across solid interfaces. (3) Hydrogen embrittlement in a wide range of materials. (4) Hydrogen mobility in metals and hydrides.

In addition there are a number of important research areas in the study of hydrides which have significance beyond the needs of energy storage. Some of these are: (1) Hydrogen diffusion in metals, which provides examples of quantum diffusion systems. (2) The effect of hydrogen on bonding and crystal structure. (3) Environmentally related failure mechanisms such as embrittlement, corrosion, etc. (4) The role of active surface sites in the transport of hydrogen across surfaces, clearly related to problems in catalysis. Hydrogen storage in metals is noteworthy because of the anticipation that particularly significant progress can be realized through the interaction of theory and experiment.

While electrochemistry and hydrogen storage in metals best meet the criteria initially stated, the other areas also offer good research opportunities. Photochemical storage of solar energy would benefit from a broad survey of endoergic photoreactions in simple and abundant chemicals, examinations of mechanisms of photosensitization, and an evaluation of catalysts appropriate for the reversion of energy rich photoproducts. Study directed to understanding the influence of redox properties of excited states in homogeneous media may be helpful in systems for the photochemical decomposition of water to hydrogen. Significant advances in mechanical storage via flywheels require improved strength to weight ratio composites, perhaps from organic fibers, and improved understanding of bonding and adhesion.

In summary, one may identify from the above a number of pervasive problems. Atomic and ionic transport, particularly through interfaces is important. Interface physics and chemistry, particularly solid-liquid and solid-solid interfaces is a recurrent theme. Of great importance in several energy systems are corrosion, hydrogen embrittlement and the need for improved understanding of the structure and properties of alloys.

F. MATERIALS FOR SOLAR ENERGY CONVERSION

The general features of photothermal and photovoltaic processes are well understood. However, the economic exploitation of the sun's energy depends critically on the development of better, longer lasting materials, more efficient conversion processes, and cheaper fabrication processes. This requires an immediate and vigorous basic research program on new materials and processes to back up the mission-oriented engineering currently in vogue. It is therefore recommended that ERDA's basic research efforts on solar materials be significantly enlarged, with the central theme being the optical and electronic properties of solids. More specific and shorter range research goals are listed below.

The major techniques being used to produce crystalline semiconductors (e.g. silicon in large area, 10 mil thick sheets) are either costly or result in materials with large densities of impurities, dislocations, grain boundaries etc. In order to understand and control the way impurities diffuse from the substrate during deposition (a major problem), research is required on semiconductor-substrate diffusion barriers, diffusion kinetics along grain bound-

aries, and methods for increasing grain size. In addition more systematic studies need to be made of the way imperfections affect the semiconductor's electronic properties (mechanisms limiting lifetimes, mobilities due to trapping, etc). Basic research which can lead to new refining and crystallization processes is also required.

The three most promising classes of amorphous semiconductors are (1) amorphous silicon and germanium (2) chalcogenide glasses and (3) organic semiconductors. Amorphous silicon doped with glow-discharge-deposited materials is of current interest. More information is needed on the effect of preparation on properties such as the density of localized states; the role of hydrogen; the local environment of dopant atoms; and carrier lifetimes, trapping and interface state densities. In the chalcogenide glasses, research is necessary on the fabrication of rectifying p/n junctions, investigation of Schottky barriers, and effects of impurities and doping techniques on electrical and optical properties. Further exploratory work is recommended on organic semiconductors because of their potentially low cost. Work on glass-transition and crystallization kinetics is necessary if one is to be able to stabilize amorphous semiconductors at high enough temperatures to be used as selective coatings for photothermal conversion.

A systematic search should be encouraged for better semiconductors to use in the photoelectrolysis of water. These materials should have the following properties: (i) an energy gap near 1.5 eV, (ii) resistance to decomposition under electrolytic operation, (iii) band edges which match the potentials of the ion species in the electrolyte and (iv) ability to sustain a surface barrier under illumination. Presently available materials either decompose rapidly in anodic operation or have a large band gap. Cathodic and electrodeless operation should be explored.

Structures using heterojunction Shottky barriers and MIS junctions in photovoltaic cells should be investigated in an attempt to lower the presently stringent requirements on crystal perfection. Studies should be made of the energy band profile of the junction and the effect of imperfections on its photovoltaic properties.

Optically transparent, low resistance electrodes (ITO, SnO_2 , Cd_2SnO_4 , etc.) offer possibilities for decrease of sheet resistance, reduction or even elimination of grid contact, use as antireflection coating, use as an IR reflection coating, etc. Improvements in the optical, infrared and electrical properties of these materials would have a large impact on solar technology.

The selective solar absorber coatings used commercially are mostly composite materials. However, the understanding of these is mostly empirical. To obtain a better understanding of high spectral selectivity, systematic studies of the optical properties of materials in the wavelength range 0.3-30 μm and temperature range 200-1000 K are recommended. These studies should include metals, semiconductors, insulators, composites, smokes and paints.

Films with a graded index of refraction or textured surface are potentially inexpensive and may give reduced reflectance over a wider band width than the commonly used resonant anti-reflection films. The practical development of such films requires more theoretical and experimental research on optical properties of inhomogeneous media.

In photovoltaic generation it is possible to decrease effective costs either by solar concentration or by utilizing a hybrid "thermo-photovoltaic" system. The former may require semiconductors which can handle current densities 100 to 1000 times greater than otherwise obtained. The latter requires semiconductors having bandgaps of ~ 1.4 eV in order to obtain solar cells that operate in excess of 100°C. Both of these problems require further experimental and theoretical work.

A systematic study of the mechanisms of degradation of a wide variety of solar materials is required, including photochemical reactions, diffusion across boundaries at high temperatures, and influence of exposure to the chemical, mechanical and thermal variation of the environment.

G. NEW MATERIALS

High priority should be given to the synthesis and determination of properties of novel materials with unusual bonding and structure as reflected in unusual electronic, magnetic, optical and thermal properties, for it is from new classes of materials that novel properties arise. Examples include materials in unusual oxidation states, materials with multiple bonding of metals, crystals with unusual anisotropy, ternary materials with a variety of stoichiometries leading to variability of properties, amorphous materials and chemically stable, high-temperature materials.

As examples (not meant to be exhaustive) we cite the following:

Metal Rich Binary Compounds (e.g. the metal rich halides of Sc and Zr, and the metal rich suboxides, phosphides, sulphides and selenides) provide areas for theoretical research on chemical bonding in solids, for investigation of property modification by stoichiometry change and, in general, for understanding the interrelationship between bonding and solid state properties.

Ternary Compounds provide opportunities for altering materials by change of stoichiometry. For example, the superconducting transition temperature of the ternary molybdenum sulphides can be varied by changing the third element. Ternary compounds of molybdenum chalcogen halides exhibiting metal-metal bonding characteristic of clusters, metal-chalcogen bonding characteristics of chalcogens and interaction of the third element with the metal-chalcogen moieties provide fruitful areas for preparing materials with unusual properties.

Amorphous materials have enhanced chemical resistance and strength. These properties may be utilized, for example, as a coating to provide corrosion resistance and/or surface hardness. New intercalation compounds with unique properties continue to be synthesized. Graphite compounds with super-acids are claimed to have conductivities comparable to copper. Alkali alloys such as K-Li or K-H intercalate, although Li or H themselves do not.

Composite materials (multi-material systems) are increasingly being utilized. Examples include: Mixed-matrix, fine-filamentary, stabilized superconductors; non-linear electrical power composites such as bismuth doped polycrystalline zinc oxide for handling faults or power lines, multi-layer semiconductor systems for power and solar devices, etc.

In order to obtain new materials, strong support should be given for novel methods of synthesis. Since energy savings result from reduction in size and amounts of material used, vapor phase methods are appropriate. Chemical vapor deposition, sputtering and evaporation all can be used to effect compounds, coating, and composites with tailored properties in the form and shape in which they will be used. Upon occasion the highly controllable methods of molecular beam epitaxy might be employed. Imaginative use of ion implantation for altering stoichiometry could be very important.

New syntheses will lead to the discovery of novel properties. In general, efforts should be directed towards systems where the expected structure or chemical bonding already suggests that the unusual properties will be forthcoming such as extreme anisotropies, equivalent sites for non-integral valency (mixed-valent crystals), amorphous materials, composites, epitaxial structures, unusual valence states, inclusion compounds, ternary and higher order compounds.

III. COMMON THEMES

The previous section has given a summary of the high priority items discussed by the individual study groups. Each, of course, focused on its own area of responsibility, and the emphasis given arose from concern about that particular area. Nevertheless, many common themes emerged, which we present in this section. Areas emphasized by several study groups are obviously of very high priority and deserve ample support.

One major theme is the critical need to find and understand the properties of new materials. While it is true that improvements of many properties can be obtained with presently available materials, these are usually in the category of 10-20% changes. Most of the major advances in the development of new and improved properties of materials in recent years have come from the discovery and synthesis of new materials. In addition to the dramatic improvement of known material properties, new materials provide a source of new physical phenomena.

Emphasis on new materials cannot help but reap significant rewards. There are presently many opportunities. Some of the areas discussed at the workshop were ternary compounds (providing, for example, the opportunity to dramatically change material properties by a change in stoichiometry), intercalation compounds (e.g., super-acids in graphite, which are claimed to have conductivities comparable to copper), amorphous materials (discussed by many study groups for their enhanced chemical resistance, high strength combined with ductility, possible use as selective absorbers for photothermal conversion, etc.), biological materials (e.g. synthetic enzyme catalysts), unusual oxidation states, anisotropic materials, organics and polymers, composites, aggregates, inhomogeneous phases and granular materials. As further novel materials arise, they should be well supported until their potential can be satisfactorily evaluated.

One area noticeably missing from the workshop was materials of geophysical or geochemical interest. The earth has been an enormous high-temperature, high-pressure laboratory for the preparation of a great variety of stable materials. Minerals offer a rich source of possible superionic conductors, binding materials for nuclear waste, etc.

The area of new materials rates high within the first priority category (exciting scientific area with a high probability for new findings). The search for new materials touches many aspects of the best features of basic research. It requires developing theoretical and empirical models to a sufficient point that their predictive powers can serve as guidelines; it requires the development of fundamentally new techniques for dealing with previously unknown properties; it stretches the imagination of the researcher to the greatest degree.

A primary barrier to obtaining better materials, be it improvements on present ones or the synthesis of new ones, is the difficulty often encountered in their preparation. Successful development of novel materials often depends critically on novel methods of synthesis. Their utilization is often prevented by the inability to make samples of the proper size and quality. The latter in turn depends critically on the availability and reliability of techniques for purification, synthesis and crystal growth. The classic example is the development of semiconductor materials. Many attractive materials, such as organics, amorphous materials, and solid electrolytes, cannot now be prepared in the desired quantity and quality. In addition, new preparative techniques are needed in many areas to improve reliability and reduce costs for commercial purposes.

Materials synthesis fits both into the first priority category (high probability of exciting new findings) and the second (providing an important base of information needed for materials science programs and energy technologies). A number of participants considered the importance of synthesis so great that they recommended that a national center for this purpose be established. Although we do not make such a specific recommendation here, we suggest that this proposal be assessed by an appropriate group.

Another almost universal concern on the experimental front was the sparsity of first-rate efforts on materials characterization. The literature contains far too many examples of work with contradictory results obtained on supposedly identical materials prepared at various institutions. In many instances it seems that sophisticated techniques exist for sample characterization which do not get utilized, frequently because of their lack of availability to many users. Unequivocal data are then not available, much to the detriment of both theoretical and experimental work. In some cases (e.g. for ceramics and amorphous materials), it appears that detailed understanding will simply not be obtained without improvements in both preparation and characterization techniques. Heavy emphasis should be placed on reliably characterizing materials so that different groups can compare their results with the assurance that they are dealing with the same materials. Unless the intrinsic properties of substances are clearly known, it will be next to impossible to decide how to tailor materials for specific purposes. Work should be encouraged in areas where good characterization is at present difficult or impossible. The idea for a national facility was discussed again in this context. Much of the equipment necessary for complete and reliable characterization of materials is complex and expensive. Thought should be given as to whether it would be worthwhile to dedicate a facility to this purpose. It was pointed out that such facilities might best be situated in the laboratories where the materials are made. This question should therefore be considered in concert with the question of a national materials preparation laboratory.

Materials characterization has the same priority as materials synthesis, since it is part and parcel of the same endeavor. They should really be considered together whenever possible.

In many areas there is an increased demand for and reliance on centralized facilities of a specialized nature, where sophisticated and expensive equipment can be made available to many users, or where their functions may be performed for the user. In addition to those mentioned elsewhere in this report, we list facilities such as synchrotron radiation (particularly a dedicated source usable on a full-time basis for EXAFS, XPS etc.), intense neutron sources, expanded computational capabilities and computing centers, and magnetic fields in the range of 200-300 kG.

Certain areas of physical chemistry are important to devising synthesis, preparation and characterization techniques, as well as to understanding material properties. These include crystal chemistry, certain thermodynamic properties of materials, phase diagrams, stoichiometry questions, etc. They fall into the second priority category (providing an important base for material science programs and energy technologies, and also perhaps as a grossly underfunded area).

The chemical and thermodynamical properties of materials are also important for understanding the structure and stability of materials. This area is of first priority in that it is critically important to many energy technologies. We are presently hampered by a serious lack of knowledge about the structure and stability of most materials, and its relation to composition and various electronic and mechanical properties. These fundamental questions are of crucial importance and are not understood except in some of the simpler materials. Much work is needed in the areas of stability, cohesion, structure, microstructure, porosity, texture and mechanical properties.

Similar understanding is required in the area of defects in many materials. Defects are often the determining factor in the use of many material properties and much remains to be learned. These studies must include impurities, vacancies, interstitials, dislocations, voids, diffusion and thermal properties, which have a pronounced effect on the microstructure of the matrix materials and are important to understanding their structure and stability.

A better understanding of all the properties mentioned should yield much information important for the critical and complex problems of corrosion and degradation. Strong emphasis should be given to programs which attempt to relate these properties in a coherent manner. More generally, such studies will go a long way toward the ideal goal of tailoring materials to emphasize their desirable properties while reducing or eliminating their undesirable properties.

Another universal theme was the need for increased theoretical research on materials, felt by almost all of the study groups. Much of the difficulty encountered, for example, in understanding structure and stability arises from the lack of comprehensive and basic theories. There exist many models and empirical correlations for the properties of a number of complex systems, but the basic understanding of these materials is very poor. A concerted theoretical attack is imperative. It was noted that in many cases it is now possible to calculate in great detail the electronic and thermal properties of

simple as well as some complex systems from something approaching first principles. It is timely to extend this work to the more complex materials of interest in many energy technologies. As one example, a need was expressed for extending the elegant theories of electronic structure and bonding which are available for metals to ceramic systems, where very basic but critical parameters are unknown. There exists a unique opportunity whose implementation requires access to large computational facilities. A relatively modest investment would lead to substantial benefits.

It was repeatedly stressed that there is a need for closer cooperation between theory and experiment. For example, it was noted that a powerful mathematical theory of composite materials exists, but it has evolved in isolation from experiment. Hydrogen storage in metals provides an example of an area where one anticipates significant progress through the interaction of theory and experiment. It is from these close interactions and mutual efforts that many of the most successful results develop, especially for the complex materials needed by energy technologies. It is important that the theorists and experimentalists concentrate on the same problems and coordinate their efforts to help guide each others progress.

Overall, theory is undersupported relative to experimental work. On a short term basis this may seem justifiable when one is seeking material properties particularly applicable to certain technologies. On an intermediate-term or long-term basis, however, such an imbalance between theory and experiment implies that resources are being used ineffectively. All too often, costly experiments do not lead to conclusive results because of lack of theoretical effort.

Theoretical activities are of first priority, having a high probability for important new findings. They are critically important to many areas of energy technology.

It is important to understand the utility of modelling in physical research. This includes theoretical models containing suitable simplifying assumptions (such as band structure calculations, empirical alloying theory, thermodynamical theories, "mixing rules" for the properties of inhomogeneous phases, etc.). Equally important, this includes experimental work on materials chosen so that the number of unknown parameters is minimized, thus allowing one to isolate various mechanisms and understand piece by piece more complex materials.

There were two other areas suggested as being important by a number of participants. One was the field of surface and interface properties, and their relation to bulk properties. Since there is a separate workshop on surface science, we did not spend much time on this question. However, the relationship of the surface to the bulk should be specifically considered to ensure that it does not fall through the cracks.

The last area we shall mention is the investigation of optical and transport properties. It was emphasized that much work should be done here and that groups working on the various classes of materials should be encouraged to obtain such data. The results, in addition to being interesting in their own right, provide much important information for the interpretation of other material properties. In this context it is a second priority area.

However, it is of first priority in cases where the optical or thermal properties themselves are of primary importance to the technology being investigated, as e.g. for solar energy.

IV. CONCLUSION

The subject of this workshop was quite broad and diverse, so that it is not easy to give a concisely ordered list of priorities. We have provided, in Sections II and III, two cuts through the subject matter, discussing it from different points of view. These complementary discussions give a full picture of the important areas included in the subject matter of the workshop.

We wish to add one further point before closing. We have not deemed it our responsibility to determine the research necessary to obtain short-range materials improvements for presently developed energy technologies. It is not that we consider these areas unimportant, but rather that we think they are best considered within the activities of the associated larger projects. We have here placed our emphasis on the long-term technological goals and have therefore concerned ourselves with the science necessary to insure the future development of materials for energy needs.

The nation must clearly understand the necessary balance between short-term and long-term technological goals. An easy response to the pressure of current energy demands is to concentrate on short-term achievements. Short-term goals, such as minor increases in the efficiency of utilization of various materials, can generally be obtained from one's current state of knowledge. However, the more radical improvements frequently necessary to meet long-term goals can be obtained only by improving the state of understanding of the basic properties and phenomena concerned. More seriously, both short- and long-term goals and the policies to achieve them may be ill-formulated simply due to insufficient fundamental research to provide the basis for intelligent planning.

ProgramWednesday, March 9

9:00 a.m.	Welcome D. L. Price (Argonne)
9:05	Introductory Remarks L. C. Ianniello (ERDA)
	I. <u>Materials Needs in Energy Technology</u> Chairman: D. L. Price
9:30	Solar Energy Technology M. Wolf (University of Pennsylvania)
10:10	Geothermal Energy Technology M. C. Smith (Los Alamos)
10:50	Coffee Break
11:10	Fusion Technology S. Harkness (Argonne)
11:50	Energy Storage Technology R. S. Claassen (Sandia)
12:30 p.m.	Lunch Cafeteria, Building 213
	<u>Materials Needs in Energy Technology (Cont'd)</u> Chairman: A. J. Freeman (Northwestern Univ.)
1:40	Nuclear Technology B. R. T. Frost (Argonne)
2:10 p.m.	Energy Conservation Technology G. Seidel (Brown)
2:50	Fossil Fuel Technology R. W. Staehle (Ohio State University)
3:30	Coffee Break
	II. <u>Status of Energy-Related Materials Research</u>
4:00 p.m.	Contemporary Spectroscopy F. C. Brown (University of Illinois)
4:50 - 5:40	Calculation of Electronic Structures A. R. Williams (IBM)
6:00	Social Hour and Dinner Cafeteria, Building 213
8:30	Meeting of Organizing Group and Study Group Chairmen - (Alvarado Room at the Ramada Inn)

ERDA Workshop Program
March 9-11, 1977

Thursday, March 10

Status of Energy-Related Materials Research (Cont'd)

Chairman: P. E. Seiden (IBM)

9:00 a.m.	Atomic Molecular Dynamics A. A. Maradudin (University of California-Irvine)
9:40	Organics and Polymers R. H. Baughman (Allied Chemical)
10:20	Coffee Break
10:45	Magnetism I. Jacobs (General Electric)
11:25	Disordered Materials B. Halperin (Bell)
12:15 p.m.	Ionic Conduction and Migration W. L. Roth (General Electric)
12:55	Lunch Cafeteria, Building 213
	III. <u>Study Groups</u>
2:00 p.m.	Study Groups Convene (See list for room assignments)
6:00	Dinner Cafeteria, Building 213

Friday, March 11

9:00 a.m.	Study Groups Re-convene
11:00	Plenary Session with Reviews by Study Group Chairmen (each 10 minutes followed by 5 minute discussion) Chairman: W. L. Clinton (ERDA)
12:45 p.m.	Lunch Cafeteria, Building 213
1:30	Study Groups Re-convene to Complete Reports
4:30	Workshop Adjourns

Study Group Participants1. Metals and Alloys

K. A. Gschneidner (AL/ISU), Chairman
 M. B. Brodsky (ANL)
 J. I. Budnick (Univ. of Conn.)
 S. Foner (MIT)
 S. D. Harkness (ANL)
 M. B. Stearns (Ford Motor Co.)
 M. C. Smith (LASL)
 R. K. Williams (ORNL)

3. Disordered Materials

E. S. Kirkpatrick (IBM), Chairman
 J. P. DeNeufville (Exxon)
 B. I. Halperin (Harvard)
 A. A. Maradudin (UC-Irvine)
 S. R. Nagel (Chicago)
 R. L. Orbach (UCLA)

5. Storage Materials

R. S. Claassen (Sandia), Chairman
 H. Birnbaum (Univ. of Illinois)
 F. A. Cafasso (ANL)
 G. Jones (Boston Univ.)
 G. G. Libowitz (Allied Chem.)
 W. L. Roth (GE)
 A. R. Williams (IBM)

7. New Materials

T. Geballe (Stanford), Chairman
 F. C. Brown (Univ. of Illinois)
 H. F. Franzen (AL/ISU)
 J. Hulm (Westinghouse)
 D. W. Murphy (Bell Labs.)
 R. W. Staehle (Ohio State)

2. Ceramics

H. K. Bowen (MIT), Chairman
 H. L. Davis (ORNL)
 I. S. Jacobs (GE)
 D. W. Readey (ERDA)
 R. W. Vest (Purdue)
 J. B. Wagner (Arizona State)

4. Organics and Polymers

C. B. Duke (Xerox), Chairman
 R. H. Baughman (Allied Chem.)
 A. N. Block (Johns Hopkins)
 V. J. Emery (BNL)
 A. F. Garito (Univ. of Penn.)
 P. J. Melz (IBM)

6. Solar Materials

B. Abeles (RCA), Chairman
 D. Adler (MIT)
 G. Seidel (Brown)
 B. O. Seraphin (Univ. of Arizona)
 M. Wolf (Univ. of Penn.)
 C. R. Wronski (RCA)

8. Organizing Group

D. L. Price (ANL)
 A. J. Freeman (NU)
 M. H. Cohen (Chicago)
 P. E. Seiden (IBM)
 W. L. Clinton (ERDA) *

ERDA Representative

L. C. Ianniello

* On leave of absence from Georgetown University

MATERIALS SCIENCES WORKSHOP ON

SURFACE SCIENCE

Held March 16 to 18, 1977 at Lawrence Berkeley Laboratory

Organizers

G. A. Somorjai, Lawrence Berkeley Laboratory
W. L. Clinton, ERDA, Division of Basic Energy Sciences
J. T. Yates, Jr., National Bureau of Standards

Participants

J. A. Apps, Lawrence Berkeley Lab.	T. E. Madey, Nat'l Bureau of Standards
W. Bauer, Sandia Labs.	R. J. Madix, Stanford University
H. Beuther, Gulf Research	J. Mayer, California Inst. of Technology
J. M. Blakely, Cornell University	C. McMahon, Univeristy of Pennsylvania
M. Brodsky, Argonne National Laboratory	D. Michels, Idaho Nat'l Engineering Lab.
R. H. Bube, Stanford University	J. Morris, Jr., Lawrence Berkeley Lab.
J. Burton, Exxon Res. & Engineering Co.	G. S. Painter, Oak Ridge Nat'l Laboratory
W. L. Clinton, ERDA, Div. of Basic Energy Sci.	P. Palmberg, Physical Electronic Industries
C. A. Colmenares, Lawrence Livermore Lab.	A. J. Perrotta, Pittsburgh Energy Res. Center
G. Cummings, California Inst. of Technology	J. A. Rabo, Union Carbide Corporation
R. Eischens, Texaco, Incorporated	J. Rowley, Los Alamos Scientific Lab.
W. P. Ellis, Los Alamos Scientific Lab.	D. A. Shirley, Lawrence Berkeley Lab.
R. P. Epple, ERDA, Div. of Basic Energy Sci.	G. A. Somorjai, Lawrence Berkeley Lab.
H. Frederikse, National Bureau of Standards	R. Staehle, Ohio State University
I. W. Gadzuk, National Bureau of Standards	D. Stein, Michigan Technological Univ.
J. Galt, Sandia Laboratories	P. Stonehart, Stonehart Associates Inc.
W. A. Goddard III, California Inst. of Tech.	J. Strozier, Brookhaven Nat'l Laboratories
D. Gruen, Argonne National Laboratory	K. Taylor, General Motors Technical Center
H. D. Hagstrum, Bell Laboratories	F. Vook, Sandia Laboratories
R. S. Hansen, Ames Laboratory	J. B. Wagner, Arizona State University
J. Houston, Sandia Laboratories	G. K. Wehner, University of Minnesota
L. Jenkins, Oak Ridge National Lab.	S. Wolf, ERDA, Div. of Basic Energy Sciences
F. P. Jona, SUNY, Stony Brook	M. Wrighton, Massachusetts Inst. of Tech.
J. R. Katzer, University of Delaware	J. Yates, Jr., National Bureau of Standards
G. Langlois, Chevron Research Co.	E. Yeager, Case Western Reserve Univ.
D. Maddox, Sandia Laboratories	

WORKSHOP OBJECTIVES

The goals of the workshop were: (1) to review the various areas of energy development and technology in which surface science plays major roles and makes major contributions, and (2) to identify the major surface-science-related problem areas in the fields within ERDA's mission in the fossil, nuclear, fusion, geothermal and solar energy technologies and in the field of environmental control.

The subjects that were discussed in the general area of Surface Science were as follows:

- Activation of Surfaces
 - A. Catalysis and chemisorption
 - B. Semiconductors, thin films, solar device surfaces
 - C. Electrodes, electrocatalysis, photon-assisted surface reactions
- Passivation of Surfaces
 - D. Corrosion
 - E. Interaction of ions with surface and near-surface regions
 - F. Grain, phase boundaries and interfacial boundaries

There were general conclusions and recommendations common to all of the study groups. These are summarized below. The specific highest priority recommendations applicable to the six specific areas of surface science are listed after the general recommendations.

WORKSHOP PRIORITIES

1. THE ORGANIZATION OF SURFACE SCIENCE RESEARCH

Surface Phenomena-A Pervasive Area in the Energy Sciences

From the very large number of specific examples discussed in this study, it is clear that surface phenomena play a dominant and widespread role in the various energy technologies. Our ability to tailor-make surfaces having desirable physical and chemical properties will be a major controlling factor in our future efforts to achieve energy conversion and energy conservation over the wide range of energy technologies. Basic research on surface phenomena, therefore, should yield concepts and data which will have a broad impact on our future ability to generate, convert and store energy.

A Major Commitment to Long-Term Research Programs

There was particular concern among the participants that much of the current funding in energy research areas could go into solving short-term problems, while the most important surface-related problems in most energy areas leading to new directions in energy technology are of a long-term nature. Although recurring energy crises always focus attention on short-term difficulties, long-term basic research must be carried out to increase our basic understanding of surface processes and materials. This long-term basic research approach should be a major component in the U.S. energy research effort.

Correlate Molecular and Macroscopic Properties of Materials

Through surface science, we gain a better understanding of the correlation between the molecular surface properties and macroscopic properties of materials. The atomic and electronic surface structures, surface composition and valency, and rates of elementary surface processes (diffusion, adsorption, reactions) should be related to the behavior of surfaces in catalysis, corrosion, grain boundary fracture, embrittlement, radiation damage, adhesion, and lubrication.

Expansion of Research at Interfaces

Surface science research should be broadened to include more studies of interfaces which are of practical importance. Future emphasis should be given to understanding surface processes at interfaces involving condensed phases (solid-solid and solid-liquid). Overlayers of great thickness compared to monolayer dimensions should be investigated over their entire range of growth. Thick-layer phenomena are of importance in corrosion, ion-surface interactions, electronic devices and grain boundary problems.

Improvement of Surface Measurement Capability-A Major Need

The development of new surface measurement techniques is a major need within the field. In addition, the calibration of existing techniques such as Auger spectroscopy, ESCA and sputter depth profiling poses major unsolved problems. Incentives should be provided for the invention of new techniques. When necessary, national facilities should be established to carry out surface research involving expensive apparatus.

National Centers for Surface Science Research

Even without coordinated national commitment to surface science research, the U.S. appears to have a leading position in most areas of the field. However, as a result of well-organized national programs in other countries (i.e., U.S.S.R., France, Germany and Japan), the U.S. Leadership role may be unlikely to continue in many subareas of surface science. It appears that making a national commitment through the establishment of surface science research centers could be of great value at present. These centers should be designed to foster effective communication between engineers and scientists who have common interests in solving surface problems and to provide access to expensive surface characterization facilities.

Education Within the Field of Surface Science

Training and retraining of U.S. scientists and engineers should have first priority in this rapidly moving field of science. Centers of research in surface science should provide education and training and exchange opportunities for personnel working in various energy technologies.

Improvement of Communications Between Scientists

The communication between basic research, development and technology needs considerable improvement. Exchange programs between personnel in national laboratories and academic institutions could improve this situation. Incentives should be provided for research by two or more investigators from various backgrounds (for example, materials science and chemistry, etc.) to carry out joint interdisciplinary research. All areas of surface science that are related to the energy mission would appear to benefit by an interdisciplinary approach.

2. RESEARCH COMMON TO ALL AREAS OF SURFACE SCIENCE

These represent general areas where investment of research funding could have the widest impact on surface science and its relation to various energy technologies.

- Studies of reaction dynamics and elementary processes (adsorption, diffusion, bonding and desorption) at surfaces, and related theoretical developments.
- Characterization of structural and electronic properties of surfaces and their influence on surface behavior.
- Study of surface modifiers: poisons, promoters, inhibitors, implanted species. Structural and chemical stabilization of surfaces.
- Surface defect characterization.
- Film growth studies (condensation, growth and evaporation).
- Development of instrumental methods for studies of external and internal surfaces under operating conditions.
- Measurement of sputtering yields and quantification of their surface measurement techniques.
- Surface studies of oxides, carbides, and sulfides.
- Studies of surface properties of new classes of materials: bimetallic clusters, composites, ceramics, polymers, ion implanted materials, intercalation compounds, etc.
- Search for substitutes for precious metals and other surface active materials that are not available in the U.S.
- Studies of the structure, composition and electronic properties of interfaces between condensed media (solid-solid, solid-liquid) and of grain boundaries, and related theoretical developments.
- Strength of interfaces: adhesion, lubrication, grain boundary cohesion, influence of environment.

3. RESEARCH RELATED ONLY TO SPECIFIC AREAS OF SURFACE SCIENCE

Catalysis and Chemisorption

- Development of chemical and physical probes of catalytic intermediates; characterization of active species in catalysis and chemisorption.
- Study of interaction of excited molecules with surfaces.

Semiconductors, Thin Films, Solar Device Surfaces

- Understanding and learning to control the nature of surface states at a free surface, and interface states at metal-semiconductor and semiconductor-semiconductor junctions.

- Study the effect of the structure and chemical composition of grain boundaries on the electrical properties.

Electrodes, Electrocatalysis, Photon-Assisted Surface Reactions

- Study of photon-assisted surface reactions.
- Study of hydrogen and oxygen electrocatalysis.

Corrosion

- Study of iron and iron-base alloy surfaces in the corrosive environments of hydrogen, sulfur, oxygen and water.
- Study of Al_2O_3 , SiN-SiC and other ceramic surfaces in the corrosive environments of hydrogen, sulfur, oxygen and water.

Interaction of Ions with Surface and Near-Surface Regions

- Simulation of radiation damage by study of low-energy ion interactions with surfaces (charge states, charge exchange, photon emission and sputtering yields.)
- Study of surface and near-surface modification under ion bombardment conditions (composition, topology, microstructure). Studies of surface passivation against radiation damage.

Grain, Phase Boundaries and Interfacial Boundaries

- Experimental and theoretical studies of correlation between free surfaces and grain boundaries with respect to segregation, diffusion, structure and two-dimensional phase equilibria.
- Determination of grain boundary and interface structure; atomic arrangements and defect structure.

PROGRAM OF THE SURFACE SCIENCE WORKSHOP

Wednesday, March 16 Chairman: G. A. Somorjai

- 9-10 A.M. Nuclear Energy Conservation and its Surface-Science-Related Problems
Carlos Colmenares, Lawrence Livermore Laboratory
- 10-11 A.M. Fossil Energy Conversion
Catalysis--Harold Beuther, Gulf Research and Development
Corrosion Problems--Roger Staehle, Ohio State University
- 11-12 A.M. Thermonuclear Fusion: The Role of Surface Science
Walter Bauer, Sandia Laboratories, Livermore
- 2-3 P.M. The Control of Air Pollution: The Role of Surface Science and Catalysis Science
Kathleen Taylor, General Motors Technical Center
- 3-4 P.M. Geothermal Energy Conversion and Surface Science-Related Problems:
John Apps, Lawrence Berkeley Laboratory
- 4-4:30 P.M. Solar Energy Conversion: Photovoltaic
Richard Bube, Stanford University
- 4:30-5 P.M. Photochemical Energy Conversion
Mark Wrighton, Massachusetts Institute of Technology

Thursday, March 17 Chairman: J. T. Yates, Jr.

- 8:30-9:25 A.M. The Theory of Surfaces: The State of the Art
G. Painter, Oak Ridge National Laboratory
- 9:25-10:20 A.M. The Atomic Structure of Surfaces
F. Jona, State University of New York, Stony Brook
- 10:20-11:15 A.M. The Electronic Structure of Surfaces
David A. Shirley, Lawrence Berkeley Laboratory
- 11:15-12:10 A.M. The Composition of Surfaces
J. Burton, Exxon Research and Engineering Co.
- 1-2 P.M. The Dynamics of Neutral Atoms and Molecules at Surfaces
Robert Madix, Stanford University
- 2-3 P.M. The Dynamics of Ions at Surfaces
G. Wehner, University of Minnesota
- 3-3:30 P.M. Solid-Solid and Solid-Liquid Boundaries
D. Maddox, Sandia Laboratories, Albuquerque
- 3:30-5 P.M. Workshop Activities
Chairman: W. Clinton

Friday, March 18

- 9 A.M.-4 P.M. Workshop Activities

Discussion groups:

Activation of Surfaces

A. Catalysis and chemisorption

Theodore E. Madey, Chairman

H. Beuther, R. Eischens, W. P. Ellis, R. Hansen,
R. Madix, G. Painter, A. Perrotta, D. Shirley,
J. Strozier, K. Taylor

B. Semiconductors, thin films, solar device surfaces

Homer Hagstrum, Chairman

J. Gadzuk, R. Bube, J. Galt, G. Cummings, F. Jona

C. Electrodes, electrocatalysis, photon-assisted surface reactions

E. Yeager, Chairman

P. Epple, W. A. Goddard III, P. Stonehart, J. B. Wagner, M. Wrighton

Passivation of Surfaces

D. Corrosion

R. Staehle, Chairman

J. Apps, J. Blakely, A. Frederikse, D. Michels,
J. Morris, Jr., P. Palmberg, J. Rowley, S. Wolf

E. Interaction of ions with surface and near-surface regions

J. Mayer, Chairman

D. Green, F. Vook, W. Bauer, G. Wehner, C. Colmenares

F. Grain, phase boundaries and interfacial boundaries

C. McMahon, Chairman

M. Brodsky, J. Burton, J. Houston, J. Jenkins, D. Maddox,
D. Stein

At the request of the organizers, all of the talks presented overviews of surface science areas and the various surface-science-related problems of energy technology. During the first day, various energy technology areas were reviewed by experts working in the field, and surface-related problems were exposed and discussed, along with their role in development and technology applications. During the second day the present state of understanding in a number of areas of surface science was discussed. These were also presented as broad reviews by active practitioners working in the respective fields of surface science. The purpose of these lectures was to provide the participants with a broad review of modern surface science and to expose the surface-science-related problems of the energy technologies. After this exposure to surface science and energy technologies the actual Workshop activities began later in the afternoon of the second day and continued through an entire third day. The participants were divided into the six study groups listed above.

The organizers provided the study groups with a series of questions to help focus the discussions. The discussions on these questions were by no means binding. Participants in the study groups were asked to consider all important areas of research and development in their broad field of responsibility. Questions asked

of the study groups were organized into two topics: the first topic was aimed at reviewing the state of surface science as related to energy technologies, its role in contributing to data base and to solving problems of existing and new technologies; the second topic was aimed at assessing the various surface science directions and goals for the future. These questions are listed below.

QUESTIONS ADDRESSED BY THE STUDY GROUPS

TOPIC 1. The state of surface science as related to energy technologies, its role in contributing to data base, and in solving problems of existing and new technologies.

- 1.1. The various fields of ERDA's mission include energy conservation, fossil, nuclear fusion, geothermal and solar energy technologies and environmental control. Identify the fields where most of the surface science problems are concentrated.
- 1.2. Enumerate the various energy technology problems that may be solved by surface science research.
- 1.3. Identify, if possible, the long-range surface science research problems where much effort should be concentrated.
- 1.4. Which areas of surface science are neglected even though research in these areas would be important in support of one or several of the energy technologies?
- 1.5. What sort of physical-chemical data are missing in surface science that would help develop new technologies or better control existing technologies?
- 1.6. What classes of surfaces need to be better understood at the basic level in order to ensure better control of surface processes?
What sort of material or process characterization is needed to help develop new technologies or better control existing technologies?
- 1.7. What theoretical research technique offers the most promise for actual predictive power?
- 1.8. Describe the experimental techniques and the type of instrumentation needed to obtain the necessary surface science data or surface characterization.

TOPIC 2. Surface science directions and goals.

- 2.1. Select several highest priority research areas which should be supported in the near future. Rank these if possible.
- 2.2. How would you organize surface science research to have maximum impact on the various energy technologies? How would you optimize the research development technology information flow?
- 2.3. What do you consider as the critical mass of research groups in surface science to provide the necessary basic materials and process control information in your area of concern? Do we have this critical mass?
- 2.4. What are the major obstacles in the way of developing close cooperation between national laboratories and industry? How could these obstacles be best removed?

- 2.5. Are there important areas of surface science research that impact on energy technology in which the best work is performed outside the U. S.? Where?
- 2.6. (a) How would you provide a mechanism to educate technical personnel for employment in the various energy technologies?
 (b) How would you provide a mechanism to retrain technical personnel already working in the energy technology fields in modern surface science?

The recommendations of the six study groups in response to these questions are consolidated under Topics 1 and 2 below.

ASSESSMENTS AND RECOMMENDATIONS OF THE STUDY GROUPS

TOPIC 1. THE STATE OF SURFACE SCIENCE AS RELATED TO ENERGY TECHNOLOGIES, ITS ROLE IN CONTRIBUTING TO DATA BASE, AND IN SOLVING PROBLEMS OF EXISTING AND NEW TECHNOLOGIES.

A. Catalysis and Chemisorption

Most catalysis and chemisorption problems are concentrated in fossil and fusion technologies and in environmental control; solar and energy conservation (through an efficient energy conversion process) are second in importance.

Energy technology problems and needs are listed in order of priority and with S = short-range goals, L = long-range goals.

Fossil: Syn Gas ($H_2 + CO$) Processing Problems

1. Reduction of purification cost, particularly S removal; development of S-resistant catalysts (S).
2. Use of surface science tools in analyzing catalyst failure, in characterizing differences between successful and unsuccessful catalysts (S).
3. Development of catalysts with high selectivity for synthesis of higher molecular weight hydrocarbons and alcohols (L).
4. Detection and processing of carcinogenic by-products (L).

Fusion and Fission

1. Chemisorption on heavily ion-bombarded surfaces (S).
2. Hot atom chemistry, particularly on carbon surfaces (S).
3. Development of catalysts for conversion (via shift) $H_2O \rightarrow H_2 + 1/2 O_2$: development of a closed thermodynamic cycle using heat from nuclear reactions to run a 4- or 5-step H_2 generation cycle (L).
4. Chemisorption in intense radiation fields (L).
5. Ferritics corrosion (L).

Solar

1. Chemisorption and external corrosion associated with solar device surfaces (S).
2. Dynamics of growth and synthesis of photoactive surfaces via gas/solid deposition processes under well-defined conditions (CVD) (L).
3. Hydrogen production from H_2O via photocatalysis involving such compounds as TiO_2 and $SrTiO_3$ (L).

Environmental Control

1. Adsorbents and catalysis for stack gas cleanup of coal combustion gases

- (e.g., SO_2) should be regenerable. NO_x adsorption and reduction (S).
 2. Materials substitutes, e.g., for Pt, Rd, and Rh in 3-way auto exhaust catalysts (S,L).
 3. Chemistry on particulates and particulate characterization (L).
 4. Catalytic combustion (L).

General Problems Impacting on Fossil, Fusion, and Environmental Controls:
 Influences of Adsorbed C, O, N, S on Surface Dynamics

1. H adsorption, dissociation, permeation;
2. Interactions of H_2O and O_2 ;
3. Catalytic activity--coke formation and S resistance, action of surface "modifiers" such as poisons and promoters.

Long-term surface science research problems (H = highest priority, L = lower priority) where much effort should be concentrated are listed as follows:

1. Reaction dynamics on well-characterized surfaces; elucidation of the basic steps of surface reaction adsorption in gas-solid interactions and related theoretical developments; interaction of excited molecules with surfaces (H).
2. Development of instrumentation to study catalysts and other well-characterized surfaces under (or applicable to) ambient conditions. Examples include but are not limited to (a) optical and acoustical spectroscopic techniques, (b) neutron scattering, (c) high energy electron microscopy (H).
3. Characterization of surface geometric, electronic, and bonding structure--theoretical as well as experimental (H).
4. Chemical and physical probes of catalytic intermediates; characterization of the active species in catalysis and corrosion (H).
5. Development of alternatives to precious metal catalysts; search for unsuspected activity in well-known materials (L).
6. Physics and chemistry of small particles: sintering, particle-support interactions and their influence on reactivity; chemistry of airborne particulates (L).
7. Structure and catalytic properties of small crystals and metal clusters (L).
8. Studies of highly exothermic reactions; search for better catalyst stability (L).
9. Surface thermodynamics of gas/surface systems (L).

Physical-chemical data needed are:

1. Rate constants for elementary reactions on surfaces;
2. Bond lengths and bond strengths of adsorbed species;
3. Surface interaction energies, heats of adsorption;
4. Surface adsorbate densities.

Research on well-characterized surfaces of the following classes of materials is imperative:

1. Alloys and mixed metals;
2. Semiconductors and insulators: oxides, sulfides, carbides;
3. Amorphous materials.

Theoretical research is needed in:

1. Determination of surface electronic structure;
2. Surface geometry and energetics of adsorption;
3. Description of dynamic processes such as breaking and formation of bonds at surfaces.

Beyond a general concern for the necessity of capital equipment expenditures for modernization and development of new surface instrumentation, we approve of the concept of national facilities or centers in support of major efforts in surface

structure determination and synchrotron radiation. The latter facility should permit a full range of UPS, XPS, and other surface science measurements. (Funds for travel to and experimental setups at these facilities should also be provided.)

B. Semiconductors, Thin Films, Solar Device Surfaces

Semiconductor and thin films are most important to ERDA's mission in the field of solar energy (solar photovoltaics in particular). Photovoltaic cells, metallization films, and protective films are also involved.

Problems involving solar energy technology may be divided into areas involving solar thermal applications; there is a need for absorbing surfaces that are environmentally stable.

Photoelectrochemical applications involve primarily a choice of a stable semiconductor system that will permit the photoelectrolysis of water with the production of hydrogen and oxygen.

Photovoltaics relates to the direct conversion of solar energy to electricity using homojunctions, heterojunctions, and metal-semiconductor Schottky junctions. Research is directed at maximizing the open-circuit voltage, quantum efficiency, short-circuit current, fill factor and solar efficiency, while minimizing recombination losses and reverse saturation current. Photovoltaics may be separated into two categories: 1) the use of single-crystal cells (presumably of Si or GaAs) with concentration of the solar radiation, and 2) the use of thin-film cells in large-area flat-plate form without concentration.

Particular problems associated with concentration involve reflecting surfaces for solar concentrators and specific effects caused by the high-intensity radiation associated with sunlight concentration. In this latter category are adhesion of the metallization electrodes and the production of defects in the photovoltaic materials. Simulated high-intensity irradiation using lasers may be useful in understanding and guiding the radiation damage found for highly concentrated solar radiation.

General problem areas related to photovoltaics may be summarized as follows:

1. Thin films with these particular properties are needed: coatings that are anti-reflective, chemically passivating, abrasion resistant, transparent, conducting, and hermetically sealing.
2. Understanding and learning to control the nature of surface states as they manifest themselves in several different ways.
 - a. Surface states at a free surface, their effect on carrier loss through recombination, and the effect of thin films, chemical treatment, and environment on the identity, character, and properties of these surface states.
 - b. Interface states that occur between two different types of material in metal-semiconductor and semiconductor-semiconductor junctions. Information is needed on their structure and on their dependence on preparation conditions and chemical treatment. The relationship of interface states to interface recombination should also be studied.
 - c. Grain-boundary effects that occur within polycrystalline layers or films. Information is needed on their structure, their effect on bulk properties, and their ways of altering properties of grain boundaries through diffusion or segregation of deliberately chosen impurities.
 - d. Metal-semiconductor interfaces are significant not only because of the role of Schottky barriers in photovoltaics, but also because of the importance of low resistance contacts to the junction semiconductors. The importance of such low-resistance contacts is accentuated in high-current-density applications such as that involving concentration of sunlight.

Areas of surface science that need added emphasis in order to support solar energy are:

1. Studies of the effect of intense long-term irradiation by light in the solar spectral region on semiconductor-metal interfaces and as a cause of defects in the surface or near-surface region of semiconductors.
2. Interface studies (solid-solid and solid-liquid interface). There is a need for chemical and atomic structure as well as electronic structure information at these interfaces, which include grain boundaries and heterojunctions, as well as metal-semiconductor and liquid-semiconductor interfaces. Some of these are coherent, and some incoherent.
3. Studies of the relation between the properties of the interfaces in (2) to the electrical properties of a structure.
4. Crystal and thin-film growth processes and the resulting kinetics on amorphous as well as crystalline substrates.

We do not suggest that funds be awarded specifically for collecting and organizing physical-chemical data, but tabulation of selected properties of materials could be useful to groups in the development and basic research areas. For example, ionization cross sections and back-scattering profiles of the elements under different excitation conditions would be useful in trying to quantify information from AES spectra; sputtering yields of materials as functions of ion energies would be helpful to surface scientists, thin film growers, etc.; data on epitaxial systems, i.e., temperature, rates, orientations, etc., for single-crystal growth, would be valuable to the device-fabrication people, as would the compilation of surface recombination velocities in well-characterized materials.

The "ordered" interfaces normally encountered in epitaxially grown layers need detailed characterization to assist and control the impact on technology uses, such as photovoltaics. Similar considerations apply to semiconductor-metal interfaces to ensure good electrical conductivity with high reliability.

To the extent that grain boundaries can be considered as surfaces, the impact on bulk electrical and transport properties needs to be defined carefully.

Segregation to and diffusion of impurities along grain boundaries are surface-related processes that require careful characterization. Studies should be directed at both the use and control of process results.

A complete quantum chemical theory of semiconductor and thin-film properties seems most unlikely, particularly when one considers the primitive predictive state of the theories of even the simplest gas phase atom-diatom molecule interactions. It thus seems unrealistic to expect that theorists will produce first-principle theories with predictive powers, at least for energy technology problems. Where then lies the role of theory?

We suggest the following possibilities. First-principle theories should be constructed on a few well-chosen systems that can be checked against carefully controlled idealized laboratory experiments. Having established the essential correctness of these theories, semi-empirical extrapolations into more tractable forms could be made. With these simpler forms, predictions of macroscopic material behavior, based on microscopic considerations, would be possible. In essence, the insight gained by a few large and idealized calculations will lead to the formulation of some "Pauling-type" rules for surfaces.

For such a development to occur, a data base of relevant physical quantities is necessary, since trends in theoretical generalizations are more likely to come from data than from extensive computations.

In the area of semiconductors, films, and solar devices, new experimental techniques are required to investigate and characterize all sorts of interfaces, such as those that occur between metals, between metals and semiconductors, between semiconductors and semiconductors, at grain boundaries, and at defects. Since surface science instrumentation is suited to the study of the vacuum-solid interface, new techniques might be devised in which atoms that are present or introduced into the interface are used as probes from which electrons are excited by radiation or in Auger processes. Such electron spectroscopy of these implanted atoms would yield information on the local chemical and electronic environment. Other possible experimental approaches to obtaining the necessary surface science data are ion channeling and backscattering, Auger spectroscopy with ion milling, and ion desorption spectroscopy.

In developing new experimental techniques, problems arise in which theoretical clarification and understanding of the measurement process are essential in order to separate measurement artifacts from data relating to the system properties. Close cooperation and collaboration between experiments and theorists is essential in this phase of surface research.

C. Electrodes, Electrocatalysis, and Photon-Assisted Surface Reactions

Electrochemistry is the direct conversion interface between chemical and electrical energy and as such is of major importance to ERDA's missions in the areas of energy conservation, fossil fuels, solar energy, and environmental control.

Many of the technological problems in electrochemistry are associated with the electrocatalytic properties of the electrodes, i.e., insufficient catalytic activity, susceptibility to poisoning, loss of electrocatalyst area, and high cost.

Laboratory techniques have recently been developed for reducing impurities at the interface to a sufficiently low level that they do not interface with the catalysis in a number of electrochemical systems. As a result, electrocatalysis has emerged as a science in the laboratory. In industrial applications, however, electrocatalysis still remains more an art than a science, with impurity effects usually greatly reducing the catalytic activity of the electrode surface. This results in reduced current densities, excessive voltage losses (reaction over-potential), higher catalyst loading requirements, shortened electrode life, and undesirable competing reactions. A major need exists for electrocatalysts of high initial activity, high tolerance to impurities in the electrolyte and reactant feeds, and long-term stability. Impurity effects are not well understood in electrocatalysis.

The objective of long-range electrocatalysis research is to develop a predictive base for a number of important electrochemical processes (e.g., H_2 , CO, hydrocarbon oxidation; O_2 reduction; H_2 , O_2 , Cl_2 generation). To achieve such an objective requires the identification of reaction pathways (including adsorbed intermediates), the relationship of the adsorption energies to electrode surface properties, solvent interactions with the electrode surface and the potential energy surfaces for the charge and atom transfer steps.

In fuel cells, and in many batteries and industrial electrolysis cells, the very high electrode surface areas used to achieve sufficient electrocatalytic activity are obtained with highly porous electrocatalytic layers or extremely small catalyst particles on a porous electrode substrate. Morphological changes, which usually occur with use, lead to a loss of this high area and constitute a severe problem that is not well understood.

Most advanced fuel cells, batteries and industrial electrolytic systems present hostile environments for the electrodes, separators, diaphragms, membranes, and

containment materials. The deterioration processes are not well understood and involve much surface chemistry.

The following are areas of electrochemical surface science receiving insufficient emphasis:

1. Photon-Assisted Reactions at Surfaces: The possibility of using surfaces to mediate the photochemical (solar) formation of fuels and conversion of light to electricity may affect future energy resources, and is a research area that most concerns ERDA's mission in solar energy. This field presently has no associated identifiable practical scale energy technologies, but within the past two years there have been two important laboratory demonstrations of light to chemical and electrical energy conversion by irradiating semiconductor electrodes exposed to liquid electrolytes. In one example, SrTiO_3 (n-type semiconducting) has been shown to efficiently convert ultraviolet light to chemical energy in the form of H_2 and O_2 from the photoelectrolysis of H_2O . Solar energy efficiency was estimated to be of the order of 1%. N-type CdX ($\text{X} = \text{S}, \text{Se}, \text{Te}$) in electrolytes containing Na_2X have been shown to serve as the photoanode in cells for the conversion of light to electricity with solar efficiency (5-8%) rivaling the values obtained for wholly solid-state devices (photovoltaics). In each case, polycrystalline semiconductors have been shown to work with efficiencies approaching those found for single crystals. These discoveries may lead to device applications and presently command a great deal of interest in the U.S. and abroad. Some of these applications and the basic research undergirding their development are outlined below.

Significant potential exists as well in the use of surfaces in non-electrode applications for photochemical fuel formation. In driving uphill reactions the problem is to build in barriers at each step that preclude back reactions. This is opposite to the goal of catalyst research which is to remove all kinetic barriers to thermodynamically favorable reactions. There is considerable merit in considering that surfaces (semiconductors, chemically modified semiconductors, organic polymers) can serve to photo-assist the conversion of raw materials (N_2 , O_2 , CO_2 , H_2O , etc.) to fuels. Promising lines of effort are those directed to evaluating the kinds of photoprocesses that can be carried out on surfaces and with special aims toward establishing unique chemical processes induced by light and an effort to promote energetic uphill reactions (e.g., $\text{CO}_2 \rightarrow \text{CO} + 1/2 \text{O}_2$) with light. The irradiation of surfaces may also serve to generate thermally active catalysts having simultaneously improved activity and selectivity. There is as yet a serious lack of real effort in this new area. Theory directed toward the establishment of surface reaction activation energies would be particularly fruitful in pinpointing the nature of the photo process desired.

2. Electrocatalysis: Electrocatalysis received considerable attention in this country in the 1950s and 1960s, principally in conjunction with fuel cell research. Most companies abandoned this work in the late 1960s. The past two or three years have seen renewed interest in electrocatalysis research in industrial laboratories of companies involved in large-scale electrolysis and electrowinning, principally as a result of escalating electric power costs. Most of the industrial research in electrocatalysis has been applied research and has not contributed much to the science.

Very little electrocatalysis research has been carried out in academic laboratories in this country; there are only two or three physical electrochemists working in this area.

3. The Electrochemistry of Oxides: Oxide films and bulk oxides play an important role as electrocatalysts, reactants in batteries, and passivation layers in corrosion inhibition. Relatively little is known about oxide-electrolyte

interfaces. With the exception of passivation films in metals, little fundamental research has been carried out on such interfaces.

4. **Electrocrystallization and Electrodeposition:** Electrocrystallization and dissolution are important in various batteries and industrial electrochemical processes, including electroplating and electromachining. Fundamental surface physics research in this area is virtually nonexistent in this country.

Supporting physical chemical data that are useful to electrocatalysis research and for which it is possible to obtain meaningful values with existing methods include the following:

1. Adsorption isotherms, heats of adsorption and electroadsorption valences for various species at metal-electrolyte interfaces; e.g., H, O, OH⁻, halides, S⁼, CO, CO₂, small organic molecules.
2. Ionic double layer properties of solid electrodes (polycrystalline and where possible, single-crystal surfaces) in aqueous solutions.
3. Standard rate constants and transfer coefficients for the H₂ and O₂ electrode reactions on various well-defined electrode surfaces under ultra-pure conditions.
4. Work functions for solid-gas interfaces.
5. Heats of wetting of metals with water.

The electrochemical interface involves an electronic conductor as the electrode phase in contact with an ionic conductor as the electrolyte phase. A wide assortment of each type of conductor is involved in energy-related technologies, particularly in the electrocatalysis area. Typical electrode phase materials include:

1. pure and alloy metals,
2. underpotential deposited monolayers on foreign metal substrates,
3. carbon and graphites,
4. metal carbides (e.g., WC, NiC),
5. intermetallic compounds (e.g., GaAs),
6. oxides (principally transition metal),
7. sulfides (principally transition metal),
8. transition metal complexes--thin films, monolayers (e.g., transition metal macrocyclics),
9. electronically conducting polymers (e.g., SN_x, polymeric transition metal complexes),
10. elemental semiconductor (e.g., Ge, Si).

In many instances these electrode materials are used in very high-area-forms with high-defect structures. Typical electrolyte phases include:

1. aqueous electrolytes, including extremely concentrated systems with all water bound to ions (e.g., KOH·H₂O, ZnCl₂·4H₂O, 96% H₃PO₄),
2. organic solvents (particularly aprotic),
3. molten salts (particularly halides, carbonates),
4. ionic conducting solids (e.g., β-Al₂O₃, Ag_xRu_yI_z).

The single most generally useful materials characterization for those various combinations of interfaces is the stability of the interface as a function of potential and temperature. Stability is more than just a matter of thermodynamics and equilibrium solubility. Often, long-term stability is achieved because of slow kinetics even though the electrode phase has high solubility in the electrolyte.

In the explanation, prediction and design of electrochemical and photon-assisted systems, reliable theoretical methods are essential to provide:

1. Heats of chemisorption of various molecules, radicals, and reaction intermediates onto electrode materials.

2. Structure of chemisorbed molecules.
3. Reactive surfaces and activation energies for charge and atom transport across solid-liquid interfaces.
4. The dependence of the above quantities upon composition and character of the electrode site.
5. For photo-assisted processes it is particularly important to consider the above quantities for excited states to learn where a photon could be used to assist a reaction and where one can get a sizeable potential barrier to prevent back reaction.
6. The above quantities would be studied as a function of potential difference across the solid-liquid interface.
7. Involving (3) and (6), we would use dynamic techniques to calculate basic rate quantities for atom and charge transfer.

It is important to emphasize that particularly for reaction intermediates the concentrations and lifetimes will be such that only theoretical methods may provide the required data.

D. Corrosion

The field of surface science is too narrowly confined with respect to the subject of corrosion. Work in surface science should contribute to understanding corrosion phenomena such as stress corrosion cracking, hydrogen embrittlement, corrosion fatigue, and erosive wear. These and other phenomena concern liquid-solid interfaces which, as a class, are under-studied in comparison to their importance to technology and society.

Table 1 suggests the variety of environments in which surface science might play a role to produce energy for industrial and domestic uses. Effort could be concentrated on:

1. Formation of a new phase on a clean surface (e.g., oxide or carbide on steel, SiO_2 on SiC) which includes investigations of nucleation growth, structural aspects, thermodynamics and kinetics of the new phase; and theoretical investigations for chemical bonding of a new layer to a substrate, distinguishing between growth on self and non-self substrates.

2. Adhesion of the new layer (experimental techniques, scaling, spalling--for liquids wettability).

Corrosion begins with nucleation and growth of a monolayer. However, it is important to study layer growth to thicknesses of several hundred Angstroms or even microns.

3. (Clean) surface characterization (solids in vacuum), which would look into electronic states; defect structure, defect distribution, and selectivity (the analogy with catalysis deserves note); and near-surface regime--the structural and compositional contrasts with the interior parts (which have a classical description).

4. Solid-liquid interface, including morphology and electronic structure of the solid near the liquid; morphology and electronic structure of the liquid near the solid; experimental approaches for studying the solid-liquid interface, e.g., optical, electrochemical, and other methods; and study of the barrier layer in the liquid-solid interface (electronic states, electric fields, compositional discontinuities, etc.).

5. Arcing (surface in very large electric fields), which would take into account effects on surface structure, evaporation and (re) condensation, and charge transfer.

Table 1. Surface science problems related to corrosion in the various energy technologies.

Class	Environment		Temp. (°C)	Solvents	Solutes	Processes Involving Surface Problems
	Pressure (atm)					
	Gas	Liquid				
Solar						
Direct	~1	~1	0 to 80	Glycol, H ₂ O	Additives, phosphates, alums	UV degrad. metal, glass corrosion, corrosion in heat storage units, particulate adhesion to transparent surfaces
Ocean, thermal, mechanical	~1	1 to 300	0 to 25	H ₂ O	Biota, seawater	Biofouling, seawater corrosion
Fossil						
Coal						
Conventional	0.05 to 30	1 to 30	0 to 700	H ₂ O, flue gases	Additives	Corrosion, ionic scales
Gasification	1 to 120	1 to 5	0 to 2000	Org. mix, slags		H ₂ S, H ₂ -alloy effects, organic scale buildup
Oil shale	0.1 to 5	~1	0 to 600	Slags	Solids	High temp. corrosion/erosion
Tar sands	0.1 to 5	~1	0 to 200	Org. mix	Solids	H ₂ -alloy effects, organic scale buildup
Oil, conventional, enhanced recovery	1 to 300	1 to 300	1 to 200	H ₂ O, petroleum	Ionic salts	H ₂ S effects, ionic salts, corrosion, scaling
Biomass						
Fermentation	~1	~1	20 to 40	H ₂ O, org. mix	Org., inorg. CO ₂	Atm. corrosion
Pyrolysis	1 to 100	1 to 100	0 to 600	Org.-inorg. mix		CO ₂ , corrosion by N- and S-containing molecules
Geothermal						
Electrical	0.05 to 20	~1	80 to 300	H ₂ O, org.	Ionic salts	Erosion/corrosion, H ₂ S, ionic scaling
Processing & heating	1 to 3	1 to 3	20 to 300	H ₂ O, glycol	Ionic salts	Ion-stimulated corrosion, inorganic scaling
Reinjection	--	1 to 150	0 to 50	H ₂ O	Ionic salts, org. additives	Rock-fluid interactions, scaling
Nuclear						
Fusion	10 ⁻⁶ to 1	~1	High T			
Fission	1 to 20	1 to 20	0 to 700 and high T	H ₂ O, liq. metal		
Environmental control	~1	~1	-20 to 50	H ₂ O, atm.	Ionic salts, trace elements	Water treatment (F ⁻ removals, etc.) Gas scrubbing (H ₂ S, Rn, etc.)

6. Surface modification/protection includes:

- a) Development of theory and experiment relating to activation of surface sites for subsequent acceptance of inhibitors (with an emphasis on organic inhibitors) or macroscopic coatings.
- b) Research into improved surface coating methods studying: gas or liquid transport, atom (or molecule) dynamics as it approaches the surface, atom (or molecule) diffusion after impinging upon the surface, e.g., surface diffusion, and film stress.

7. Corrosion of materials, e.g., metals, ceramics, polymers, composites. Theory and experiment relating to: oxidation, sulfidation, and carburization or other gas effects.

Note: Emphasis on metals and glass is through "chemisorption" or monolayer growth, whereas the emphasis on ceramics and glasses is on their defect structure and physical properties once a discrete product layer has been formed.

8. Interaction between environment and mechanical properties would stress theory and experiments investigating adsorption and chemisorption with respect to surface energies, crack growth and defect configuration at the intersection with the "contaminated" surface; and relation of above to "engineering" properties, e.g., stress corrosion, cracking, corrosion fatigue, hydrogen embrittlement, slow crack growth, etc.

Surface "science" studies are presently heavily concentrated on metals and semiconductors and involve low pressure ($\leq 10^{-4}$ Torr) and low temperature ($\sim 300^\circ\text{K}$) conditions. Current techniques of surface science should be applied to a wider range of materials and experimental conditions. Specific recommendations regarding areas of research currently neglected are as follows:

1. Some theoretical effort should be devoted to the topic of surface structure (electronic, vibrational, defect, etc.) at elevated temperature. Experiments on the detection of surface defects and their effect on binding and transport properties are required.
2. Further work deserves to be done on the structure and reactions at the interface between metals and relatively high pressure (~ 1 atm) gases using techniques such as LEED, electron, ion and optical spectroscopies, ellipsometry, etc.
3. Surface characterization of nonmetallic materials is required. This should include covalent and ionic crystals and oxide semiconductors, as well as some more complex systems such as slags, molten salts, and polymeric materials.
4. The defect structure of scales (oxide and oxyanion salt films) is of importance in connection with growth and passivation characteristics. Further data on the electrical and thermal conductivity of scales would be valuable.
5. The structure of solid-solid interfaces requires further study for the development of strongly adherent protective coatings on metals. High spatial resolution techniques would be valuable.

Several types of physical-chemical data are needed to help develop passivation coatings and understand corrosion phenomena. They include: 1) thermodynamic properties of concentrated electrolytes; 2) thermodynamic properties of compounds; 3) phase diagrams for two dimensional systems, for example, pressure, temperature, thickness diagrams for the oxidation of metals; 4) atom or molecular diffusion coefficients on metal surfaces; 5) atomic structure of various substrate-adsorbate systems; and 6) parameters which govern the growth rate of surface films.

The industrial use of energy involves its conversion from one form to another or into a different medium. In both cases a physical interface is involved and important heat transfer events involving atomic and molecular activity occur at the phase boundaries.

The nature of the phase boundary in the context of heat transfer is an interfacial region, a tubular zone having a finite thickness often much greater than a monolayer, which provides a transitional space for the homogeneous phases on either side. Since the two sides frequently have different temperatures and different compositions, some irreversible chemical phenomena take place.

Study of this kind of interface involves a logical extension of surface science. In principle, a classical surface would be studied by beginning from a clean condition, proceeding through nucleation events for the development of a new phase on the substrate, and continuing with the lateral extension of the new phase and its extension into the "free" space of the "z" direction, reaching thicknesses of many atomic layers.

The medium in the free space can usefully be a gas, perhaps dilute at first. However, more useful information will come from the study of the effect of denser gases and ultimately condensed fluids. Such endeavors mark a transition from surface science, as traditionally practiced, to a science of interfaces.

Additionally, the dynamic nature of industrial processes deserves scientific attention. The process is microscopically a series of molecular events which can be evaluated by study of the thermodynamics, statistical mechanics, chemical bonding, and other science concepts, taken in real time. Such an approach would be a science of interfacial processes.

Although a large variety of interfaces is possible, the ones of greatest importance to energy development are few in number. Significant among these are aqueous-metal interfaces in which corrosion and scaling occur due to the dissolved components. In many cases heat transfer is important, especially with respect to gas-metal interfaces in reaction vessels. Aqueous-oxide and gas-oxide interfaces are important in the context of ceramics or when the metal substrate presents an oxide surface to the contacted fluid.

Very little scientific information about the interfacial region is available. Structural information would be valuable. Surface bonding modes for molecules and ions are expected to be different from gas-solid counterparts, since solvation competes for the molecular association on one hand and the solvent and extraneous ions compete for surface sites on the other hand. The consequences of these near-surface phenomena control the usefulness of the equipment. In principle they can be described in terms of such concepts as electron sharing, statistical mechanics, etc. If scientific data were available concerning chemical bonding and the principles of intermolecular competition, better estimates could be made of the engineering parameters required for design of novel systems or the incorporation of novel combinations of materials into practical designs.

Of chief importance to an interface description are the geometry and the composition and distribution of components. Resolution in space involves three dimensions, of which the z direction can be of the order of microns. Lateral resolution should provide information about growth rates of developing films and, in some experiments, the character of nucleation sites for growth of scale or corrosion products, or the initiation of etch pits or corrosion attack.

A few techniques apply--namely ellipsometry, high voltage electron microscopy (HVEM) particularly with environmental chambers, energy loss analysis or both, and laser Raman spectroscopy. The first technique yields information on film thickness and the spread of growing films in situ. HVEM can give in situ data at high resolution, perhaps identifying nucleation sites or processes occurring at a spreading edge. Raman techniques yield information about molecular species or bond types; of particular significance are newly developed techniques using crossed laser beams which stimulate a small volume of fluid and can be ranged through the interface, including the z direction.

Because these techniques are new, the real opportunities for studying thick interfaces are just becoming available. These tools promise information about the interfacial region that includes real-time analysis with good spatial resolution.

Because of the complexities associated with corrosion phenomena, a range of instrumental techniques are required for the study of surfaces and surface-related phenomena. They are as follows:

1. Electron microscopy, including high resolution EM (this technique might cause radiation damage to the surface), raster emissions, energy loss spectroscopy, application of environmental chambers, and scanning electron microscopy.
2. Field ion microscopy.
3. Optical methods, including Raman-laser spectroscopy (particularly with respect to molecular surfaces), optical microscopy (reflection, ellipsometry), and high-intensity light.
4. High-vacuum electron and ion emission techniques for surface analysis, including Auger electron spectroscopy, scanning Auger spectroscopy, ion scattering spectroscopy (ISS), secondary ion mass spectrometry (SIMS), electron spectroscopy for chemical analysis (ESCA), and exoelectron emission.
5. Miscellaneous spectroscopic techniques, such as Newton spectroscopy, and Mössbauer spectroscopy.
6. Electrochemical techniques, including electrochemical potential distribution, and general electrochemical methods.

E. Interaction of Ions with Surface and Near-Surface Regions

The technologies of fission, fusion, fossil, solar, and geothermal energy have surface, near-surface, and interface problems that are crucial to their success. For example, magnetic fusion progress is now limited by a need to solve the plasma contamination by first wall surfaces. The interaction of energetic ions with surfaces is a highly successful research area providing basic insight and data for applied energy problems. The two major areas of application are ion-surface modification and ion-surface analysis. Included in ion surface modification is ion implantation, which beneficially modifies the near surface (corrosion protection, solar cell junctions, erosion, and wear), and provides tailored surface environments for particular applications. The study of basic phenomena such as sputtering, diffusion, solubility, phase diagrams, corrosion, oxidation, and radiation damage simulation plays an important role in this work.

Table 2 enumerates the various energy technology problems that may be investigated by ion-surface modification.

Long-range science research problems are:

1. Chemical and physical sputtering, including back reflection and gas re-emission;
2. Near-surface modification of composition, microstructure, and topography;
3. Adsorption and desorption phenomena;
4. Chemisorption;
5. Influence of impurities on sputtering phenomena, surface migration, near-surface diffusion and solubility.

Neglected but important surface science research areas are: systematic application of ion beams to surface analysis and surface modification with specific technological interactions (e.g., corrosion, erosion, embrittlement, catalysis).

Table 2. The role of ion beams in energy technology.

Energy Field	<u>Surface Modification</u>	<u>Surface Analysis</u>
	Implantation of Ions	SIMS, RBS, Nuclear Reactions, ISS, Sputter Auger and ESCA
Fusion	First wall-plasma simulation (sputtering, desorption). New superconducting films. Coatings for laser fusion and beam fusion. Pellet technology. Ion polishing of mirrors. Corrosion of cooling ducts.	Confinement experiment analysis. First wall analysis.
Fission	Neutron damage simulation. Waste disposal studies. Corrosion by liquid metal coolants. Isotope separation via sputtering.	Cladding vessel analysis. Fracture analysis.
Fossil	Hydrogen diffusion barriers, to avoid embrittlement. Catalyst modification. Modification for erosion and wear surfaces. Corrosion of vessels.	Catalysts analysis. Hydrogen containment vessel analysis. Fracture analysis.
Solar	Sputter deposition for mirrors photovoltaic junction contacts, and passivating layer formation. Production of thermal absorbing layers.	Mirror and composite layer analysis. Solar thermal absorbing coatings.
Geothermal	Drill surface modification. Erosion and high wear surfaces. Nonsticking corrosion-free surfaces.	Analysis of interface between deposits and metals. Adhesion analysis of strippable layers.
Environmental		Automotive catalyst degradation analysis. Pollution analysis of solid, liquid, and gas samples.
Conservation	Corrosion in thermal storage media (molten salts, organics).	Surface analysis of storage media such as metal hydrides.

Needed physical-chemical surface data are:

1. Low-energy sputtering data (i.e., sputtering yield of engineering materials);
2. Data elucidating the sputtering process in compound materials and data on sputtering thresholds;
3. Formation of compounds with high-dose ion beams;
4. Formation of near-surface diffusion barriers;
5. Data on diffusion, segregation, and embrittlement.

Classes of surfaces that need to be better understood are: supported metal catalysts, engineering surfaces (e.g., fusion, first walls, corrosion processes), and semiconductor interfaces and junctions. There is also a need to develop new technologies to control existing technologies, and to develop higher resolution surface barrier detectors and long lasting electron detectors. The ion surface analysis tools listed in Table 2 are particularly useful for process characterization, but need to be refined and improved to meet future needs.

Theoretical research is needed in:

1. Monte Carlo theory (ion beams interaction with surfaces);
2. statistical chemical theory;
3. an improved data base on which to base theory;
4. sputtering theory including impurities and surface morphology.

The instrumentation and experimental techniques needed for surface characterization are: (1) ion beam technology coupled to electron spectroscopies, and (2) techniques to examine the surface/liquid interface.

F. Grain, Phase Boundaries and Interfacial Boundaries

A primary concern in the field of energy technology is the stability of materials under service conditions. Failure of materials commonly involves loss of cohesion or adhesion at interfaces as a consequence of embrittlement or corrosive processes. Such phenomena can involve either internal reactions which alter interfacial structure and/or composition or reactions with the external environment. In order to predict and control these phenomena, a basic understanding of interfacial structure, composition, and reactions is required.

Important problem areas to consider here are:

- Embrittlement of crystalline materials, such as steel, Ni-based alloy, refractory metals, noble metals, and ceramic materials.
- Effects of aggressive environments (e.g., H_2 , H_2S , liquid metals, aqueous solutions) on materials.
- Adhesion of joints and coatings.
- Control of microstructure by surface-related phenomena (e.g., texture formation in Si steels for transformer applications).

The underlying scientific problem areas include:

- The understanding of the interface structure: crystallography, composition, defect structure, phase relationships, and dynamic behavior (diffusion in various potential gradients, and chemical reactions).
- Measurement of interface strength to determine fundamental quantities amenable to theoretical analysis: normal strength and shear strength of grain boundaries and other interfaces, i.e., bonded joints, coatings, etc.
- Factors that control strength of interfaces: structure-atomic arrangement; and composition-atomic species.

- Factors that control solute segregation to interfaces: thermodynamic, kinetic, and atomic structure of interfaces.

Areas of surface science which need to be extended or developed are listed below in order of priority.

1. Experimental and theoretical studies of correlations between free surfaces and grain boundaries with respect to segregation, diffusion, structure, and phase equilibrium (2-dimensional)
2. Determination of grain boundary and interface structure, atomic arrangements, defect structure: develop diffraction techniques to probe grain boundary structure (i.e., LEED, RHEED); examine other non-diffraction techniques for this purpose (e.g., FIM); improve spatial and depth resolution of electron spectroscopy; develop the technique of combined high resolution electron microscopy (e.g., lattice imaging) and electron spectroscopies (Auger, energy loss, etc.).
3. Determination of grain boundary composition: atomic species, bonding, (i.e., what atoms are present and how are they associated), and particularly the development of quantitative AES, which consists of research on calibration of AES for quantitative chemical analysis; theory of Auger emission effects of atomic environment, line shape analysis, and angular resolved AES; theory and technique of depth profiling of chemical composition.
4. Development of surface techniques for measuring thermodynamic activities in solid solutions (e.g., effects of solute interactions in alloy steels); thermodynamic and kinetic modeling of interfaces and interface reactions, including 2-dimensional phase equilibria, to predict segregation behavior in multicomponent systems.
5. Development of theoretical modeling techniques to understand the physics of cohesion and adhesion. For example, how are charge transfer/atomic volume effects handled in developing a theory of intergranular cohesion as a function of composition?
6. Studies on grain boundary reactions, including development of techniques for directly studying surface reactions and relating them to grain boundaries; determination of relevant impurities in specific alloy systems involved in environment/grain boundary interactions; and determination of the mechanisms of these interactions.

TOPIC 2. SURFACE SCIENCE DIRECTIONS AND GOALS

A. Catalysis and Chemisorption

The highest priority research areas to be supported in the future, and the organizing of surface science research so that it has maximum impact on energy technologies have previously been discussed under Topic 1. Suggestions are offered now for a related consideration - the optimization of information flow, by (1) sponsoring international and national meetings and workshops of a topical nature; (2) encouraging a fellowship program for industrial-national laboratory-university exchange.

Close cooperation between national laboratories and industry is beneficial. A major obstacle to this is the proprietary nature of the catalyst industry. Perhaps catalysts could be used with an agreement not to analyze catalyst composition.

Excellent work in catalysis and chemisorption is being done outside the U.S. at the German surface physics and chemistry "putsch" in Jülich, Munich, Garching. It should also be noted that major catalysis institutes in France (Lyon), Japan (Hokkaido), and Russia (Novosibirsk) represent national commitments to catalysis which the U.S. has not undertaken.

An ERDA-sponsored retraining fellowship program would be a good means of educating technical personnel for the various energy technologies, or retraining those already in energy technology for modern surface science.

B. Semiconductors, Thin Films, Solar Device Surfaces

The most significant area of future research involves the characterization of interfaces and grain boundaries. This characterization should include the structural, electrical, chemical, and metallurgical properties of the interface or grain surface. Furthermore, it should also include information on the effects of such an interface on the surrounding bulk. Metal-semiconductor and semiconductor-semiconductor interfaces should be added to the presently investigated metal-metal interfaces to enhance their relevance to the energy program.

A second research area concerns the determination of the atomic and electronic structures of surface and interface defects and the effects of these defects on mechanical properties.

Since many techniques of surface science have not been extensively compared with one another, it is recommended that multiple investigations of the same property be conducted with different techniques, and multiple types of measurements taken on the same sample. To date, correlations involving atomic structure have been weaker in this regard than correlations involving electronic structure.

Finally, particular attention should be paid to the quantification of the basic investigative and characterization techniques.

A surface science research group, if it is to be effective, must have a critical mass. Although this may be achieved by cooperation among people from different institutions, the group should include both theoretical and experimental capability and adequate experimental equipment. Second, it is desirable that the same institution should include a research group as well as a development activity in relevant energy technology. Such an interaction is likely to have a positive effect on both groups, and would also be an important way of optimizing the research-development-technology information flow. The research funding agency can improve this information flow further by holding suitably timed topical conferences to which personnel from the different functional groups are invited. Efforts to

stimulate cooperation between groups (rather than simple competition for research funding) should be sought.

The precise number of people constituting the critical mass in any given group is likely to vary with the specific activity of the group, but in general the co-existence of and the close interaction between experimentalists and theorists is beneficial and often necessary. In most areas, the minimum number may be three or four professionals if adequate technical and computational support is available. It is suggested that a minimum of four or five groups working on the same or similar problems in different geographical areas may be the number required to sustain interest, create competition, and establish the important system of checks and balances that is necessary for progress.

Major items concerning cooperation between national laboratories and industry involve work scheduling and specific goals. Basic research is the proper activity of a national laboratory, but areas of investigation should be selected and supported on the basis of a long-term technology strategy. National laboratories should be part of the planning cycles leading to these technology strategies, and might pay specific attention to the following:

1. Time phasing of industrial technology needs should be emphasized.
2. Technology development should be followed from initial concepts, through proof of concept and reduction to practice.
3. Laboratories might serve as effective technology demonstration sites to illustrate utility and reliability.
4. Laboratories might also serve as test sites for system study efforts.

There are few areas outside the U.S. where better work has been done in the area of surface science. One area is that of high-resolution electron energy loss spectroscopy done in Germany, although this work leans heavily on original work done at NBS in the U.S. Possibly the training of researchers in electron microscopy (SEM, TEM) is stronger outside the U.S., particularly in England. Equivalent work on photoemission has been done in Germany, on field or photoemission of polarized electrons in Switzerland, and on ISS in Germany.

The task of educating or retraining technical personnel can range from developing awareness to developing skills. At one extreme, short courses, workshops, and carefully distributed applications reports can do much to promote the role and effect of surface science on the energy technology community. The development of surface science technical skills is an entirely different problem and will probably require an extended association (6 months to 2 years) of an individual with a functioning surface science laboratory. Programs similar to the American Vacuum Society's program in vacuum technology might serve as models.

C. Electrodes, Electrocatalysis, and Photon-Assisted Surface Reactions

High-priority research areas are in:

1. Electrocatalysis

Hydrogen electrocatalysis (anodes and cathodes): Studies of mechanisms, rate constants, and transfer coefficients on various electrode surfaces for which data are not available; hydrogen electrosorption studies using electrochemical methods; relation of these quantities to electronic structure of catalyst, electrolyte composition; impurity effects (including CO, H₂S, NH₃); choice of surfaces for study to be guided by expected heats of H adsorption and volcano curve considerations; special emphasis on non-noble metal catalysts and acid electrolytes.

Oxygen electrocatalysis (cathodes and anodes): Parallel studies to those for hydrogen electrocatalysis; catalysts to be examined to include defect-transition

metal oxides, adsorbed transition metal ions, and stable complexes on carbon and graphite substrates; doped carbons and graphites, derivatized carbons and electronic conducting oxides; special emphasis on non-noble metal catalysts in acid and alkaline electrolytes.

2. Morphological changes in high-area electrocatalyst systems. Research to establish mechanism of sintering and restructuring of high-area electrocatalysts, particularly noble metals on carbons and graphites.

3. Dendrite and other morphological changes with metal electrodes (e.g., Zn in aqueous electrolytes, lithium in molten halides). Studies of electrocrystallization and electrodisolution as functions of potential, electrolyte, poisons, and temperature; studies of electronucleation, adatom and adion mobilities.

4. Wettability of electrode surfaces: surface energies and contact angles. Determination of the factors controlling interfacial energies and contact angles through measurements with various electrode materials in aqueous electrolytes and molten salts; effects of adsorption, chemical interactions.

Longer range surface science research in electrocatalysis consists of (a) theoretical studies in calculation of heats of adsorption, potential energy surfaces for charge and atom transfer, and rates for component steps; and (b) experimental studies on single crystal surfaces: electrochemical measurements of adsorption isotherms, heats of adsorption and rates for hydrogen and oxygen electrode reactions on noble metal single-crystal surfaces including high-index surfaces; LEED, Auger-ESCA characterization of surfaces with special transfer techniques; comparison of electrochemical measurements with counterpart measurements at gas-solid interfaces.

To expedite information flow annual workshops with representation from the relevant scientific disciplines and the potential users are recommended. Such workshops should be integrated into the grant-reporting structure so that grantees as well as government researchers are expected to attend and report on their research results.

There is no critical mass of research groups in the theoretical area in electrochemical surface science in the U. S. In the experimental area, the critical mass in fundamental science is at best marginal, and probably below critical mass, particularly with respect to electrochemists with a strong surface chemistry-physics background. This area warrants at least six to eight academic groups focusing on electrocatalysis; the present number is much smaller (3 or 4). The critical mass in applied research is principally in industrial laboratories where proprietary interests interfere with their close cooperation with national laboratories.

One way to promote cooperation between national laboratories and industry is to give the national laboratory access to the proprietary information with the condition that it be treated as classified. Such an arrangement does not help information flow with the academic community, however.

The principal international center for basic research in electrochemistry including electrocatalysis is the Institute of Electrochemistry of the Soviet Academy of Sciences in Moscow, with approximately 450 scientists. In addition, the Karpov Institute of Physical Chemistry and the Soviet Academy's Institute of Physical Chemistry have several hundred electrochemists engaged in basic research in electrochemistry with a heavy emphasis on passivation phenomena and corrosion.

Other world centers of fundamental research in electrochemistry surface science which surpass any single group in the U. S. include the electrochemistry group in the Institutes of General and Inorganic Chemistry in Kiev (Ukrainian Academy of Sciences); the Fritz-Haber Institute of the Max Planck Society in West Berlin;

the CNRS and University research groups in Paris and Bellevue, France; the electrochemistry group at the University of Southampton under Professor M. Fleischmann and G. T. Hills. There is also substantial research in electrochemical surface science in Japan, Czechoslovakia (Institute of General Chemistry, Prague), Yugoslavia (Belgrade, Skopje, Zagreb), Italy (Milan), Bulgaria (Sofia), and Canada (Ottawa).

To educate and/or retrain technical personnel in modern surface science, two proposals are made: the academic community benefits greatly from sabbatical leaves which help a faculty member to catch up with studies in his own field and to enter new research areas. Industrial and government scientists should be allowed sabbatical leaves taken in academic or other laboratories where they have an opportunity to study and gain experience and relevant techniques in modern surface science; the second proposal is to hold small workshops where surface scientists have an opportunity to summarize new developments and where technologists can communicate their particular problems. This is a good way to close the feedback loop between fundamental research and technological development work.

D. Corrosion

The highest priority for corrosion research in surface science involves three considerations: a model system, specific environments and specific substrates.

The model system is a solid surface in a molecular environment which may be either gas or liquid. It should be considered at three stages: adsorption at specific sites, lateral spreading of the first layer, and growth of multiple layers. The interaction of the substrate should be considered since its structure may change in the process of interaction, e.g., the substrate may become ordered.

Specific substrates should be considered for the following:

1. metallic substrates should emphasize iron and iron base alloys;
2. ceramic materials used as containers for high-temperature processes, e.g., Al_2O_3 ; ceramic materials used for turbine blades, e.g., SiN-SiC ;
3. glasses as used for container materials; and
4. polymeric solids used as structural materials.

Gaseous and aqueous environments should be studied, where dissolved species are mainly hydrogen, sulfur, and oxygen with a secondary emphasis on chlorine, nitrogen, and carbon.

Currently surface science research efforts directly related to corrosion problems largely do not exist. Efforts to encourage institutions and research groups to work on corrosion problems and develop equipment to perform multi-evaluations/measurements on reacting surface interfaces would appear to be valuable pursuits. A call from users/technologists for handbook type data compilations for the research community might provide valuable resource documentation as well as promote professional interactions.

The reduction of obstacles to cooperation and information flow between national laboratories and industrial firms depends upon development of appropriate incentives on both sides. Similarly, stronger interactions between and within the various ERDA divisions would provide needed research and development technology information flow.

Areas of surface work relevant to corrosion being carried on outside the U.S. are the following: 1) energy loss spectroscopy in Germany; 2) high-voltage and high-resolution electron microscopy in Germany, England, and Japan; 3) electrochemical kinetic studies of film-free alloys in the USSR; 4) organic inhibitors in the USSR; 5) molten salt electrochemistry in the USSR and Germany.

E. Interaction of Ions with Surface and Near-Surface Regions

Ion beam analysis, simulation of radiation damage, and modification of materials can have a major impact in the energy field. The rank order of the highest priority research areas is:

1. Low-energy ion interactions with surfaces, including charge states, charge exchange excitation, photon emission, and sputtering yields.
2. Surface and near-surface modification using ion beams (composition, topology, microstructure) including: diffusion and solubility measurements (surface, near-surface, and grain boundary), measurement of equilibrium or steady state phase diagrams, and production of new materials and metastable phases, and solubility and segregation under high flux and fluence conditions.
3. Corrosion, oxidation, and passivation by use of ion beams.

Our recommendations for optimizing information flow cover two areas. First, information transfer should occur on the working level. This can be effected by funding the travel and experimental equipment of applied scientists to work at laboratories and universities struggling with basic problems. Also, consulting funds could be provided for basic scientists to work at applied labs. Second, joint science-technology surface conferences (e.g., on corrosion and catalysis) should be established.

Surface analysis experimentation is capital intensive especially when coupled with ion beams. At present only a few labs have critical mass capacity. Therefore interaction between labs is necessary for rapid and efficient progress.

Some lack of motivation to interact exists because of industrial proprietary restrictions. Also, basic researchers in universities need to know real problems to guide their research. Perhaps some of these obstacles could be removed by organizing joint science-technology conferences in special surface science areas. Basic groups must be encouraged to support basic labs and universities.

Areas of foreign superiority are listed below.

1. Great Britain: surface modification for corrosion research.
2. Germany: ion scattering and surface analysis for first wall problems.
3. Denmark: atomic collisions theory.
4. USSR: ion scattering and sputtering.
5. Japan: ion implantation for large-scale semiconductor manufacture.

Exchange programs with laboratories and universities would retrain technical personnel working in various energy technologies. We note that the Europeans and Japanese are using this method to educate and retrain their people effectively.

F. Grain, Phase Boundaries and Interfacial Boundaries

Recommendations for surface science directions and goals are listed below.

- Support the development of specific equipment such as the LEED diffractometer and equipment for high spatial resolution electron diffraction and spectroscopy.
- Provide more realistic funding for acquisition and operation of advanced capital equipment.
- Recognize the primary role of individual interactions to accomplish research-development-technology information transfer. Hence, programs should be developed which encourage scientists from different disciplines to work together, to meet periodically in small groups, and to develop interpreters who can work at the interfaces between disciplines. Specifically, ERDA should encourage interdisciplinary pairs or small groups, small technical meetings or focused topics involving people from different disciplines, designation of individuals in the

larger laboratories to be responsible for promoting interaction between various groups, attendance at technical meetings by active research and development personnel

- Provide funding for scientists to travel to and reside at national facilities so that these resources can be more effectively utilized.

MATERIALS SCIENCES WORKSHOP ON

X-RAY, NEUTRON, AND ELECTRON SCATTERING

Held April 13 to 15, 1977 at Oak Ridge National Laboratory

Organizers

M. K. Wilkinson, Oak Ridge National Laboratory
 A. Bienenstock, Stanford University
 M. Blume, Brookhaven National Laboratory
 W. L. Clinton, ERDA, Division of Physical Research
 J. J. Rush/J. M. Rowe, National Bureau of Standards

Participants

S. C. Abrahams, Bell Laboratories	B. Morosin, Sandia, Alb.
B. W. Batterman, Cornell University	A. H. Narten, Oak Ridge Nat'l Lab.
A. Bienenstock, Stanford University	L. Passell, Brookhaven Nat'l Lab.
E. Bloom, EPRI	S. W. Peterson, Argonne Nat'l Lab.
M. Blume, Brookhaven Nat'l Lab.	E. Prince, Nat'l Bureau of Standards
G. S. Cargill III, IBM Research	A. Rahman, Argonne Nat'l Lab.
R. S. Claassen, Sandia, Alb.	D. H. Reneker, Nat'l Bureau of Standards
W. L. Clinton, ERDA, Physical Research	J. J. Rhyne, Nat'l Bureau of Standards
J. M. Cowley, Arizona State Univ.	J. M. Rowe, Nat'l Bureau of Standards
R. G. Donnelly, Oak Ridge Nat'l Lab.	J. J. Rush, Nat'l Bureau of Standards
P. Eisenberger, Bell Laboratories	S. Schnatterly, Princeton University
R. Gronsky, Lawrence Berkeley Lab.	J. L. Scott, Oak Ridge Nat'l Lab.
J. M. Hastings, Brookhaven Nat'l Lab.	S. M. Shapiro, Brookhaven Nat'l Lab.
R. W. Hendricks, Oak Ridge Nat'l Lab.	C. G. Shull, MIT
H. Herman, SUNY Stony Brook	J. Silcox, Cornell University
J. Kasper, GE R&D Laboratories	S. K. Sinha, Argonne Nat'l Lab.
J. Khan, Lawrence Livermore Lab.	C. Stassis, Ames Laboratory
J. S. King, Univ. of Michigan	D. K. Stevens, ERDA, Physical Research
T. A. Kitchens, Los Alamos Sci. Lab.	R. P. Stromberg, Sandia, Alb.
G. H. Lander, Argonne Nat'l Lab.	J. W. Tester, Los Alamos Sci. Lab.
U. Landman, Univ. of Rochester	J. Wachtman, Nat'l Bureau of Standards
F. W. Lytle, Boeing Aerospace Co.	S. A. Werner, Univ. of Missouri
J. P. McTague, UCLA	M. K. Wilkinson, Oak Ridge Nat'l Lab.
H. A. Mook, Oak Ridge Nat'l Lab.	H. L. Yakel, Oak Ridge Nat'l Lab.
R. M. Moon, Oak Ridge Nat'l Lab.	

I. SCOPE

The ERDA Workshop on X-ray, Neutron, and Electron Scattering was attended by leading scientists in the United States with special expertise in the three scattering techniques and related theory and by authoritative scientists and engineers closely associated with energy technologies. In selecting participants, the Organizing Committee took special care to ensure that the desired objectivity of the Workshop would be achieved. All aspects of the various scattering techniques were represented, and the participants came from a wide variety of industrial, academic, and government laboratories. About half of them represented organizations that were not affiliated with ERDA.

The first day of the Workshop was devoted to overviews of energy technologies and to general discussions concerning them. Overviews were given on Energy Storage (R. S. Claassen), Energy Conservation (R. G. Donnelly), Fossil Energy (J. Wachtman), Geothermal Energy (J. W. Tester), Solar Energy (R. P. Stromberg), Fission Energy (E. Bloom), and Fusion Energy (J. L. Scott). The speakers emphasized some of the specific energy-related materials problems and helped to identify the basic research necessary to solve such problems. Scientific overviews were given on the second morning, and because of the tight Workshop schedule, only very recent developments in the three fields of scattering were discussed. Overviews were presented on Electron Scattering (J. M. Cowley), X-ray Scattering with Synchrotron Radiation (P. Eisenberger), and Small-Angle X-ray and Neutron Scattering (H. Herman). The last half of the Workshop was devoted to discussions within Study Groups and to plenary sessions for coordinating the Study Group recommendations.

Although this Workshop was organized on the basis of techniques, Study Groups were organized according to properties of materials to ensure that each Group would have a mixture of scientists with a variety of knowledge and experience. The five Study Groups were: (1) Crystalline Structures, (2) Non-Crystalline Structures and Surfaces, (3) Dynamical Properties of Materials, (4) Magnetic Properties of Materials, and (5) Defects, Inhomogeneities, and Polymers. Each Study Group was asked to determine the most important areas of research that should be pursued by ERDA, to specify those research areas that were particularly relevant to energy technologies, and to make recommendations for the development and utilization of special equipment. In their deliberations, the participants were mindful of the dual role of ERDA in materials science. Most obvious is ERDA's responsibility to support research that will help to solve problems associated with existing energy technologies. However, equally important is ERDA's responsibility to ensure that its unique facilities and scientific expertise are used for research that can lead to a better fundamental understanding of materials. Such research is necessary not only because it increases our knowledge of condensed matter, but because this knowledge is essential in developing capabilities for predicting the properties of materials which will be needed to solve future technological problems. It is difficult to conceive of research utilizing these scattering techniques which would not bear ultimately on the nation's energy problems.

The complete Study Group reports are given in Section III, and they constitute the major part of this report. Recommendations by the Workshop are discussed in Section II, which includes a list of priorities that were selected from the Study Group reports by members of the Organizing Committee.

II. WORKSHOP PRIORITIES

There was unanimous agreement among the participants that x-ray, neutron, and electron scattering investigations provide some of the most important information that can be obtained on condensed matter and that these investigations should be strongly supported by ERDA. Knowledge of the structural and dynamical properties of materials is a prerequisite to understanding the results of nearly all other research, and the scattering techniques must be fully exploited to obtain that knowledge. These investigations fall under the highest priority established by ERDA for materials science research; they include important national research that utilizes unique ERDA facilities, scientific areas with a high probability of new findings, and basic research critically important to energy technology.

All Study Groups strongly recommended that increased efforts be made to ensure the most effective utilization of unique national facilities by outside scientists as well as in-house staffs. The success of this user-oriented program would require stable central support by ERDA to operate the facilities instead of fragmentary support by users, so that reduction of individual programs would not jeopardize the operation of a facility. A modest amount of support would also be required to make the user mode of operation attractive and convenient for scientists from other institutions; a highly practical form of support would be travel and incidental expenses provided by the facility. Since this Workshop dealt specifically with techniques, many recommendations were made for the support of new facilities and equipment. However, no consideration was given to specific types of new sources, because National Academy of Sciences panels have examined or are examining the need for such sources. There were strong recommendations for state-of-the-art equipment for all techniques; such equipment is essential if the investigations are to remain at the forefront of research throughout the world. The Study Groups also recommended a wide variety of important problems for almost every conceivable class of materials. Three research areas of particular significance are materials under extreme environments, non-crystalline materials, and polymers, because relatively few scattering investigations have been performed in these areas.

This Workshop was the only one in the ERDA Workshop Program that was based on techniques, and these techniques are utilized in research areas covered by all other workshops. The high priority recommendations from every workshop for scattering research indicate the strong impact that this research will have on the solution of materials problems in existing energy technologies. In many research areas, the probability for this impact is apparent, such as hydrogen diffusion and bonding studies which could lead to better materials for safe hydrogen storage and transport, investigations of fast-ion conductivity which could help to develop better batteries and fuel cells, and experiments on fluxoid pinning which could produce better high-field superconducting magnets. Many more examples are given in the Study Group reports. However, such examples should not obscure the fact that the central effort of these techniques is concerned with the important role of ERDA to provide a better understanding of materials through long-term research. Scattering investigations have been the key experiments in deducing and testing our present concepts of condensed matter, and these concepts have provided the basis for developing new classes of materials with special properties. An important example is the contribution of neutron scattering to understanding magnetic interactions in rare earth metals and alloys, which has led to new high field permanent

magnets that significantly increase the efficiency of electrical devices. Future energy technologies will undoubtedly require new classes of materials with properties that are not yet defined, and ERDA must support critical basic research that will be the foundation of those technologies.

There are so many exciting areas of research utilizing x-ray, neutron, and electron scattering that it is essentially impossible to assign priorities that would be completely acceptable to all participants. Every Study Group report lists a number of recommendations, and these reports should be read in full. All items mentioned were recommended for some level of funding; those areas and applications of marginal scientific merit were not even discussed. Members of the Organizing Committee have culled a list of priorities from the Study Group reports, which are concerned with the development and utilization of equipment. No areas of materials are listed, because the types of materials to be investigated will be strongly influenced by high priority recommendations of the other workshops. The following priorities summarize steps that are necessary to ensure creative utilization of ERDA facilities in helping to solve materials problems in both present and future technologies:

- There should be continued strong support for high quality basic research with x-ray, neutron, and electron scattering techniques. Special emphasis should be given to the support of research at major ERDA facilities, including the dedicated synchrotron radiation facilities that will be available within a few years. Microscopic information obtained with these unique facilities is essential in understanding the physical properties of materials; it is a prerequisite for other research.
- Increased support should be provided for more effective user-oriented programs of research. Such programs would require stable central support of major unique state-of-the-art ERDA facilities and special funds to make these facilities attractive and convenient for outside users.
- The ERDA effort in electron microscopy should be expanded. Support should be given to state-of-the-art atomic resolution instruments and to high performance scanning transmission electron microscopes with energy analysis.
- Apparatus for studying materials in extreme environments should be developed. Scattering experiments with specimens at high temperatures, pressures, and magnetic fields are necessary to provide better engineering materials.
- Facilities and equipment should be provided for the production and use of epithermal neutrons ($E > 200$ meV). These facilities would be important for studies of amorphous materials, itinerant magnetism and electronic excitations.
- Neutron and x-ray small-angle scattering facilities should be developed for many types of studies (polymers, superconductors, voids, precipitates). Special attention should be given to the development of area detectors.
- Increased support should be provided for programs in crystal growth and materials characterization.
- Techniques for EXAFS measurements should be developed for applications to surfaces and low Z elements.
- There should be expanded support for theoretical investigations that couple closely to the ERDA experimental programs.
- A renewed effort should be made to obtain better monochromating and analyzing crystals for conventional neutron scattering research and for research using neutron spin polarization analysis.
- Ultra-high resolution spectrometers should be developed for energy analysis of x-ray and neutron scattering.
- An improved data base for research materials should be provided which includes both experimental measurements and critical evaluations.

III. STUDY GROUP REPORTS

A. CRYSTALLINE STRUCTURES

*S. C. Abrahams, Chairman; J. M. Cowley; J. S. Kasper;
B. Morosin; S. W. Peterson; E. Prince; H. L. Yakel*

1. INTRODUCTION

Knowledge of the crystalline structure of a given material is prerequisite to nearly all further fundamental studies. Contemporary crystallography is already using the new high flux x-ray and neutron sources and high resolution electron microscopes to make important advances, and these will be accelerated as new national facilities become established. These facilities will be of maximum national value only if use by qualified scientists from across the country is encouraged. A highly practical form of encouragement would be support of travel and incidental costs, provided by the facilities, without the necessity for each scientist to raise this by individual grant proposals.

The impact that crystallographers have on materials and physical research would be heightened if they initiated new materials synthesis and crystal growth programs, rather than depend only on those crystals that happen to become available. The rate of growth of fundamental and applied information could increase rapidly with synthesis and growth of new crystalline materials likely to be of physical interest on the basis of past crystallographic studies. An example would be the formation of highly oriented or single crystal polymers or elastomers for mechanical energy storage applications.

Crystallographic information has been produced so rapidly in the last decade that improved methods of retrieval and correlation have become necessary. In the case of organic, metal-organic and protein crystals, crystallographic data is being developed on a machine readable data base, but the only comparable base for inorganic and metal alloy crystal structures is *Crystal Data*. A data base is necessary that includes not only atomic coordinates, etc. but also physical and mechanical properties--perhaps also chemical. This would enable retrieval of all materials known, for example, with correct sized channels for Li^+ transport, or with interatomic spacings for epitaxial overgrowths.

The Crystalline Structures group has made a careful selection of topics in techniques and materials studies that are considered to lie at the cutting edge of crystallographic research and that also are likely to have a beneficial impact on ERDA's goals. Each topic is of considerable importance and should be supported at some level. Ratings have been made of each and are given in Section 4.

2. MATERIALS OF SPECIAL INTEREST

This section contains materials oriented areas in which crystallographic research is expected to yield particularly fruitful results.

- (a) Development of new alloys and superalloys with improved physical and mechanical properties can answer materials problems that now

severely limit energy producing and converting devices such as fusion reactors or coal gasifiers. Basic relationships between the desired properties and the crystalline structures of these superalloys will be derived from detailed diffraction studies of both average lattice arrangements and fluctuations from the average. Tailoring of new alloys for specific uses will follow from coupling such structural results with a knowledge of likely defect configurations (dislocations, grain boundaries, etc.). Where elements of the alloy have only slightly differing scattering cross sections, it will be imperative that the experiments be performed with radiations that maximize those differences--e.g., neutrons, or x-rays at synchrotron radiation sources.

(b) Superionic conductors have already found use in the energy program mainly in battery applications but they have potential use in fuel cells and as ion-transporting media. They also present several interesting scientific challenges as to mechanisms of conduction. The most definitive information has come from structure studies combining conventional single crystal structure determination with quasi-elastic neutron scattering studies. Superionic conductors offer great opportunities for both scientific and practical advances, for example, β -alumina and AgI.

(c) Catalysis is a field of great importance to the national economy in which the impact of full application of a wide array of structural tools, including diffraction very prominently, is just beginning to be strongly felt. The chemistry of metal-cluster compounds is reaching the stage where they can be designed to simulate, structurally and chemically, various so-called active configurations or sites of heterogeneous catalysts. The basic structural tool essential in these studies is diffraction (x-ray, neutron, or electron). The new advances resulting in both homogeneous and heterogeneous catalysts are due to elegant collaborative studies involving both structural and catalytic science. In a related area of organometallic hydrides, neutron and x-ray diffraction structural studies are providing new leads to the mechanisms of hydrogen abstraction, the activation of the C-H bond of hydrocarbons, and catalytic decomposition of small hydrocarbons such as methane and ethylene. Another area of great future potential is that involving biocatalysts or enzymes to accomplish a wide range of chemical transformations of industrial importance. Diffraction methods promise the only effective tools for structural investigation of these biocatalysts and effective development of this potentially fruitful area requires active participation of the materials scientist.

(d) The ease with which small molecules and metallic atoms can be inserted into and modify the properties of layer type compounds in important ways offers a technological challenge. Molecules as diverse as NH_3 , HNO_3 , Br_2 , FeCl_3 , XeF_6 , ferrocene, etc. or atoms such as Na or K can often be easily introduced between the layers of graphite, TaS_2 , NbS_2 and other similar materials. Properties such as strength, electrical conductivity and superconducting transition temperature are often greatly modified. Very little is yet known of the structure-property relationships in this relatively new field. Diffraction techniques, including the use of the new profile refinement methods for polycrystalline patterns, are the

methods of choice for providing the structural information which is required to develop further this materials area.

(e) One-dimensional conductors have unique physical properties such as Peierl's and spin-Peierl's transitions and offer a splendid opportunity to check the refined theories that have been developed for the one-dimensional state. There also remain other interesting aspects concerning the physics of the one-dimensional conductor that need to be investigated. It is essential to have very well determined structural data for an understanding of the physical and chemical properties. Also, there remains some prospect of achieving unusually high conductivities with non-metallic systems such as, for example, TTF-TCNQ and TTF halides. Crystallographic studies are also necessary on materials with two-dimensional properties.

(f) Responses of crystalline materials to high fluences of damaging radiation will be crucial in determining their usefulness in fission or fusion reactor environments. Diffraction experiments, probably with radioactive specimens, will be required to characterize the phase transitions or modifications that may occur. These effects are special instances of phase transition phenomena--a field in which applications of new diffraction methods will give basic clues to mechanisms at the atomic scale. Dynamic experiments at high flux sources should be of unique value.

(g) Physical property changes taking place at phase transitions continue to be of considerable importance. A program for investigating the change in crystal structure, both far from and close to the transition temperature or pressure, should be undertaken with a view to relating these, often large, changes to the associated macroscopic property changes.

(h) It is desirable to study single crystals of superconductors at low temperatures and under applied stress to avoid the twinning commonly encountered with phase transitions in the region of the onset of superconductivity. It would be worthwhile to undertake accurate structural characterizations as a function of temperature with single crystals in order to ascertain small changes in lattice parameters and structural parameters and particularly to obtain electron densities in order to determine the changes in bonding effects.

(i) Hydrogen is an important candidate both as the future fuel for transportation and as the working fluid to be used in heat engines and refrigeration devices. Metal hydrides offer considerable promise as efficient storage devices for those applications. A wide range of metals and alloys needs to be examined in order to develop an ideal combination of hydrogen absorption kinetics, decomposition pressures and recyclability. These appear to be strongly structure dependent properties and extensive structural studies, particularly by neutron methods, are strongly indicated.

(j) A number of salt hydrates which have rather high heats of transition of hydration have been proposed for energy storage. The properties of these systems such as heats of transformation, transition temperatures, vapor pressure and chemical stability, which are important for energy

storage, are structure sensitive and related to the extensive hydrogen bonding. Thus, structure and phase studies, emphasizing neutron methods, should be of particular value in understanding the properties and behavior of model systems and in designing or selecting superior salt hydrates. The information gained concerning hydrogen bonding and water configuration in these systems is of general scientific interest.

(k) Ceramic materials (high temperature oxides, both insulators and semiconductors) which can be employed as coatings for exhaust flues, heat exchangers and, in particular, for conducting and separator elements in MHD generators should receive crystallographic study. The relationships of structure to stability and conductivity properties require continued elucidation. The effects of ionic and impurity transport might be better understood using the high magnification capabilities of newly developed electron microscopy techniques.

(l) Crystals undergoing changes of many orders of magnitude in conductivity as a function of temperature, especially from insulator to metallic, should be prepared and studied crystallographically (both with x-rays and with neutrons). The vanadium and titanium oxides have been extensively studied, but not many other materials. Similarly new piezoelectric, ferroelectric and ferroelastic crystals should be prepared and their structures studied as a function of temperature, stress or field.

(m) Structure studies (morphology, thermal expansivities, lattice matching) should be made to characterize potential photovoltaic materials, particularly long term electrical effects of nonstoichiometric compounds (e.g., Cu_{2-x}S on CdS or $\text{Cd}_x\text{Zn}_{1-x}\text{S}$), the growth of such crystalline films by chemical vapor spray pyrolysis techniques, amorphous to polycrystalline transitions in Si as well as other new photovoltaic materials.

3. CRYSTALLOGRAPHIC TECHNIQUES

Development of the following techniques is essential for the most successful application of crystallographic methods to understanding the properties of materials:

(a) The advent of electron microscopes having resolution for directly interpretable images in the range 1.5 to 2.0 Å, especially at high voltages (0.5 to 1 MeV), represents a major advance in the capabilities for research on the structure of materials. These microscopes allow the possibility of the direct visualization of the arrangements of atoms in both well ordered and disordered crystals and around crystal defects. They provide information on the atomic structures of crystal surfaces. The most immediate applications will be to the radiation resistant materials such as alloys, semiconductors and ionic conductors which are of relevance for energy research. The acquisition of at least one, and preferably more, such instruments in the country must be regarded as of high priority. Because these instruments are still in the developmental stage, adequate support facilities and staffing for instrumental research are essential.

(b) Structural research for many materials problems is being revolutionized by the introduction of high-flux sources including synchrotron radiation sources of x-rays, pulsed neutron sources and field-emission guns for electron microscopes. While the availability of these sources is of great importance, it is equally important that funds be made available for adequate associated instrumentation necessary to allow them to be used efficiently and effectively. For all three radiations, area-sensitive detectors capable of operation at high count-rates and attendant data-handling devices are required for the data collection. For x-rays and neutrons a variety of monochromators and spectrometers are required and neutron polarizers are of increasing importance. Special requirements for high vacuum, high pressure or high temperature specimen environments often arise in materials research.

(c) In all of the presentations on the various energy technologies it was very evident that there was an enormous need to develop techniques for studying the structure of materials under extreme environmental conditions--high temperature and/or pressure, extreme stress conditions, etc. (such as those to which minerals ~ 5 km below the earth's surface are exposed)--in order to determine the conditions of phase equilibria, the factors controlling compressive strengths, and the modes of failure under these conditions. For studies under these conditions the use of energy dispersive techniques, as described in Section 3(d), will be very important. The design of temperature/pressure sample cells is much easier if there is only a single scattering angle and therefore only two small windows, one for the incident beam and one for the scattered beam.

(d) There is a need for development of energy dispersive diffraction techniques, particularly in connection with studies of materials under extreme conditions of temperature and pressure. For neutrons, time-of-flight (TOF) methods are the obvious ones to use in connection with pulsed sources, but even with steady state reactors conventional TOF techniques using choppers are appropriate in some applications. The resolution of solid-state x-ray detectors, especially at low x-ray energies, may need some improvement while the necessary sources of white radiation and data handling instrumentation must be developed.

(e) The advent of more and more complex (and expensive) research tools has resulted in a great need for development of new computational methodology. This includes studies of the optimum data collection strategies for use with one and two dimensional position-sensitive detectors, as well as analytical tools such as data fitting and graphical display of results. An example is profile analysis, which involves the detailed fitting of a powder diffraction pattern to a model. In many cases this is the only method available for obtaining structural information about important materials that are not readily prepared as single crystals.

(f) In association with the new techniques of scanning transmission electron microscopy, the use of field emission guns of high brightness has allowed chemical analysis of specimen areas of around $100 \text{ \AA}$ diameter by both x-ray microprobe analysis and energy loss spectroscopy. The extension to even smaller specimen regions appears possible. Also,

electron diffraction patterns can be obtained from specimen regions 20 Å in diameter or less (a few hundred atoms). This represents an important extension of previous capabilities, with obvious application to many significant areas of energy related research such as, for example, the identification of microconstituents of fossil fuels or of alloys and the determination of the structure of aggregates of foreign atoms on grain boundaries.

(g) The very high brightness of synchrotrons and fluxes of pulsed neutron sources should be exploited on structure studies involving time-dependent phenomena. These include temperature dependent systems (phase-changes, thermal expansion mechanisms, annealing), chemical changes in nonstoichiometric and clathrate compounds, crystallization (glass-ceramic) and solid state polymerization phenomena to mention a few examples. Coupled with environmental control techniques mentioned elsewhere, structural and compositional phase equilibria in high temperature materials (ceramics, MHD oxides, metal-metal hydride equilibria) can rapidly be determined. Such pulsed sources may also be employed in transient phenomena (electrical or optical pulsing).

(h) High flux sources should be exploited for more quantitative diffuse elastic scattering studies on lower dimensional systems. Quantitative information on correlation effects in solids prior to the onset of phase transitions deserves special attention. Neutron sources should be useful in percolation studies on hydrides, helium in metals (and alloys) as well as in other solid-solid alloy transitions.

(i) Fundamental understanding of the properties of materials and the stabilities of their structures ultimately rests on complete descriptions of bonding electron distributions. Combined x-ray and neutron diffraction techniques that uncover these distributions in light element compounds have been developed but must be expanded and improved if possible. This work will complement efforts to predict crystalline structures through modeling calculations based on known potential functions of atoms and atom groups.

(j) Structure studies of the alloys used in such extreme environments as the blades of gas turbines would benefit greatly from the ability of neutrons to penetrate the bulk material, facilitating studies of preferred orientation, grain size, and phase homogeneities in these materials. Actual components can be examined nondestructively before and after exposure to real conditions of use.

4. DETAILED SCIENTIFIC PRIORITIES

The activities described in Sections 2 and 3 have been placed in three priority groups, within each Section. This priority was determined primarily on the basis of fundamental scientific interest, modified by the possibilities of useful impact on ERDA's goals. Within a priority group, each activity is equally important. Only activities regarded as valuable have been presented, with marginal activities omitted from this report.

Materials of Special InterestHighest Priority (#1)

- (a) Alloys and superalloys
- (b) Superionics
- (c) Biological, organometallic, metal cluster and inorganic catalysts

Priority (#2)

- (d) Intercalation compounds
- (e) One- and two-dimensional property materials
- (f) Radiation effects on phase diagrams
- (g) Phase-transitions: structure-property

Lowest Priority (#3)

- (h) Superconductor crystallography
- (i) Storage hydrides
- (j) Storage hydrates
- (k) MHD ceramics
- (l) Dielectrics
- (m) Photovoltaics

Crystallographic TechniquesHighest Priority (#1)

- (a) Atomic resolution electron microscopy
- (b) Instrumentation for high flux sources
- (c) Structural studies under extreme conditions
- (d) Energy dispersive x-ray and neutron scattering

Priority (#2)

- (e) Development of computational methodologies
- (f) Picoprobe analysis and diffraction
- (g) Time dependent high flux experiments

Lowest Priority (#3)

- (h) Diffuse scattering with high fluxes from single crystals
- (i) Bonding electron studies
- (j) Texture studies in bulk materials

5. CONCLUSIONS AND RECOMMENDATIONS

Three areas of materials research and four areas of technique development have been identified as having highest priority for scattering research on crystal-line structures. Additional areas of considerable importance have also been discussed (Sections 2 and 3). It is recommended that all identified areas receive support. General recommendations, outlined in Section 1, are to take steps to maximize use of new national facilities for scattering research, to upgrade materials synthesis and crystal growth skills, and to develop a comprehensive machine-readable data base of crystallographic and associated physical and chemical data.

B. NON-CRYSTALLINE STRUCTURES AND SURFACES

*G. S. Cargill III, Chairman; P. Eisenberger; J. Khan;
U. Landman; A. H. Narten; L. Passell; A. Rahman*

1. INTRODUCTION

An important frontier in basic materials science research is concerned with liquids, with non-crystalline (amorphous) solids, and with surfaces. These systems present new challenges to the materials scientist in that both the structural and dynamical behaviors are more complex and are more difficult to evaluate than those for the perfectly periodic crystalline systems with which so much of our basic research has been concerned over the past decades. Improved structural characterization of liquids, of amorphous solids, and of surfaces is a challenging and important first step in extending basic understanding of these materials and in developing methods for predicting their properties in environments of technological importance. Considerable progress is being made in structural characterizations of these systems using well established x-ray, neutron, and electron scattering techniques, and the continued usefulness of these will be enhanced by availability of more intense and better instrumented scattering facilities. More recently developed and developing techniques of extended x-ray absorption fine structure (EXAFS) measurements and interpretation in terms of local atomic arrangements should provide further information on atomic scale structure of these classes of materials. Continued technological development of structural research capabilities for liquids, amorphous solids, and surfaces will be an important component in improving basic understanding and technological utilization of these materials.

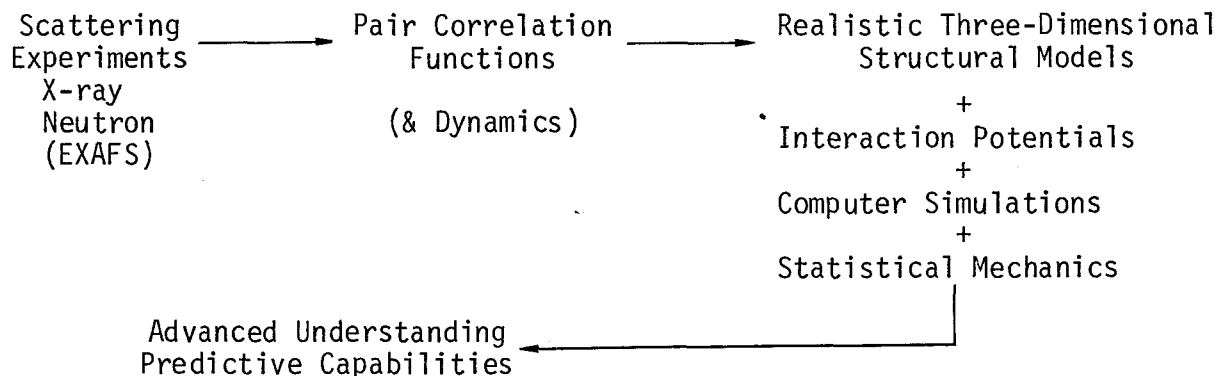
In this report we emphasize the importance and accessibility of structural information for liquids, non-crystalline solids, and surfaces. The need for further development of liquid state theories is accentuated by present and anticipated future needs to predict properties of both simple and complex liquids in extremes of temperature, pressure, and radiation exposure, environments which severely limit possibilities of direct physical measurements. Resurgence of interest in non-crystalline solids is largely due to discoveries of several new classes of such solids during the last decade, e.g., amorphous metallic alloys and various types of amorphous semiconductors, and to increasing recognition of possible technological applications for these solids. Studies of surface structure, using well characterized clean or over-layer surfaces, are widely pursued and provide the background for microscopic investigations of surface catalytic reactions and surface diffusion. Improved understanding of catalytic processes at surfaces is a particularly strong motivation for studies both of single crystal surfaces and of non-uniform catalytic surfaces.

Discussions and rankings of research priorities in this report are divided according to subject areas: (1) liquids, (2) non-crystalline solids, and (3) surfaces. A separate section of the report contains discussions of major facility improvements for research on non-crystalline structures and surfaces. In these research areas there was a common feeling that national laboratory facilities, i.e., neutron and x-ray sources, must be made more attractive and convenient for use by visiting researchers. Common to surfaces and non-crystalline solids research areas were questions about mechanisms for proprietary research at national facilities; the lack of such mechanisms limits the

usefulness of national laboratory facilities for some researchers in U. S. industrial R & D laboratories. Common to the three research areas discussed by this study group was the view that research progress is being hampered by continuing decreases of support for relevant theoretical work.

2. LIQUIDS

Scattering measurements on liquids are an important component in further development of a fundamental theory of liquids; the role of scattering measurements in this development is indicated by the following diagram:



We believe that basic studies of multicomponent liquids should be particularly encouraged. Examples of liquid systems which should be studied, in order of their apparent scientific and technological importance, are listed below:

- (a) Molten salts--possible importance in both coal gasification technology and fusion technology
- (b) Liquid metal alloys--energy storage (battery) technology
- (c) Superionic conductors ("lattice liquids")--energy storage (battery) technology
- (d) Diffusion of hydrogen in liquid metals--fusion technology
- (e) Aqueous solutions of inorganic salts, dependence of structure and dynamics on concentration, homogeneous and heterogeneous nucleation of precipitation--geothermal energy technology
- (f) Liquids consisting of simple polyatomic molecules
- (g) Rare gas liquids

Scattering studies of such liquids should be closely coupled with computer simulation experiments and statistical mechanical analysis. Extended x-ray absorption fine structure experiments were included in the above diagram, although the usefulness of such measurements in liquid structure research has not yet been demonstrated. Determinations of partial distribution (pair correlation) functions for binary liquid systems should be pursued by neutron scattering with isotopic substitution (when appropriate isotopes are available) in combination with x-ray scattering, and also by x-ray scattering, using selected wavelengths from synchrotron radiation to modify atomic scattering factors via anomalous dispersion. Neither of these methods for determining partial distribution functions has been widely applied, although this type of experimental data is essential to further progress in understanding multicomponent liquids.

3. NON-CRYSTALLINE SOLIDS

Scattering measurements on non-crystalline solids are the most direct available probe of atomic scale structure for these solids. A diagram similar to that included in the preceding section on liquids could be drawn to illustrate the contribution of scattering measurements to advanced understanding of amorphous solids: such scattering measurements provide guidance in construction or generation of realistic three-dimensional structural models for non-crystalline solids, and the scattering measurements provide critical tests for such models. Several applications of x-ray, neutron, and electron scattering to structural problems of non-crystalline solids are listed below, in order of their apparent scientific and technological importance:

(a) Scattering experiments for single component non-crystalline solids should be extended to polyatomic systems, to determine partial distribution functions using isotopic substitution in neutron scattering (when appropriate isotopes are available) in combination with x-ray scattering. The practicality and accuracy of obtaining partial distribution functions by x-ray scattering, using selected wavelengths from synchrotron radiation to modify atomic scattering factors via anomalous dispersion, should also be evaluated. Such scattering measurements should be closely coupled with efforts to construct or generate realistic three-dimensional structural models for non-crystalline solids. We particularly recommend support of structural studies of polyatomic metallic alloys of the transition metal-metalloid (Fe-B, Co-P, etc.) and inter-transition metal (Nb-Ni, Zr-Cu, etc.) types. Metallic glasses are of potential technological importance because of their mechanical strength and ductility and, in certain cases because of their magnetic properties. Glassy metals are also expected to be less susceptible to radiation damage than crystalline metals. Understanding and improving these properties would certainly be aided by the development of better models for atomic arrangements and chemical ordering in these materials. Multicomponent, covalent and mixed metallic-covalent amorphous solids are also attractive candidates for such structural studies.

(b) Scattering measurements should be used to determine the nature and extent of structural variability, especially for those families of non-crystalline solids mentioned in the previous paragraph. Structural variability is expected because such solids are never equilibrium states of matter; both atomic scale structure and microstructure are expected to depend on preparation conditions, thermal treatments, and exposures to radiation. Experimental data on such dependences are very limited, especially for the newer classes of non-crystalline solids, but this information is very important in evaluating the usefulness of the new materials in a variety of technologies, as well as in developing better understanding of their basic physical properties.

(c) Small-angle scattering measurements, using neutrons, x-rays, and electrons, are needed to determine the extent of structural and chemical homogeneity in various types of non-crystalline solids. High resolution electron microscopy and selected area micro-electron diffraction should also be useful probes in such studies. Information on homogeneity is as important as reliable partial distribution functions in obtaining realistic and useful structural models for non-crystalline solids.

(d) Crystallization of non-crystalline solids and corrosion and other forms of chemical attack on these materials are well suited to study by electron microscopy; scanning high energy electron diffraction permits real-time *in situ* studies of thin non-crystalline films in well controlled thermal and chemical environments. Although both crystallization and corrosion processes are likely to be too complicated for detailed analysis in terms of present theories of stability of amorphous solids, more information on these processes is certainly important in many near-term possible uses of amorphous solids, and availability of additional experimental information may aid development of phenomenological understanding of these processes.

Failure to include discussion of structure research on non-crystalline polymers in this report reflects the lack of experience of members of this Study Group with polymers. We regret that we cannot make critical recommendations concerning this area.

4. SURFACES

Further studies of surface structure are essential in improving understanding of physical properties of surfaces and of interaction processes which occur at or near surfaces; such improved understanding should aid in development of numerous components in various energy technologies. Studies of well-characterized surface systems are needed, as well as development of improved techniques for characterization of surface systems in more complicated, technologically important conditions and environments. The following is a listing of areas of surface research involving scattering studies of structure and/or dynamics, in order of their apparent scientific importance, biased somewhat by current and anticipated technological needs:

(a) Microscopic investigations of surface reactions, especially those involving catalysis, and of surface diffusion should be initiated and encouraged, with particular attention to effects of surface structure, topology, and defects on such reactions and diffusion. Progress in these areas requires further development of experimental techniques (field ion microscopy, high resolution electron microscopy, ion and neutral atom scattering, and inelastic neutron scattering) coupled with theoretical studies of stochastic and computer simulation models for the surface processes. These experimental and theoretical methods should also be extended to study thin film formation, faceting, and sintering.

(b) Support should be continued for low energy electron diffraction (LEED) studies of single-crystal surfaces, including continued development and evaluation of spin-polarized LEED techniques. Surface structure determinations both for clean metal and semiconductor surfaces and for overlayer systems of adsorption on such surfaces require both improved theoretical methods for practical deduction of surface structures from LEED intensity data, including improved computational methods and optimization strategies for analysis of complex surface structures, and further collection of such data, with hardware improvements for more rapid and efficient intensity measurements, e.g., channel plate detection and automated, computer control of LEED experiments. Surfaces with overlayers of particular interest involve reactive adsorption: initial stages of oxidation, carburization, and sulfurization. Structure studies of

non-reactive adsorption overlayers provide data on phase transitions and other cooperative behavior for two-dimensional systems. Structure studies of alloy surfaces may reveal differing degrees and forms of chemical ordering on surfaces relative to chemical ordering of bulk material. Spin-polarized LEED studies of magnetically ordered surfaces provide similar comparisons of magnetic ordering and its temperature dependence on surfaces relative to that of bulk material.

(c) Development of better methods for characterizing non-uniform surfaces, both polycrystalline and amorphous, should be encouraged. Such characterization should include accurate determination of pore-size distributions, of effective surface areas, and of active site distributions. Small-angle scattering measurements, with x-rays or neutrons, may be useful in studies of pore sizes and surface areas; surface-EXAFS measurements may provide information on active site distributions. Information obtained by these methods should complement that available by traditional chemical techniques.

(d) The usefulness and reliability of surface-EXAFS measurements in determining local bonding in surface structures should be evaluated, using cross-checking with LEED results for simple surface systems to which both techniques are well suited. The surface-EXAFS technique may be particularly useful in studies of local bonding in cases where LEED is not applicable, e.g., small cluster catalytic systems and overlayers on polycrystalline and amorphous surfaces, and its further development, both experimental and theoretical, should be encouraged.

(e) Studies of surface elementary excitations (vibrational, magnetic, and electronic) and their correlation with surface structure require further development of techniques for high resolution LEED and spin-polarized LEED measurements, as well as further development of theoretical methods for analyzing such measurements. Capabilities of inelastic neutron scattering to provide similar information should also be evaluated and extended.

(f) The utility of high resolution electron microscopy to provide information on atomic scale surface structures should be evaluated.

5. MAJOR FACILITY IMPROVEMENTS

The following is a discussion of several facility improvements which we believe are important for further progress in research on non-crystalline structures and surfaces. Items are listed in order of their importance to these research areas:

(a) An intense, pulsed or continuous, short wavelength ($< 0.5 \text{ \AA}$) neutron source is needed for partial distribution function measurements with polyatomic liquids and non-crystalline solids. Instrumentation for these measurements should include a curved, linear position sensitive detector for simultaneous data collection over large angle regions. Even shorter wavelength neutrons ($< 0.1 \text{ \AA}$), with high intensities, are needed for higher resolution distribution function measurements with non-crystalline solids. Intense neutron sources are also needed to investigate the usefulness of neutron scattering as a probe of structure and dynamics of overlayers in large surface area systems, including real catalysts in technologically important environments.

(b) Synchrotron radiation facilities should be made available, with appropriate instrumentation, to investigate the practicality of using anomalous dispersion effects with x-ray scattering to determine partial distribution functions in multicomponent liquid and non-crystalline solid systems.

(c) Facilities for neutron and x-ray small-angle scattering studies of non-crystalline solids should be improved: a well-instrumented cold source is needed and area detectors suitable for high data rates expected with synchrotron radiation x-ray sources must be developed and made available. These facilities are needed in studies of phase separation, voids, and other defects and heterogeneities in non-crystalline solids.

(d) Spectrometers optimized for synchrotron radiation in the 500-1500 eV range are needed to permit applications of EXAFS and surface-EXAFS methods to elements of low atomic number ($Z = 8 - 13$).

C. DYNAMICAL PROPERTIES OF MATERIALS

*J. M. Rowe, Chairman; T. A. Kitchens; J. P. McTague; H. A. Mook;
P. M. Platzman*; S. Schnatterly; S. M. Shapiro; S. K. Sinha*

1. INTRODUCTION

X-ray, neutron, and electron inelastic scattering are, in general, complementary rather than competitive techniques. The nature of the radiation and of its interaction with condensed matter tends to determine the relative utility of the three types of scattering for different measurements. For example, neutron scattering has been the technique of choice for the study of atomic and molecular vibrations because both the energy and wavelength of neutrons are well-suited to the characteristic energies and distances of condensed matter. However, with the advent of new, intense x-ray sources and new electron scattering techniques it can be expected that both of these types of inelastic scattering will become increasingly important in this area. In fact, one of the most exciting possibilities is the direct intercomparison of results for x-ray, neutron, and electron scattering studies of electronic excitations, a field which will open up as the new x-ray and spallation neutron sources are developed and exploited.

The basic role of inelastic scattering in materials research has been (and will likely continue to be) in the area of detailed tests of solid state theory rather than in the more directly relevant areas of interest to the materials engineer. Nonetheless, a firm base in solid state physics is essential to the nation's future technology and thus it is entirely appropriate that this research be carried out by the Materials Sciences Program of the Division of Physical Research at ERDA.

It is true that several of the areas of inelastic scattering have significant potential for short-range impact on materials technology. Specific examples are neutron scattering studies of hydrogen in metals, the use of electron

*Unable to attend meeting, so written contribution only.

inelastic scattering as a microanalytical tool (for which basic research into scattering cross-sections is essential), the study of interatomic forces under extreme temperatures and pressures, and the study of the dynamics of defects in crystals. An example of the latter would be the study of the split interstitials in metals.

In our report, we have evaluated current and future research areas primarily on their scientific potential rather than on their short range impact on materials engineering. We have also, however, indicated those areas most likely to couple more directly to technological problems. In the next section, we discuss five general areas of research in order of their scientific importance (most important first). In Section 3 we list specific problems grouped into three broad classes, with priorities assigned to each class but not within classes. Section 4 contains our specific instrumentation recommendations, while the last section presents our overall conclusions and recommendations.

2. SCIENTIFIC AREAS OF INTEREST

(a) Solid State Physics - Many Body Effects

The most important advances in solid state physics theory in the past twenty years have been in the field of many-body theory and the statistical mechanics of elementary excitations, co-operative phenomena and phase transitions. The most direct and dramatic tests and verifications of these results have been obtained from scattering techniques (including light scattering). X-ray and electron inelastic scattering can directly measure the dynamic structure factor $S(\kappa, \omega)$ for the electrons in solids while neutron scattering can measure the enhanced spin susceptibility $\chi(\kappa, \omega)$ of electrons. In principle, all three techniques can measure $S(\kappa, \omega)$ for the atoms in materials, although neutron scattering seems likely to dominate this field as it has in the past. In the next few paragraphs we list some areas which seem particularly ready for exploitation by inelastic scattering techniques.

One of the most important and fundamental interactions in solids is that between the electrons and phonons. This interaction is responsible for normal state resistivity, for superconductivity, and in some cases for crystalline stability of metals. The study of phonon dispersion relations and phonon lifetimes in normal and superconducting metals by neutron inelastic scattering is one of the most powerful probes of the details of this interaction, as one is able to obtain information at selected values of wave-vector. The information obtained in this way is unique, and it affords the most critical tests of the theory of the electron phonon interaction. (See e.g., the APS meeting at San Diego where the neutron scattering results clearly dominated all discussions of the properties of Nb.) This field of study will clearly continue to grow in importance as measurements are extended to other superconductors and as resolutions are improved to allow better measurements of phonon lifetimes. Another area of enormous impact and potential is the study of soft mode instabilities driven by electronic charge density waves and metal insulator phase transitions. Again, the measurements of the phonon properties offer the only detailed microscopic probe available for the study of these effects.

This leads naturally to the next topic to be considered in this section-- structural phase transitions. Our understanding of these transformations in which the symmetry of materials is changed has been increased dramatically

in recent years by the neutron scattering studies of appropriate soft modes. Since in many cases these soft modes occur at finite wave vectors, they can only be studied directly by neutron scattering. Although there has been much progress to date, enormous areas of research remain to be exploited. It is clear that a detailed understanding of the phenomenon of phase transformations is essential to future energy related materials research, especially when one considers the range of temperatures and pressures at which materials must be used.

A new field which offers great promise is the study of electronic excitations by a combination of electron, neutron, and x-ray scattering. As the new neutron and x-ray sources become available and as electron techniques are further developed, this intercomparison will lead to a rapid development of this field. We fully expect that new concepts and conclusions will come from this effort which we cannot now predict. Suffice it to say that several experiments would be done immediately if facilities were available and that there is an overwhelming probability of totally unexpected phenomena to be explored.

The study of quantum systems (primarily helium) has been one of the triumphs of neutron inelastic scattering. From the first demonstration that Landau's prediction of an elementary excitation spectrum with unusual energy dispersion for superfluid He^4 was correct through to the most recent experiments on liquid He^3 and He^3 - He^4 mixtures, the results of neutron scattering experiments have been of critical importance in the testing and sharpening of old concepts. Recent experiments have attempted to exploit the fact that at high enough energy and momentum transfer one can measure more or less directly the momentum distribution $n(p)$ of the ground state in He^4 . Recent experiments on thin films of He^4 adsorbed on grafoil (i.e., a 2 dimensional quantum system) have challenged the Feynman concept of the roton.

(b) Disordered Systems

In this category, we include specifically solids with defects, alloys, glasses, amorphous solids, liquids, and surfaces. The dynamical properties of these systems are among the least understood in solid state science today and present the most challenging problems for both theory and experiment.

In the case of solids with defects, considerable theoretical progress has recently been made by the use of Green's function, average t-matrix and coherent potential techniques. These calculations have been motivated by the existence of high quality experimental data on the vibrational properties of such systems which can be used as a direct test of such theories. Recent efforts include the study of split interstitials in neutron irradiated metals, a topic of great interest to reactor technology. The framework for the theory of these interstitials has been tested by studies of $(\text{CN})^-$ ions in KCl--a good example of the interplay of basic research with studies of more technological interest. The extreme example of solids with defects is of course an alloy where the concentration of "defects" may reach 50%. The study of alloy systems has led to important new insights into the coherent potential model as well as other statistical mechanical techniques for the study of large concentrations of defects. This area offers continuing opportunities for studies of new techniques for theoretical treatments, especially including computer simulation.

The glassy and amorphous solids are one stage less tractable than alloys, and this is reflected in both the experimental and theoretical situation. The loss of translational symmetry renders the concept of non-interacting phonons for which wave vector is a good quantum number (a concept which was enormously useful in studies of crystalline solids) untenable. Although in some cases (tetrahedrally bonded semiconductors) cluster calculations have been moderately successful, in other cases computer simulation appears at present to be the only useful computational technique. In order for further progress to be possible, new theoretical treatments must be found, and these can only be tested by careful comparison with high quality inelastic scattering data.

Liquids are the extreme example of disordered condensed systems. Here one has all the complications of the amorphous state plus rapid diffusion to contend with. However, recently there has been substantial progress in reaching a good phenomenological understanding of the statistical physics of liquids through a combination of neutron scattering and molecular dynamics simulation. This has led to renewed vigor in attempts to derive statistical mechanical models for liquids and to test these models by comparing them to the very detailed data available. The major present experimental need is for more data in the important region of energy and momentum transfer in which the well understood hydrodynamic picture begins to break down. Presently available facilities cannot provide sufficient flux and resolution for these critical studies, but the proposed pulsed neutron sources should open up this area. Progress in the understanding of more complicated liquids such as molten salts, liquid mixtures and molecular liquids is of course predicated on a satisfactory picture of simple liquids.

The dynamics of surfaces and of layers adsorbed on surfaces is a subject of intense current research interest, and is also an area offering more direct contact with energy technologies. The fundamental characterization of interfacial layers has been advanced considerably over the past decade by tools such as LEED and Auger spectroscopy. However, the study of surface and adsorbed layer dynamics is only beginning to be studied. Neutron inelastic scattering is not a surface specific probe but it can be (and recently has been) used in special cases to observe directly the dynamics of both chemisorbed and physisorbed species on graphite surfaces and to observe the phonon densities of states of small particles where surface effects are important. Inelastic LEED is a surface specific technique which provides information about the electronic states of both clean surfaces and adsorbed layers. These techniques will provide significant new information essential to a fundamental understanding of surfaces.

(c) Measurements in Extreme Environments

At the present time, most experiments are done at temperatures between 4-700 K at atmospheric pressure, and there has been little effort to make measurements over the full range of pressure and temperature at which materials are used. Quite recently, measurements have been made at temperatures down to 0.003 K and at pressures up to 40,000 atmospheres with temperatures down to 4 K. There is a real need to extend the ranges of pressure and temperature at which measurements can be made and to conduct systematic studies of materials under these extreme conditions. This should be done both for simple materials (e.g., alkali metals) where a comparison with anharmonic phonon calculations is meaningful and for more complex materials (e.g., ceramics) where simple

empirical knowledge is the primary goal. The ultimate aim of this two pronged attack is to achieve an understanding of materials in environments such as are found in real engineering applications. With the advent of new high flux pulsed sources (both x-ray and neutron) the study of shock waves and of other transient phenomena will be possible. This will allow achievement of even higher pressures, temperatures, and magnetic and electric fields than can presently be contemplated.

(d) Mechanisms of Diffusive Motions

The microscopic details of the diffusion process of atoms in condensed matter is a subject of considerable current interest both scientifically and technically. The outstanding examples of such motions are the superionic conductors (e.g., CaF_2), hydrogen in transition metals, atoms or molecules adsorbed on surfaces, and liquids. The neutron scattering technique is very well suited to these studies--in fact it offers a unique probe whereby one can actually probe distances of the order of single diffusive steps. The method requires measurements near zero energy transfer (quasi-elastic scattering) and hence requires instruments with high energy resolution (0.1-200 μeV). There are several examples of successful recent measurements-- Ag^+ ions in AgI , H in Pd, $(\text{SH})^-$ ion reorientation in RbSh and the self diffusion in liquid argon. In these experiments, it has been possible to establish the dominant mechanism of diffusion and in some cases to infer the path of diffusion. However, it is very difficult to interpret many of the results and further progress will depend upon a close, continuing interaction with both theoretical developments and computer simulation.

(e) Vibrational Spectroscopy

Within this rather broad category we include the study of molecular vibrations, density of states measurements by incoherent scattering, and the study of complex solids such as polymers through the observations of the scattering associated with hydrogen. The information available from such experiments is more limited than that discussed in the preceding sections, but, provided that model systems are carefully chosen, it is possible to derive information that is both useful and unique. For example, it is well known that there are no selection rules for neutron incoherent scattering, and thus, in principle, one can directly obtain information about molecules not obtainable by optical techniques. There are, however, experimental limitations which must be carefully considered. In spite of these restrictions the technique is a useful complement to the much more generally applicable techniques of Raman and infrared spectroscopy. The new pulsed neutron sources offer some advantages for this type of work.

3. DETAILED SCIENTIFIC PRIORITIES

In this section we list those activities discussed in Section 2 in four groups by priority determined by probable scientific impact only. All of those topics presented below are important--we did not assign priorities to less significant studies, but rather simply omitted any such programs. We have indicated by asterisks those activities which we feel will contribute most directly to shorter range energy-related technology (two asterisks are more directly energy related than one). Finally, some of the lower priority items

should perhaps be considered by other programs within DPR, e.g., molecular spectroscopy by molecular sciences, since these programs might well assign higher priorities than those given here. Listings within priorities are alphabetical.

Priority (#1)

- * Amorphous solids and glasses
- Electronic excitations
- * Electron-phonon interaction
- ** Interatomic forces in extreme environments
- * Structural phase transitions
- * Surface dynamics

Priority (#2)

- * Excitations in defected crystals and alloys
- Dynamic structure of liquids
- Quantum solids and liquids
- * Surface diffusion
- * Superionic conductors

Priority (#3)

- ** Alloys in extreme environments
- Diffusion in liquids
- ** Hydrogen in metals - diffusion
- Momentum distributions $n(p)$

Priority (#4)

- ** Incoherent scattering (polymers, hydrogen bonded solids)
- Molecular spectroscopy
- Rotational diffusion

4. EQUIPMENT NEEDS

We have tried to examine the need for new major equipment expenditures in this field. We have explicitly excluded neutron, x-ray, and electron sources from our deliberations since National Academy of Sciences panels have examined or are examining the need for such equipment on a national basis (not restricted to ERDA). It was clear to this panel that the major need is to develop state-of-the-art facilities at the proposed new sources. Without such efforts, these sources will not be properly exploited. At the same time, we recognize the need for specialized instruments to do some of the work recommended highly in Section 3. We have attempted to assign priorities to these needs, and once again, we have only presented those needs which are most pressing--thus many perceived needs are not mentioned on the grounds that they will be attended to by normal means in the laboratories. The list below is in order of priority, with the most important first:

- (a) Development and construction of ultra high resolution neutron spectrometers to achieve energy resolutions between 0.1 and 2.0 μeV .
- (b) Development of high resolution bent crystal x-ray inelastic scattering spectrometers to allow high resolution studies of electronic and possibly atomic excitations using synchrotron radiation sources.
- (c) Development of a broad range of neutron time-of-flight instrumentation including position sensitive detectors and data acquisition systems to allow full utilization of the proposed pulsed neutron sources.

(d) Development of pulsed sample environmental techniques to achieve the most extreme conditions (e.g., 10^6 gauss magnetic fields).

5. OVERALL CONCLUSIONS AND RECOMMENDATIONS

Neutron inelastic scattering has been and will continue to be the technique of choice for studies of the thermal properties of materials. Electron inelastic scattering is the technique of choice for studies of valence electron excitations. New, high intensity sources of high energy neutrons and the new synchrotron radiation source at Brookhaven will open up new possibilities for intercomparison of results obtained from the three techniques. There are many exciting areas of solid state physics which are open to exploitation in the near future and these are the areas (see Section 3) which should be emphasized. The equipment necessary for a full exploitation of these ideas is ranked by priority in Section 4. Finally, we emphasize that a continuing close interaction between theory, experiment and computer simulation is essential to continued progress.

D. MAGNETIC PROPERTIES OF MATERIALS

*C. G. Shull, Chairman; J. M. Hastings; G. H. Lander;
R. M. Moon; J. J. Rhyne; C. Stassis; S. A. Werner*

1. INTRODUCTION

Because of their unique characteristics (neutrality, spin moment, energy and momentum with associated De Broglie wavelength) thermal neutrons are excellent probes of magnetic phenomena and materials. Magnetic materials are widely exploited in many forms of technology and a full understanding of the basic phenomena behind their properties is important in technological improvements.

In simple form, a study of the neutron interaction with magnetic materials provides information on an atomic scale of the magnitude and directional configuration of atomic magnetization and the correlation energy and range of these magnetization units. This microscopic picture of the magnetic materials, unavailable from other exploratory techniques, is intimately connected with the bulk macroscopic properties of the material. Aside from the technical interest in such studies, the neutron scattering studies have provided a wealth of information about electronic wavefunctions as they exist in condensed atom systems and on magnetic interactions between atoms, and this information has served in a very stringent way to test, and give guidance to, theoretical investigations.

In considering the various techniques of x-ray, electron, and neutron scattering as tools in studying magnetic materials, the latter undoubtedly occupies a unique position. Although electrons because of their spin moment will also exhibit magnetic interaction, this is overwhelmed by the dominant Coulombic interaction and electron scattering has not been useful in this area. Similarly x-ray scattering has not been useful because of the lack of a sensible interaction with magnetization units. Accordingly our Study Group has concentrated on outlining the various areas of neutron investigation and suggesting the relative importance and significance of these.

In Section 2 we briefly discuss various areas of research in which neutron scattering has played an important role and give our assessment of the need for further work in each area. No significance should be attached to the order of presentation. In Section 3 we assign priorities to these areas based on scientific merit and also indicate which areas have important short-term technological impacts. Finally, in Section 4 we list some desirable improvements in neutron scattering techniques as applied to magnetic materials.

2. SCIENTIFIC AREAS OF INTEREST

(a) Magnetic Structures

Our understanding of important classes of materials such as ferrites, rare-earth metals and intermetallic compounds has been greatly enhanced through magnetic structure determinations using neutron diffraction techniques. The need for magnetic structure determinations will surely continue. Understanding the structure of magnetic materials is important in controlling material properties and in developing new materials with desirable magnetic properties. A knowledge of the magnetic structure of a solid is always necessary before dynamical studies are undertaken; it gives the first clue toward understanding the nature of the exchange and anisotropy energies.

A wide variety of magnetic structures have now been observed including helical, sinusoidally modulated components, conical, antiphase domains, linear antiferromagnetic, ferrimagnetic and others. Neutron diffraction has been essential in determining these structures. An important feature of structure determinations in ferrimagnetic materials is the determination of the temperature variation of the magnetization associated with different sublattices. As more complex materials come under investigation, it is likely that the variety and complexity of known magnetic structures will increase.

For most structures determined to date a high-flux source has not been necessary, and in many cases, powder samples have been adequate. For complex structures, single crystals may be needed, and for cases involving simultaneous magnetic and crystal transitions the polarization analysis technique is necessary. This technique is actually desirable for all magnetic structure determinations because it allows a clean separation of nuclear and magnetic scattering, but has been little used because of intensity limitations.

(b) Magnetic Form Factors

The magnetic moment density in solids is derived from those electrons outside of closed shells--the same electrons which are responsible for all the interesting chemical and physical properties of materials. By carefully measuring the magnetic form factors (or scattering amplitudes), a precise description of the spatial distribution of these outer electrons is obtained. This information is closely related to a fundamental theoretical concept--the electronic wavefunctions of the outer electrons. Accurate calculations of solid state wavefunctions are essential in understanding a wide variety of physical phenomena. The neutron measurements serve as an important benchmark to test the accuracy of various theoretical approximations. Close interactions between experimentalists and theorists have been growing and should be encouraged.

The basic technique in these measurements involves polarized neutron beams. A wide variety of form factors for ferromagnetic materials have been measured in the past and it is expected that this work will continue. High-flux sources are not necessary for ferromagnetic samples. In recent years this work has been extended to paramagnetic metals, to dilute alloys of magnetic atoms in a non-magnetic host, and to diamagnetic materials. For these experiments long counting times are needed and a high-intensity source is a great help. We anticipate that measurements on these weakly magnetic systems will continue.

Because of the fundamental nature of form factor measurements and their close relationship with the theory of solids, these measurements are widely regarded as among the most valuable that can be made with neutrons.

(c) Magnetic Phase Transitions

Many diverse systems exhibit the phenomenon of a second-order phase transition ranging from the order-disorder transition of an alloy such as β -brass to the superfluid transitions in liquid ^4He . The behavior of all these systems with "continuous transitions" is observed to be similar in the neighborhood of the transition. Indeed, beginning around 1965 with the development of the phenomenological concept of universality the hypothesis was put forth that the classification depended upon the dimensionality of the system and the symmetry of the order parameter. Within a given class, the critical properties are presumed to be identical. At about the same time another phenomenological theory called scaling appeared. Near the critical point various physical quantities (susceptibilities, specific heat, correlation length, order parameter, etc.) either diverge to infinity or go to zero. The critical behavior of the quantities is given by a power law with a so-called "critical exponent." Scaling theory predicts that there are only two independent exponents.

A magnetic system in the neighborhood of the transition from a disordered paramagnetic state to an ordered magnetic state undergoes a second-order transition. Neutron scattering, both elastic and inelastic, has provided the broadest test of these concepts and has helped to establish their validity. In 1971 a momentous series of papers by K. Wilson and co-workers utilizing the renormalization group method changed their phenomenological theories into real calculations of critical point behavior. This approach provides a realistic calculational method for a many-body problem and its predictive power must be tested. Neutron scattering measurements on magnetic systems can provide these tests as well as new directions.

(d) Magnetic Excitations

Our understanding of magnetic excitations in insulators is now very good. This has come about largely through the inelastic neutron scattering technique. The situation for metals is quite the reverse; in fact, our understanding is really very limited. Current theories of magnetism in metals divide the excitations into two classes. The first class is the collective excitations, in which almost all of the "magnetic electrons" (unpaired 3d electrons in the transition metals) contribute. These are the spin waves, and there are thought to be two branches, an "acoustic" branch for which $\omega \rightarrow 0$ as $q \rightarrow 0$, and an optic branch. The second class is the Stoner excitations naively viewed as those arising from magnetic excitations of a single electron. This

single particle continuum of excitations covers a broad range of energies. Only the acoustic magnons have been observed, so far. The difficulty in observing the single particle modes with neutrons arises from the fact that they occur at relatively high energies (~ 0.1 to 2 eV). Use of the epithermal neutrons from a pulsed-spallation source may allow us to directly observe these excitations for the first time.

(e) Crystal-Field Excitations

The measurement of 4f-shell-crystal-field energy levels has led to an increased understanding of all bulk magnetic properties (such as magnetization and specific heat) of these systems. These quantization states are, in fact, as important in characterizing the system as the atomic structure. For metallic systems, neutron scattering is the only tool available. Since the crystal-field potential contributes the dominant term to the bulk anisotropy, its measurement and understanding can contribute directly to applied science. A recent example is the tailoring of rare-earth magnetostrictive devices to reduce the bulk anisotropy.

(f) Valence Fluctuations

In mixed valence compounds elements can exist in two discrete valence states and fluctuate between them. Although the concept is an old one in chemistry, its understanding at a basic level has received considerable stimulation from recent solid-state physics efforts. Neutron experiments are now providing important and unique information on the fluctuation process and the lattice interactions involved. In rare-earth systems the energies of the two states are close together, whereas in transition metal or actinide systems the energy differences are much greater. To study such processes will require greater fluxes of high-energy neutrons.

(g) Superconductivity

The magnetic scattering of neutrons is a powerful technique in the investigation of Type II superconducting materials. Indeed, neutron scattering proved for the first time that the magnetic field penetrates the material in tubes called fluxoids (each carrying one flux quantum) arranged in a periodic array. It has been demonstrated that neutron scattering can characterize the fluxoid structure and also provide important information about its perfection, the flux distribution inside an individual fluxoid, and the nature of the pinning forces. Most experimental investigations have been performed on pure Nb and much remains to be learned by extending these measurements to technologically important materials (such as Nb_3Sn) and to systems containing magnetic and non-magnetic impurities. In addition, magnetic neutron scattering techniques can be used to investigate the coexistence of ferromagnetism and superconductivity in certain materials as well as the related phenomenon of reentrant superconductivity. Another interesting potential application of magnetic scattering is the study of the field penetration depth in various materials. Thus we feel that magnetic scattering techniques together with inelastic neutron scattering investigations of the precursor transformations and of the electron-phonon interaction in various materials can substantially further our understanding of superconductivity.

(h) Disordered Systems and Amorphous Materials

The field of amorphous magnetism has seen its birth and early development all within the last 10-12 years and currently shows significant promise both from the viewpoint of basic scientific investigation and from the potential for important applications. An example is the transition metal glasses (e.g., $\text{Fe}_{0.8}\text{B}_{0.2}$), which show remarkably high permeability and very low hysteretic losses, and for which applications include magnetic shielding, transformer cores, etc. Likewise, the rare earth based systems (e.g., GdCo_2) show promise for computer bubble memory applications and for thin-film memories.

Scattering techniques can have a significant role to play in this area as well as in the associated studies of spin glasses and concentrated disordered alloys. Aside from the obvious atomic structure investigations, these studies include the effect of topological disorder on the exchange interactions (probed through inelastic neutron scattering), magnetic moment density and distribution (studied by polarized beam techniques) and magnetic clustering or "micro-domain" effects (small q scattering techniques). In addition, the entire question of local environment and/or disorder effects on magnetic interactions may be investigated by diffuse scattering in disordered alloys.

The study of amorphous and disordered systems depends heavily on future developments in two areas of scattering techniques: (1) more efficient neutron polarizer with high intensity, and (2) development of low-angle scattering facilities with polarized neutron beams combined with an inelastic scattering capability.

The types of studies which can be anticipated in the amorphous disordered phenomena all can be grouped into three broad classes: (1) low q inelastic studies of acoustic mode magnons and domain configurations, magnetic roton phenomena, magnetic density of states studies and optic magnon or excitonic excitations, (2) studies of phase transitions in amorphous systems and disordered systems to test scaling and phase transition theories, and (3) studies of short-range magnetic order and localized mode interactions.

(i) Hard Magnetic Materials

The class of compounds including ReCo_5 , $\text{Re}_2\text{Co}_{17}$ and $\text{Re}_6\text{Co}_{23}$, where Re is a rare earth metal, are very interesting from the technological point of view, being high temperature ferro- or ferrimagnets with relatively high coercivities and anisotropy fields. Theoretically, the ReCo_5 magnets should have very high energy products, but the commercially prepared materials fail by a considerable factor (~ 10) to match the predictions of single crystal studies, due at least in part to nonstoichiometries and defects related to the 2-17 and 6-23 compounds. These compounds, derived by modifications of the 1-5 structures, have relatively poor anisotropy fields. Neutron scattering is being used to study the magnetic structures of these compounds and in particular to determine the effects of substitutions of one transition metal for another on some of the inequivalent sites in the 2-17 and 6-23 compounds. It is hoped that by judicious choice of the composition, one can tailor the material to be highly performing despite slight deviations from perfect composition or defects in the growth of the material tending toward the 2-17 or 6-23 compounds. Only a thorough understanding of the basic magnetic properties of these various compounds will enable one to arrive at the optimum material.

(j) Magnetic Domain Studies

The techniques of neutron radiography and neutron topography have been applied to the study of magnetic domain structure in only a limited number of cases, e.g., Fe, Cr and NiO. These techniques, especially using polarized neutrons, are potentially very potent for the study of domain nucleation, domain wall motion due to applied fields and strains, and magnetic inhomogeneities. We should expect that this area of neutron research will grow as neutron photographic techniques are pushed into the submicron region.

3. SCIENTIFIC PRIORITIES

In this section we give an indication of our judgment concerning the scientific importance of those areas discussed in Section 2. We established two categories--one of high priority and the other of lower priority, and placed each of the research areas in one of these two categories on the basis of their probable scientific merit. In addition, those areas marked with an asterisk have a high probability of producing a short-term technological pay-off.

High Priority

- Magnetic form factors
- Magnetic phase transitions
- Magnetic excitations
- * Superconductivity
- * Disordered systems and amorphous materials

Lower Priority

- Magnetic structures
- Crystal-field excitations
- Valence fluctuations
- * Hard magnetic materials
- * Magnetic domain studies

4. TECHNIQUE DEVELOPMENT

We list below several desirable advances in experimental technique which would either open up new areas of research or significantly improve data acquisition rates in established research areas. Some of these advances are associated with the proposed pulsed sources and others can be realized with the existing steady-state sources.

(a) Improvement in polarized beam technology. Polarizing crystals of higher reflectivity are needed to allow the further development of the polarization analysis technique. Polarizing filters for white beam applications are needed for pulsed sources. The development of layered polarizing monochromators and supermirrors for relatively long wavelengths is also important.

(b) Polarized-beam small-angle scattering instrument. Such an instrument would be useful for studying magnetic inhomogeneities in alloys and for magnetic colloids. The addition of energy analysis would be valuable in the study of amorphous magnetic materials.

(c) Pulsed source development. The high epithermal spectrum available from pulsed neutron sources would allow a much more complete study of magnetic excitations in 3d metals and some 4f materials than has been

possible with steady-state sources. In addition, the pulsed nature of the neutron beam could be exploited to study time-dependent phenomena, such as relaxation effects.

(d) Extreme sample environments. Further development of high pressure techniques would allow the study of pressure-induced magnetic phase transitions and a more complete study of the valence fluctuation phenomenon. Most neutron instruments are equipped to cover the temperature range from ~ 1.5 K to 300 K on a routine basis. An effort should be made to extend the routine operation into the mK and kK regions.

E. DEFECTS, INHOMOGENEITIES, AND POLYMERS

*B. W. Batterman, Chairman; R. Gronsby; R. W. Hendricks;
H. Herman; J. S. King; F. W. Lytle; D. H. Reneker; J. Silcox*

1. INTRODUCTION

Defects and inhomogeneities have been recognized as having all pervasive influence on the properties of real materials and the subject has some considerable maturity. Scattering techniques using x-rays, neutrons and electrons form the most direct probe of defects and thus have to be considered at the heart of defect characterization studies. In the following, the Study Group identifies problems that are ripe for attack using current techniques and understanding. At the same time, it is noted that support for instrumentation development and acquisition has fallen far short of needs over the past seven years and a substantial shortfall exists. Thus, attention will have to be paid to ensuring that the instrumental base is adequate to tackle these problems.

The Study Group recommends that ERDA support research at the synchrotron radiation facility as well as the facility itself and that limited support for new work should be provided in the individual laboratories that will use the Brookhaven facility. For electron scattering, strong support was voiced for the funding of scanning transmission electron microscopy instrumentation with high brightness sources and state-of-the-art energy analysis modes. It was felt that development of such instruments should proceed on a regional basis. Strong support was registered for a national facility for high resolution microscopy to provide ultimate point-to-point resolution of 1 Å. In neutron scattering, concern was registered about continued support for the existing national facilities, such as Brookhaven and Oak Ridge. It was recommended that continued support and strengthening of these facilities continue to be an ERDA policy. Support should also be provided for the neutron facilities at NBS and at feeder institutions such as MURR and MIT who will train the new scientists in the areas of neutron diffraction. It was strongly recommended that new facilities such as the IPNS be supported vigorously.

In the specific areas of basic research supported by ERDA, we will present a number of recommendations, all of which we feel are important. We have ranked these recommendations in three categories to establish a relative priority. Starting with the highest priority, which we will designate Category A, we present the individual areas and some brief comments.

2. CATEGORY A

(a) Chain Configuration in Bulk Polymers and Relationship to Useful Properties (Deuterium Decoration)

Decoration of polymers with deuterium enables one to characterize by neutron scattering chain geometry in bulk polymers and thus facilitates establishment of the relationship between bulk properties and chain geometry. The long standing problem of the effects of sample preparation and deformation on chain geometry can be attacked as soon as experimental facilities are available. In this regard small-angle neutron scattering facilities are needed immediately. The workers in the polymer area are cognizant of these problems and are ready to work on them when facilities are made available. The ability to establish the relationship between structure and properties in polymers will have a large impact on the national energy problem with the use of improved plastics in transportation systems, electrical power distribution systems, conduits for the transport of gaseous fuels and water, membranes for chemical separation processes, and other applications due to the increased durability of articles made from polymers.

To put polymers in perspective, it should be pointed out that the polymer industry sells about 25 billion dollars per year of polymers for use in plastics, elastomers and fibers. In 1974 only 1.4% of the nation's total use of natural gas and petroleum was used as a petrochemical feedstock to make plastics. On a volume basis fabrication of a steel or aluminum part uses two to three times the fuel required to synthesize and create a plastic part. Hence increased use of plastics as replacements for metal parts will impact favorably on energy problems. Support of neutron scattering facilities, particularly low-angle facilities, to study deuterated polymers will facilitate the use of polymers in energy conserving applications.

(b) Atomic Detection in the Early Stages of Void Formation

A prominent feature of irradiation in both fission and fusion systems is the formation of voids which seriously affect mechanical properties. Quantitative means of direct evidence of low Z elements such as helium in the early stages of void formation or even in the voids themselves has not been adequately developed. A promising new approach to quantitative detection of such gases as helium would be the use of electron energy loss analysis using a high intensity electron source. Such systems have already demonstrated detection of the order of 5000 Fe atoms with the sensitivity of better than 500 atoms using the Fe-M_{2,3} inner core excitation. The helium K excitation has roughly comparable cross sections and should therefore be detectable in comparable quantities. With current instruments optimized for this purpose, even better performance may be expected. Extensions of the approach to other low Z elements can be readily expected.

(c) Grain Boundary Structures and General Cluster Formation and Composition at the 10-100 Å Level

Segregation of second phase elements at grain boundaries and at cluster formations in general is a common problem in all materials. It is an area of extreme technological importance since virtually all engineering materials are utilized in polycrystalline form. First wall problems in reactor vessels, for

example, have been traced to hydrogen and void trapping in grain boundaries. Structural ceramics for turbine application are also known to be embrittled due to the presence of glassy phases and grain boundaries. Clearly, the relationship between grain boundary structure and properties will allow many of these problems to be controlled. New techniques now offer the possibilities of chemical and structural characterization at the 100 Å level. High resolution electron microscopy can now provide images that reflect the projected potential along the boundary, and analytical electron microscopy can provide identification of second phase particles and to a limited extent their electronic structure and their chemical composition through energy loss analysis. We strongly urge support for the technology that will lead to improved high resolution electron microscopy and analytical electron microscopy.

(d) Real Time Measurements of Defect Dynamics with High Intensity Sources

The motion of dislocation structures, crystal transformations and interfaces can be studied in real time using topographic techniques associated with synchrotron radiation from a storage ring. This will aid considerably in the fundamental understanding of dislocation dynamics and dislocation-associated interfacial motion. The real time study of crystallization behavior within amorphous systems and in liquids can be studied by analogous methods. Furthermore, the growth of defects due, for example, to plastic deformation, creep or radiation, and the growth of second phase precipitate particles *in situ* can be studied with these high intensity sources, thereby permitting an evaluation of the kinetics of the system. High intensity sources can include as well high brightness electron guns for analytical and high resolution microscopy. However, the new and exciting possibilities on the horizon are the very intense time-structured synchrotron radiation sources.

(e) Development and Support of Analytical Electron Microscopy at the 10-100 Å Level

For several of the areas of research that we recommend in this report, state-of-the-art achievement in analytical electron microscopy is an essential parameter. Therefore, the support of STEM instruments with energy analysis capability at the cost of approximately \$300,000 per unit should be a major support category for ERDA's basic research program. Microanalytical detection of atoms in the 10-100 Å regime can be achieved with instrumentation now becoming available commercially. The key features of these instruments are high brightness electron guns which provide high beam intensities in small (5 Å) probes, non-dispersive x-ray detectors, good vacua, and electron energy loss capabilities. The latter are particularly sensitive to low Z elements where the photoelectric yield is low and afford high collection efficiencies as the result of the strong forward scattering into the detector apertures. The potential of this instrument and the ancillary techniques have been established as well as rudimentary quantitative procedures. There now needs to be extended development to provide quantitative data. Up until the present time, electron microscopy and diffraction have been dominated by the use of photographic techniques. Since the dynamic range of a photographic plate is limited, the observations have been substantially qualitative. Diffraction theory, on the other hand, has become quite precise with the extensive use of computer techniques. It is now ripe for this field to become much more quantitative experimentally. Thus, it is essential that we proceed with the development of state-of-the-art electron counting and the development of

advanced techniques for identification and separation of elastic and inelastic components of electron micrographs and diffraction patterns.

(f) Support for a National Facility for Small-Angle Neutron Scattering

The Study Group feels that the construction of a user-oriented dedicated small-angle neutron scattering instrument with an area detector and associated data acquisition and analysis systems is of very high priority. It has been demonstrated by experiences in Europe that data from such an instrument would contribute significantly to our understanding of the structure of polymeric materials, of phase transformations in alloys and glasses, of voids in neutron irradiated alloys, and of cluster formation in general. Almost all of the areas of materials research considered in this report would benefit substantially by the availability of such a small-angle neutron scattering facility.

(g) Local Non-stoichiometry in Refractory Oxides and Alloys

Deviations from stoichiometry in compound oxides and alloys give rise to one and two-dimensional defect structures. These defects (point imperfections and planar defects) are important influences on mechanical behavior and are amenable to study by diffuse scattering techniques using either neutrons or x-rays. Cases in point include oxides of titanium, vanadium and iron and most metallic alloy systems. Complementary analysis by atomic resolution electron microscopy can yield information on the character of these defects, their interfacial structure and the localized compositional changes which they induce. Data of this type have already been achieved in minerals and complex oxides having much larger unit cells. Applications to technologically significant materials, however, require the development of high voltage, high resolution microscopy as well as analytical electron microscopy techniques.

(h) Local Order and Void Nucleation

The development of low swelling alloys is of critical importance to the development of advanced fission and fusion reactors. It is well known that alloy composition (both gross and impurity) plays a critical role in determining the behavior of alloys which are exposed to high neutron fluxes. It has long been anticipated, but only recently demonstrated, that local atomic order in alloys of the same composition can also have a very significant effect. The Study Group believes that the use of analytical electron microscopy and diffuse neutron and/or x-ray scattering at both large and small angles can contribute unique and significant information to the understanding of such effects and should thus be an important component of an alloy development program. In this effort, the use of high-angle scattering to study short-range order and small-angle scattering to study clustering should be vigorously pursued.

3. CATEGORY B

(a) High Resolution Electron Microscopy

With the advent of stable high voltage electron accelerators and low aberration lens design, it appears feasible that point-to-point resolution of $\approx 1.5 \text{ \AA}$ can be achieved in the near future. Meeting the cost of such an instrument as well as the necessary support instrumentation and staff would be best accomplished by establishing a user-oriented shareable national facility. It is strongly

recommended, based on needs shown throughout this report, that the first such facility be set up as soon as possible in order to provide scientists in this country with the capability for atomic resolution electron microscopy.

(b) Hydrogen and Gases in Metals

In high temperature environments a variety of ferrous metal alloys can dissolve large quantities of hydrogen. This gas diffuses rapidly and is able to coagulate and embrittle the material. Transmission electron microscopy and small-angle neutron scattering methods are able to study and characterize the incipient gas formed products. To study hydrogen storage systems in these materials the formation of "reversible hydrides" must be investigated by diffuse, small and wide angle scattering methods and high resolution transmission electron microscopy.

(c) Inhomogeneities in Glasses

Glasses, either oxide or of the metallic glass variety, can give rise to important small-angle scattering effects. These are due to voids or in the case of mixed oxides for example, inhomogeneities, which can be precursor phases or actual phase separation processes. These phenomena represent an important aspect of either materials improvement or property degradation. Optical, chemical and mechanical properties can also be influenced by devitrification, a process which can be accelerated by radiation, impurities and thermal treatment. Small-angle scattering methods represent a key probe in evaluation of these defects.

(d) Defects in High Temperature Superconductors (Al₅ Compounds)

It is clear that the ultimate transition temperature for superconductivity is closely related to the crystalline order in these compounds. Not only is the transition temperature affected but also the current carrying capabilities while in the superconducting stage. A vigorous program of support in the development of these materials, both from a fundamental point of view and from a technological one, is essential for supporting expansion in fusion and magnetohydrodynamic energy related areas.

(e) Advanced Detection Systems for Synchrotron Radiation Studies

The very high flux, pulsed nature of synchrotron radiation will require an entirely new system of detectors. Certain applications (for example, fluorescent EXAFS) will require very fast photon counting. Other uses will require ionization detectors with their inherent amplifiers and voltage to digital conversion. All need improved stability and linearity. Development of area x-ray detectors will allow utilization of the beam for small angle scattering studies as well as other real time diffraction problems. The pulsed nature of the synchrotron beam will permit dynamic studies of material properties on time scales of the order of nanoseconds but will also require an interface and switching capabilities with the appropriate detector. Utilization of the beam for lithography and diffraction topography will require a high resolution capability such as a photoresist and a method for reading it such as electron microscopy. The Study Group recommends that an aggressive program of detector development be initiated immediately in order to meet not only current experimental needs but also to allow for the long lead time which

will be necessary to develop detectors required for the new national facility proposed at Brookhaven National Laboratory and for the expanded facility at Stanford.

(f) Supported Catalysts and Substrate Interaction

The problems of heterogeneous catalysis are very much involved with the role of the catalytic atom with the defect structure of the catalyst support. The interaction of the substrate with the catalyst has long been obvious from catalytic evidence but there has been no generally available tool for studying it. The advent of high flux sources will now make this possible by three techniques: (1) EXAFS can look at the support from the catalytic atom outwards, (2) small-angle scattering can describe the bulk void structure, and (3) scanning electron microscopy can determine surface topography of both the support and the aggregation of catalyst atoms. These determinable parameters are intimately related to the performance and lifetime of real catalytic materials and would result in a quantum jump in our understanding.

4. CATEGORY C

(a) Characterization of Coal

An understanding of the microstructure of coal is prerequisite to the understanding of coal gasification. Analytical electron microscopy is a demonstrated tool for the characterization of such structures while small-angle x-ray scattering plays a significant role in the evaluation of the specific surface of microporosity. Such research, when coupled with other analytical techniques, can make significant contributions to a basic understanding of coal.

(b) Radiation Induced Creep

Although radiation induced creep is a long standing question in the fast breeder program, almost no reliable in-pile data exist and theoretical modeling is contradictory and incomplete. It is predicted to play a major role in reactor structural behavior and our base of understanding is definitely inadequate. We therefore recommend that continued studies with all available techniques be applied to creep as induced by simulated in-pile irradiation.

(c) Membranes and Transport in Polymeric Materials

Development of improved membranes for energy efficient chemical separation processes, for separators in electrochemical batteries and fuel cells, for desalination of brackish water, and for heat exchangers may lead to significant opportunities for energy conservation. We recommend strongly that, coupled with our suggestions in Category A on the structure of polymers, considerable effort be given to understanding transport phenomena across polymeric membranes.

MATERIALS SCIENCE WORKSHOP ONLOW TEMPERATURE RESEARCH AND SUPERCONDUCTIVITY

Held April 18 to 20, 1977 at Brookhaven National Laboratory

Organizers

M. Strongin, Brookhaven National Laboratory
 W. L. Clinton, ERDA, Division of Physical Research
 J. E. Mercereau, Cal. Inst. of Technology
 J. C. Wheatley, Univ. of California, La Jolla

Participants

P. B. Allen, SUNY, Stony Brook	W. D. Gregory, Georgetown Univ.
A. C. Anderson, Univ. of Illinois	R. A. Hein, Naval Res. Lab.
M. R. Beasley, Stanford Univ.	C. Henning, ERDA-DMFE
W. H. Butler, Oak Ridge Nat'l. Lab.	E. J. Kramer, Cornell Univ.
J. Clarke, Univ. of Cal., Berkeley	D. M. Kroeger, Oak Ridge Nat'l. Lab.
J. R. Clem, Ames Lab.	R. H. Kropschot, Nat'l. Bur. of Standards
W. L. Clinton, ERDA-Physical Res.	J. E. Lukens, SUNY, Stony Brook
J. G. Cottingham, Brookhaven Nat'l. Lab.	M. B. Maple, Univ. of Cal., La Jolla
J. G. Dash, Univ. of Washington	J. E. Mercereau, Cal. Inst. of Technology
G. J. Dick, Cal. Inst. of Tech.	H. F. Morrison, Univ. of Cal., Berkeley
D. H. Douglass, Univ. of Rochester	R. Richardson, Cornell Univ.
R. C. Dynes, Bell Labs.	J. M. Rowell, Bell Labs.
D. K. Finnemore, Ames Lab.	M. Strongin, Brookhaven Nat'l. Lab.
S. Foner, MIT, Nat'l. Magnet Lab.	M. Suenaga, Brookhaven Nat'l. Lab.
E. Forsyth, Brookhaven Nat'l. Lab.	R. D. Taylor, Los Alamos Sci. Lab.
F. Y. Fradin, Argonne Nat'l. Lab.	J. M. Turner, ERDA-DMFE
J. R. Gavaler, Westinghouse	R. Voth, Nat'l. Bur. of Standards
D. M. Ginsberg, Univ. of Illinois	G. W. Webb, Univ. of Cal., La Jolla
A. L. Giorgi, Los Alamos Sci. Lab.	J. C. Wheatley, Univ. of Cal., La Jolla
A. M. Goldman, Univ. of Minnesota	M. C. Wittels, ERDA-Physical Res.
K. E. Gray, Argonne Nat'l. Lab.	

SCOPE

The workshop summarized here discussed the related areas of low temperature physics and superconductivity and their relationship to the energy technologies ERDA is developing.

In the low temperature part of the workshop traditional areas of low temperature physics were discussed, such as research on quantum fluids and other unique phenomena at low temperatures. New areas more directly related to ERDA's energy mission, where low temperature research is already starting to play an important role, were also discussed. These include surface science, nonequilibrium and non-linear phenomena, and thermophysical technology.

The superconductivity part of the workshop covered broad areas of solid state physics and the materials sciences. There were five study groups in the superconductivity area: Materials, Type-II Superconductivity, Non-equilibrium Phenomena and Superconducting Devices, General Superconductivity, and Understanding and Attaining High T_c 's.

Besides two days composed of study sessions, the first day of the workshop involved talks on the various energy technologies where superconductivity and low temperature research play a major role. The presentations covered applications of superconductors for fusion magnets, energy storage, electrical power transmission, surface science, and geophysical exploration. Other talks covered cryogenics and energy technology, refrigeration cycles, and the use of heat engines for solar heating applications.

WORKSHOP PRIORITIES

Priority One

New materials -- ternary systems, metastable alloys, new methods of preparation.
High T_c superconductivity -- intuitive chemical search for high T_c compounds, investigations of the possibilities of an excitonic mechanism of superconductivity.
Areas of low temperature physics -- thermophysical technology and novel physical systems.
Understanding the mechanism of flux pinning in superconductors -- the relationship between microstructure and J_c .
Nonequilibrium and nonlinear phenomena.
The use of SQUIDs in geophysical exploration and other areas.
Facilities for materials characterization.
Special ERDA facilities.

Priority Two

Improvement of known alloys and compounds.
Role of mechanical strain, radiation damage and instabilities on properties of superconductors.
ac losses, rf breakdown and the role of the surface.
Fundamental mechanisms that limit superconductivity.
Boundary effects.
Calculation of the coupling constant λ .

Priority Three

Radiation damage on nonsuperconducting materials that are used in radiation environments at low temperatures.
General studies of magnetism and superconductivity.
Studies of dimensionality and anisotropy.
General studies of the physical properties of materials at low temperatures.
Josephson junction research -- especially arrays.
General studies of non-phonon mechanisms of superconductivity.
Superconducting metal hydrides.

LOW TEMPERATURE RESEARCH

Study Group Members:

J. G. Dash, Chairman
 A. C. Anderson
 R. H. Kropschot
 R. Richardson
 J. C. Wheatley

A. Novel Physical Systems at Low Temperatures

The research we have selected for emphasis in this category should be supported primarily because it is fundamentally new science. It is part of the national investment for future technologies. There are exciting new discoveries still to be made in low temperature physics. There is no certainty that any of the investigations can be applied to technological advances in the short term but this is frequently the case with fundamental research. This general area was the breeding ground that produced superconductivity, an effect that only 20 years ago appeared as little more than an interesting mystery with few applications. We feel strongly that ERDA should play a role in the support of fundamental research in this area because of its close scientific relationship to some of the technologies it is trying to develop.

Some examples of physical systems that are either currently yielding, or are very likely to yield, significant new science or general physical insights are: superfluid ^3He , quantum fluids and solids; spin polarized atomic hydrogen; and composite and amorphous materials. In listing these examples we do not intend to exclude future studies of other physical systems at low temperatures. These are the subjects most interesting to this particular panel in 1977.

Superfluid ^3He is still a very new research area. It is simultaneously a spin 1 "superconductor" and an anisotropic superfluid. It has novel magnetic, transport and thermal properties and it has a variety of collective modes not found in any other substance. The fundamental question of why the transition occurs at temperatures between 1 mK and 3 mK and in various p-wave states is quite relevant to the general theoretical understanding of superconductivity. A great deal remains to be done in this system.

The area of quantum fluids and solids is also ripe for the production of new physics. We list a few examples of interesting topics in this system.

Solid ^3He undergoes a nuclear magnetic phase transition near 1 mK. Studies of this subject can be expected to produce significant advances in both theory and experiment.

Vacancy and impurity motion in both solid ^3He and solid ^4He could lead to new collective modes and possibly to a "superfluid solid".

The boundary layer of liquid ^3He has some remarkable magnetic properties at low temperatures. It may be that there is a ferromagnetic surface phase with a physical behavior that is distinctly different from the superfluidity in the bulk liquid or the nuclear magnetism of the bulk solid.

Finally, a new pairing transition may eventually be found in ^3He in dilute mixtures with liquid ^4He as the cryogenic technology develops to permit even

lower temperatures to be reached.

The system of spin polarized atomic hydrogen is an important new area. The technical problems in creating a stable polarized system are very difficult. The effort should be encouraged because of the potential new physics and chemistry that might be revealed. The unique quality that the system will provide is a new quantum statistical medium.

Amorphous materials and composite materials are systems in which little is yet understood about equilibrium properties at low temperatures. The systematic similarities found in a wide class of amorphous materials are quite striking. The interesting physical problem is how to understand microscopic disorder on a variety of length scales in order to produce theoretical models that are as successful as the Debye model of crystals or the Fermi surface descriptions of normal metals.

B. Surface Science

Surface science is at a takeoff point today, similar to Solid State Physics in the 1930's. There are strong advances in experiment, partly due to new high area uniform substrates, and partly novel applications of sensitive techniques for studying monolayers and few-layer films. Theory has developed highly detailed realistic models, with some notable successes in predicting and explaining observations. The control and characterization of surfaces and surface films are key factors in many areas of direct and indirect importance to energy technology, e.g. catalysis, corrosion, thermal accommodation and heat transfer, cryopumping, radiation damage induced wall erosion, adhesion, wetting, welding, fracture, fatigue, wear and lubrication. In addition we believe that surface physics and adsorption merits support as fundamental science, for its intrinsic interest and as a testing ground for our understanding of bulk matter.

We recommend two general areas for special encouragement and support:

1. The use of physical adsorption for surface characterization. Its special advantages are sensitivity to weak surface features on an atomic scale; faceting, growth morphology, long range crystalline order, and imperfections. There are presently available high resolution techniques for determining aspects of the substrate character from the properties of the adsorbed films, and a high probability for new inventions and improvements in the near term future.
2. The study of physical adsorption as a novel form of matter. In monolayer films of helium and other light molecular gases there are two-dimensional and substrate-ordered phases. Some of these phases are analogues of bulk matter while others can be mapped into important theoretical models. In multilayer films one can study fundamental mechanisms of nucleation, growth, and the evolution to bulk behavior.

C. Fluctuation, Nonequilibrium and Nonlinear Phenomena

Availability of new measuring and analytical methods, theoretical ideas, and computational techniques make possible significantly deeper and more detailed investigations of fluctuational phenomena and nonequilibrium/nonlinear behavior. Studies of fluctuation phenomena can probe dynamical physical and thermal processes

in materials near thermal equilibrium. Large departures from equilibrium or from linearity lead to novel phenomena in heat, mass, and charge transport which cannot be understood in terms of conventional linearized theories and which in the past have led to new technologies.

By way of description, one can include, under fluctuations, noise processes in materials, and hence in instrumentation. Research on noise processes is often facilitated by the utilization of low temperatures. The scope of investigation should even include terrestrial noise, especially as it limits the application of SQUID technology to prospecting and other geophysical studies.

Nonequilibrium behavior in superconducting metals and junctions is already under investigation. Nonlinear behavior in fluids causes strong instabilities which play an important role in heat and mass transport. A convenient mode of studying these phenomena on a laboratory scale is the utilization of cryogenic fluids.

D. Thermophysical Technology

Research in this area is intended to lie on the interface between basic thermal science and its implementation as technology. It is intended to span a temperature range from somewhat above room temperature to the lowest temperature. The end result of the work relates to the energy mission of ERDA, for example in conservation and in the utilization of low grade heat. The work itself emphasizes science, discovery, and measurement rather than specific hardware development, based on current knowledge, to solve a specific problem. Some possible lines of work, with priorities set primarily by quality of principal investigator and of proposal, are as follows: (a) Improved or conceptually new approaches to heat engines, heat pumps, and cryogenic refrigerators. This includes thermophysical studies of the working substance, especially if it is operated under novel conditions. (b) New approaches to heat and mass transfer, emphasizing especially nonlinear phenomena. Included here are thermal "superconductors" of all types and also problems in heat regeneration. (c) Novel studies of thermal insulation. (d) Fundamental work studying the thermophysical properties of composites. Such materials are of great technical importance now and should become even more so. This work leads to the development and characterization of both well-known and new materials for industrial applications.

The development of the SQUID magnetometer illustrates the principle motivating a program of Thermophysical Technology. The discovery by Josephson lead to superconducting devices having applications in geophysical prospecting, medicine, laboratory standards, and so on. However, the path from basic science to practical technology requires extensive innovation. For example, essentially nonmagnetic materials and special thermal insulation are required; a suitable refrigeration system needs development; and electromagnetic interference at extremely low levels must be controlled before such a device provides wide public benefit. Some of the problem areas have long been addressed by engineers and scientists alike. The new innovations required cut across a number of disciplines and can best be devised by basic science.

E. Theory and Modeling

It is necessary to develop and maintain a strong theoretical program as an integral part of the other elements of the Superconductivity and Low Temperature Program. The objective is to provide the fundamental understanding, prediction

techniques (such as scaling and modeling) and to provide the necessary coupling with the ultimate users -- wherever they may be. Theory and experiment must proceed in concert, theory motivating experiment and vice versa, in order to optimize productivity.

GENERAL SUPERCONDUCTIVITY

Study Group Members:

D. K. Finnemore, Chairman
 D. M. Ginsberg
 A. M. Goldman
 W. D. Gregory
 M. B. Maple
 R. D. Taylor

There is a wide scope of research necessary to bring an understanding of the multifaceted field of superconductivity. In some cases fundamental studies of problems related to device development are appropriate. In other cases, the study of new phenomena is appropriate. The need for research in selected areas is discussed briefly and an outline of topics with priorities is appended.

Boundary Effects

Boundary effects at a superconductor-normal metal interface frequently play an important part in determining the performance of devices. For example, in multifilamentary cables which are used in magnets, motors, generators, and transmission lines, the spatial variation of the superconducting order parameter near a super-normal boundary governs the configuration of quantized magnetic vortices, and therefore influences the motion of vortices and flux bundles. This motion in turn limits stabilization against quenching of the superconductivity. The fundamental understanding of these boundary effects requires various types of data, such as those coming from electron tunneling, measurements of electrical and thermal conductivity, and observations of neutron scattering to determine current and field profiles near boundaries. It is important that the properties of composite materials be determined, since the properties will yield vital information about boundary effects. This type of work will require that new methods be developed for producing a wide range of composites. Once a detailed microscopic understanding of boundary effects is acquired, it will be important to use that understanding to develop macroscopic equations, suitably averaging over microscopic variables, for engineering or design purposes. In a closely related problem, the proximity effect may be used to obtain a microscopic characterization of materials with high T_c . This has been demonstrated by the recent observation of the signature of the phonon spectrum of a superconductor in the I-V characteristic of a tunnel junction in which the tunneling was into the normal half of a superconductor normal proximity sandwich. With further experimental and theoretical work it may be possible to develop this technique to yield quantitative data for proximity induced superconductors.

Time-Dependent Superconductivity

Many superconducting devices of the future will require operation under conditions which are significantly removed from equilibrium. It is, therefore, important that new experimental and theoretical results in this area be extended to study the dynamics of phenomena such as ac losses and relaxation effects. This study must be based on a comprehensive framework within which time-dependent and nonequilibrium phenomena can be examined. This subject is fundamental in that it requires the combination of the full theory of superconductivity with nonequilibrium

statistical mechanics. The study of superconductors away from equilibrium may be the best quantitative probe of nonequilibrium statistical mechanics, given the high state of development of the theory of superconductivity and the control of the experimental configuration possible using superconducting materials and low temperatures. An important goal of research in this area is the development of macroscopic partial differential equations for time-dependent phenomena which can quantitatively characterize ac loss phenomena and serve as engineering design equations. With sufficiently general tools, a diversity of applications might be addressed, from power lines to the generation and detection of radiation by arrays of Josephson junctions.

The study of fluctuation effects associated with the onset of superconductive order in homogeneous systems can be developed into a probe of the nonlinear phenomena associated with phase transitions. Such studies may be used to test the renormalization group approach to phase transitions. The study of fluctuations, which have been well-characterized in the past, can serve as a diagnostic tool in the investigations of anisotropic systems and systems of reduced dimensionality. From a technological point of view, continued development of the understanding of noise and fluctuation phenomena are important to the optimization of the performance of superconducting devices which may evolve from the SQUID.

Magnetism and Superconductivity

Theoretical and experimental investigations of the interaction between superconductivity and magnetism are valuable in establishing a fundamental understanding of both phenomena. Magnetic ions can have dramatic effects on the properties of superconductors. Spin-flip scattering depresses T_C sharply, but antiferromagnetic coupling between impurity atoms and conduction electrons can cancel the effect of an externally applied field, raising H_{C2} very significantly, even by 100 kgauss or more. There is theoretical and experimental evidence which strongly suggests that the virtual excitation of crystal field levels can be a fundamental interaction which causes superconductivity. Superconducting ternary rare earth compounds provide an excellent new opportunity to study the influence of long-range ordering of magnetic ions on superconductivity. The effect of magnetic ions on the transport properties of superconductors is largely unexplored, and deserves attention.

Microscopically Inhomogeneous Systems

Real superconducting devices frequently have characteristics which are affected significantly by microscopic inhomogeneities. For example, the surfaces of superconducting cavities have a surface impedance (energy loss) which indicates the presence of networks or layers of oxides. In addition, the effects of electron and phonon scattering during transport in such inhomogeneous media must be known to understand the limitations of many devices, such as SQUIDs. Percolation theory and effective medium theory are being applied to these problems, but this theoretical work is in its very early stages and should be extended, in concert with transport experiments.

Nonlinear Effects

The whole area of superconductivity in regimes where nonlinear effects are important is slowly beginning to open for study and totally new effects may be observed. For example, solitary wave propagation may occur in Josephson junction

strips. This sort of phenomena needs further study.

Superconducting Metal Hydrides

The superconducting hydrides and deuterides are of great interest because there are large variations in T_c which can be controlled continuously and systematically by changing experimental parameters such as hydrogen concentration, isotopic mass, and alloy composition. In addition, the band structures are known well enough that there is a reasonable hope of calculating the fundamental effect of zero point motion of the hydrogen, anharmonicity, the breakdown of the Born-Oppenheimer approximation, and spin fluctuations. This is an excellent prototype system for developing a thorough understanding of the fundamental interactions which control the occurrence of superconductivity.

Dimensionality and Anisotropy

The development of useful devices often requires an understanding of the effects of limited dimensionality. This understanding is important in the development of devices such as microbridges or devices using thin films, layered compounds, or submicron particles. The utilization of real materials can be made possible by an understanding of the role of anisotropy, and even of the detailed band structure. Among materials which deserve further investigation are single crystal metals, polymers and possible superconducting organometallic compounds.

Mechanisms for Superconductivity

The search for new mechanisms for the pairing of superconducting electrons constitutes a problem of both fundamental interest and immense potential application to energy technology through the possible development of structures with superior superconductive properties (e.g., higher values of T_c , H_{c2} , J_c , etc.). These mechanisms include excitons, triplet pairing, virtual coulomb excitations of crystal field levels and the already established electron-phonon interaction. Although the excitonic mechanisms have attracted a great deal of interest in recent years, only a few systems have been explored experimentally. Critical experiments on known but unusual superconducting systems, such as layered compounds and doped semiconductors, are needed to ascertain whether the excitonic mechanism is involved in their superconductivity. Realistic theoretical calculations are needed to guide exploratory experimental work on new systems.

In view of the recently recognized role of triplet spin pairing in superfluid He^3 , it appears to be fruitful and timely to explore this mechanism within the context of superconductivity. Virtual coulomb excitation of crystal field levels has recently been proposed on theoretical grounds to be a viable pairing mechanism, and is also worthy of investigation. Further systematic studies of the electron-phonon interaction with respect to model or practical superconducting systems are highly desirable.

Very High Pressure Studies

The recent development of inexpensive diamond anvil presses provides a valuable opportunity for a wide-ranging study of superconductors at pressures in the 100 to 300 kilobar range. This type of research may lead to the discovery of new superconducting phases and to an understanding of the volume dependence of

superconducting interactions. Materials with higher T_c may be discovered as a result of such investigations.

Special Experimental Facilities

Some aspects of superconductivity research are vitally dependent on major facilities which provide tools such as synchrotron radiation or neutron scattering. For example, in the A-15 compounds, local disorder has a strong effect on the superconducting properties, and it is essential to determine the detailed nature of this disorder to understand the mechanisms which are operative. Synchrotron radiation (with EXAFS) provides a probe to obtain this microscopic information. In another area, it is important to understand the magnetic field and current distribution in high- J_c superconducting materials. Small angle neutron scattering provides a probe for samples which have a periodic array of superconducting filaments.

Central facilities should be provided at a few places for producing and characterizing samples. These facilities would be available to a wide range of visiting scientist users. They should probably be established at national laboratories; the provision of operating personnel as well as space and equipment is required. Provision should be made for on-site in situ experimentation. A formal survey of university, government, and industrial laboratories where special facilities might be available to outsiders would be helpful and would help avoid unnecessary duplication of efforts in the future.

GENERAL SUPERCONDUCTIVITY*

I. Boundary Effects

- 1* Composites
- 1* Pinning of vortices at interfaces
- 1 Proximity effect tunneling
- 1* Development of macroscopic equations for engineering design
- 2* Stabilization
- 2 Electron and phonon transmission through interfaces
- 3* Joints or welds between superconductors
- 3 Super-Normal-Superconductor (SNS) junctions
- 2 Growth of new crystallographic phases by epitaxy
- 2 Surfaces, rf cavities

II. Time-Dependent Superconductivity

- 1 Nonequilibrium phenomena
- 1 Development of macroscopic equations for engineering design
- 2 Fluctuations
- 3* ac losses
- 3 Arrays of Josephson junctions

III. Magnetism and Superconductivity

- 1* Magnetic impurities including enhancement of H_{c2}
- 1 Coexistence of superconductivity and magnetic order
- 2 Effect of crystal fields on superconducting properties

IV. Microscopically Inhomogeneous Materials

- 1 Effective medium theory and percolation theory
- 2 Amorphous materials
- 3* Effects of strain

V. 2* Nonlinear effects

VI. Superconducting Metal Hydrides

- 2* Enhancement of T_c
- 2* Tunneling spectroscopy
- 2* Isotope effect mechanisms

VII. Dimensionality and Anisotropy

- 2 Band structure and energy gap anisotropy
- 2 Restricted dimensionality; films and layer compounds, microbridges, submicron particles
- 3 Organometallics and polymers

VIII. Mechanisms for Superconductivity

- 1 Excitons
- 1 Triplet pairing
- 2 Virtual excitation of crystal field levels
- 3 Electron phonon interaction
- 1* Yet to be discovered

IX. Very High Pressure Studies (0.1 to 1.0 megabars)

- 2 Unusual superconducting phases

X. Special Experimental Facilities

- 1* EXAFS
- 2 Small angle neutron scattering for distribution of currents and fields in superconductors
- 1* Neutron studies of phonon dispersion curves and linewidths
- 1* Sample preparation and characterization

*In this priority list (1 high, 3 low) the stars indicate unusual energy relevance.

NONEQUILIBRIUM SUPERCONDUCTIVITY AND SUPERCONDUCTING DEVICES

Study Group Members:

J. Clarke, Chairman
 G. J. Dick
 K. E. Gray
 J. E. Lukens
 J. Mercereau
 H. F. Morrison
 J. M. Rowell

This subject has been broken down into five sections: nonequilibrium superconductivity, superconducting electronics and techniques, quasiparticle tunnel junctions, superconducting cavities, and materials and fabrication.

NONEQUILIBRIUM SUPERCONDUCTIVITY

Nonequilibrium phenomena in superconductors currently represent one of the most interesting and important basic research problems in superconductivity. Since most applications of superconductivity involve a nonequilibrium state, the results have implications beyond basic physics. There is a need for more experimental and theoretical work.

Superconductors can be perturbed from equilibrium by, for example, quasiparticle injection by tunneling or passage of a current across a normal-superconductor interface, by electromagnetic irradiation, by a thermal gradient, by exceeding the critical current of a microbridge, or by pulsed magnetic fields. For sufficiently large perturbations, the superconductor is driven into the normal state.

The primary interest is in the rate of the relaxation processes. A major problem is the removal of the perturbation energy by phonon transport across the superconductor surface. Coupled with this is the necessity to ensure that the effects are not due to simple heating. An extension of measurements to superconductors such as Nb and Nb₃Sn should be strongly encouraged. Three examples of nonequilibrium situations in larger systems worthy of study are the fact that surface fields considerably in excess of H_{c1} can be obtained in rf cavities without flux penetration; the thermal/magnetic instabilities of magnet windings where detailed studies of heat flow and boundary resistance in realistic geometries would be of value; and the fast transition from the superconducting to the normal state of thin films, which has promise both as a power switch and as a magnet protective device.

SUPERCONDUCTING ELECTRONICS AND TECHNIQUES

SQUIDS

SQUIDS (Superconducting Quantum Interference Devices) have been developed into reliable instruments for the measurement of very small changes in magnetic field (10^{-14} T Hz^{-1/2}) and magnetic field gradient (10^{-13} T m⁻¹ Hz^{-1/2}), for the sensitive measurement of magnetic susceptibilities (10^{-9} MKS) and for the measurement of tiny voltages (10^{-15} V Hz^{-1/2}). The present generation of SQUIDS

probably has sufficient sensitivity for most applications except gradiometry: There is a well-defined need for gradiometers with a sensitivity of 10^{-15} to 10^{-14} T m⁻¹ Hz^{-1/2}, for example, in geophysical measurements. SQUIDs and gradiometers should make much more extensive use of the narrow linewidth (1 μ m or less) thin-film techniques available from the semiconductor industry. These techniques are suitable for the mass production of SQUIDs, and should also result in high reliability, particularly if an all-niobium technology is used. SQUIDs made from superconductors with a high transition temperature (for example, Nb₃Sn) should be developed. These devices could be operated at the temperatures of 12 K or higher that should soon be available from closed-cycle refrigerators.

The applications of SQUIDs are numerous and important. SQUID magnetometers and gradiometers should be used in surveying for geothermal sources and mineral deposits using both active and passive electromagnetic techniques. A second geophysical application is to monitor possible resistance and magnetization changes along a fault that may be precursors to an earthquake. SQUIDs could also measure changes in the magnetic moment of molecules adsorbed on the surface of a catalyst. SQUIDs should be more widely used in biomedical applications.

High Frequency Electronics Applications

To realize the promise of Josephson junctions as millimeter and submillimeter detectors, mixers and generators, the single most important problem is to understand the upper frequency limits of the various device geometries. Very small, high current density, low capacitance tunnel junctions are needed in this application. For inherently low capacitance junctions such as microbridges, it is important to understand the fundamental limitations imposed by heating and relaxation processes.

The replacement of a single junction with an array may lead to significant improvements in the performance of Josephson devices at high frequencies. The recent application of fabrication techniques from the semiconductor industry to arrays has solved many problems in this area. Coherent arrays may also achieve the higher power and narrower linewidth required for Josephson generators to be useful. For mixers and amplifiers, the impedance matching properties of non-coherent arrays appear useful.

Josephson detectors and mixers are subject to strong competition from other superconducting devices, notably the super-Schottky diode and the bolometer.

The operation of the super-Schottky diode, which utilizes single particle rather than pair tunneling, needs to be extended to higher frequencies, and its operating limits explored. In our view the present level of effort should be sufficient to achieve this. At present, the superconducting bolometer is the most sensitive broad-band far infrared detector. This device should be more widely exploited.

Computer Elements

Josephson junctions are in use as high-speed (10^{-10} sec) low dissipation (10^{-15} J) storage and logic elements for computers. IBM has mounted a very large effort in this area. However, there is a need for continuing research into

both the basic circuit elements and the configurations in which these elements may be optimally coupled together. The ultimate goal of this research is to produce a very compact ultrahigh speed computer. It is our feeling that smaller groups would be encouraged to enter this field if recent results from large laboratories were disseminated promptly.

Superconducting Gravimeter

A superconducting gravimeter with very low long-term drift has been developed for measuring tiny changes (10^{-10}) in the local gravitational constant. This instrument has potential application in monitoring the depletion of geothermal sources and in detecting small changes in ground level that may precede an earthquake. We recommend that instruments of this type be more widely exploited.

Refrigeration

It is to be hoped that several superconducting devices that operate at 12 K or higher will be available within a few years. There is therefore a strong need for a closed-cycle refrigerator capable of attaining this temperature that has a very low level of magnetic, electrical, and mechanical noise. This development would have a major impact on the wide-scale use of superconducting devices.

QUASIPARTICLE TUNNEL JUNCTIONS

Inelastic Tunneling Spectroscopy

Inelastic tunneling, which probes the vibrational spectrum of molecules trapped in the tunnel oxide (but only when the barrier is aluminum oxide?), is an existing tool which is being developed for catalysis-related studies. Good progress is being made in this development.

Elastic Tunneling Spectroscopy

Quasiparticle tunneling, by which the energy gap and electron-phonon coupling strength in superconductors can be measured, is well understood. Its use has been confined largely to soft metals and it should be applied much more broadly to transition metals, and to their alloys and compounds, where the information obtained would be compared with the rapidly increasing theoretical understanding of these materials. Some obstacles to this are the materials and surface problems to be discussed below.

Phonon Generation and Detection

Tunnel junctions have been used to generate and detect phonons of twice the gap energy ($0.5 < 2\Delta < 7$ meV). This technique deserves more utilization, for example to study phonon transport through solids, liquids, solid/solid and solid/liquid interfaces (the liquid being helium or hydrogen).

SUPERCONDUCTING CAVITIES

High Q superconducting resonators have several practical applications. The most important use, and the one that has principally prompted their development, is for the construction of particle accelerators with much lower power requirements

and better energy resolution than is possible using conventional techniques. The development of practical machines, however, has been held back largely by the inability to achieve in full scale resonators the very high fields and Q's which have been achieved in small, pure niobium cavities. This problem is being dealt with in the machines presently built or planned by accepting a level of performance in the superconducting surface which is far below its ultimate capability. Even at those lower levels, however, a reduction in total accelerator power consumption by a factor of ten can be achieved, and on this basis several development projects for heavy ion boosters are presently underway. Other applications of cavities include their use as very stable frequency sources, and their possible use to store or transmit microwave energy or to generate microwave energy efficiently using parametric amplification.

The most exciting materials development relating to cavity applications is the possibility that much higher microwave fields than are presently available might be obtained through the use of superheating in type II materials. Research is needed toward an understanding of the mechanism of flux penetration in these materials, and, on a more mundane level, toward the construction of supercurrent carrying joints.

In a longer time scale, cavity development might yield the highly efficient accelerators which have been proposed for nuclear fuel generation or fusion pellet ignition by heavy ions.

MATERIALS AND FABRICATION

A pervasive and outstanding problem, which has limited our progress in the reliable operation of cavities, transmission lines, SQUIDs and computers, and in the use of tunneling for studies of transition metals and A-15's, is the lack of basic knowledge of the surface properties and oxidation of these materials.

For example, niobium, which has the high H_{c1} desirable for a cavity, has not reproducibly given the expected high performance because of the lack of control over surface properties. Losses in a transmission line tape have been shown to depend strongly on surface morphology. Both SQUIDs (using tunnel junctions) and computers ideally need a metallization which can be evaporated onto a substrate at temperatures below 100°C, adheres well to insulating substrates, resists abrasion, forms an insulating oxide reliably and uniformly, and produces tunnel junctions with "clean" characteristics which are stable in time and with thermal cycling. Tunneling studies of transition metals, alloys and compounds often indicate that the surface of the materials (defined in this context as a few coherence lengths) has a depressed energy gap and T_c compared to the bulk, and hence bulk parameters cannot be determined.

To solve these problems, chemically and structurally well-characterized surfaces of transition metals, alloys and compounds, including new materials such as Chevrel phases, must be studied, not only in the "clean" state but as a function of oxidation and contamination, for example to parallel the condition of a cavity surface. This requires use of well-developed surface analysis tools (electron microscopy, Rutherford backscattering, Auger, LEED). As a function of surface condition and morphology, the energy gap, flux entry field and losses as a function of magnetic field should be known, preferably on the same surface.

A less serious problem arises in the fabrication of SQUIDs, arrays of junctions, and computer circuits, where it is desirable to achieve small tunnel junctions ($1\text{ }\mu\text{m} \times 1\text{ }\mu\text{m}$). These dimensions can be achieved now using lithography techniques developed in the semiconductor industry, but some encouragement seems necessary to introduce these techniques to groups making superconducting instruments.

PRINCIPAL RECOMMENDATIONS

In our view, the highest research priorities in this field are:

- (1) The continuation of experimental and theoretical work on nonequilibrium superconductivity to gain a deeper knowledge of the fundamental physics involved.
- (2) Research on the surface properties and problems of superconducting materials.
- (3) Continued development of SQUID-based devices, and particularly their application to geophysical measurements and to other areas.

MATERIALS

Study Group Members:

R. A. Hein, Cochairman
 M. Suenaga, Cochairman
 M. R. Beasley
 R. C. Dynes
 J. R. Gavaler
 A. L. Giorgi
 C. Henning
 G. Webb

Prologue

This report presents the results of two days of discussion on materials research germane to low temperature physics and technologies. Our workshop was directed to place emphasis on superconducting materials. Topics listed in the summary and our conclusions are the ones that survived free and lively exchanges among the panel members as to their relative importance and merits to the overall program of the Division of Basic Energy Science and to the scientific community at large. The priority ratings were determined by written ballots.

1. Introduction

Superconductivity is both a science and a technology. Recognizing this duality of interest and being sensitive to the mission of ERDA, this report considers tasks which are of both technological and scientific importance. It is the consensus of this panel that superconducting technology will have its greatest impact in the area of magnetic confinement for fusion reactors. Other clearly recognizable important energy related areas are those concerned with the generation, storage, transmission and conversion of electrical power. Superconductivity will also impact on those technologies which can exploit the unique quantum properties of the superconducting state, i.e. Josephson devices for sensors, switches, etc.

In this report we had restricted our discussions to those nine task areas deemed to be the most important from both a scientific and technological point of view. The priorities in these 8 selected areas are noted with area headings while the Appendix defines all symbols used in this report.

1.0 New Materials (High Technological and Scientific Interest)

Concurrent with efforts to improve the technologically important parameters of known superconductors, it is strongly recommended that a well planned, balanced program be supported to investigate the possibility of synthesizing new metallurgical phases of superior superconducting properties. For example, recent successes with other ternary systems XRh_4B_4 , where X=Rare Earth element, has once again highlighted a possible close correlation between magnetic ordering and superconductivity in homogeneous phases. One cannot mention new superconducting phases without immediately thinking about metastable phases. This has been emphasized by recent data with regard to the high T_c (A-15) phase of Nb_3Ge . It should be strongly pointed out that synthesis of new materials is not only relevant to the technological applications, but also extremely valuable to understanding superconductivity.

2.0 Improvements of Technologically Important Parameters of Known Superconducting Alloys and Compounds (High Technological Interest)

In light of the pressing needs of ERDA's ongoing fusion research, we strongly recommend that the BES support efforts in basic metallurgical studies leading to useful conductors of the higher T_c and H_{c2} superconductors. To do this one must delineate those chemical, physical and processing variables which improve $J_c(H)$, T_c , and $H_{c2}(T)$. Particular attention should be focused on basic metallurgical understanding of those processing techniques which are compatible with the ultimate commercial production of useful lengths of multifilament conductors.

Based on the minimal acceptable design goal of a 12T magnetic field (acting on the conductor), we believe the A-15 compounds should be given highest priority; however, due to their remarkably high J_c and H_{c2} values at 4.2 K, we believe that the B1 compounds, the Chevral phases, and the Laves phases should also be exploited to ascertain the true potential of useful conductors of such compounds.

3.0 Fundamental Limits to Superconductivity (High Scientific Interest)

Here we mean identification and quantitative understanding of the fundamental mechanisms (including real metal effects) that limit the physical properties of superconductors (e.g. T_c , H_{c2} , J_c , radio frequency, and power frequency losses) and their relation to material parameters both physical and chemical. Some concrete examples in this area are: the relationship between T_c and lattice instabilities, between H_{c2} and Pauli paramagnetic limiting and Fermi surface anisotropy, and say between J_c and sample microstructure. Progress toward this goal requires close coupling between materials work and theory. It can be expected to lead to a firmer scientific base for the applications of superconductivity, new generalizations and concepts in solid state physics, and new insights into profitable areas for the search of new superconducting materials.

4.0 Structural Instabilities and Mechanical Properties (High Technological and Scientific Interest)

Effects of lattice softening and structural instabilities on the superconducting properties of many high performance materials of current interest are not well understood. This overall problem is further complicated when one considers these materials as components of composite conductors. Work, both theoretical and experimental, should be encouraged to understand the role of stress, strain and structural instabilities upon J_c and H_{c2} of composite conductors. These effects constitute a practical problem as well as a problem of high intrinsic scientific value.

5.0 Low Field ($H_{c2} < H < H_c$) Properties (High Technological Interest)

Recent experimental results with several A-15 compounds have clearly shown that the magnitude of surface ac magnetic fields at which losses first increase are not governed by the magnitude of H_{c1} as previously believed. This has significant consequences to the viability of ac transmission lines and has opened the possibility of using such materials as the basis for microwave pulse power supplies and accelerators using high Q cavities. In addition the scientific value of understanding the basic cause for such behavior must be highly rated as it relates to our basic concepts involving fluxoid creation and propagation in the mixed state.

6.0 Radiation Damage

It is well documented that high T_c compounds of the A-15 structure are seriously degraded when subjected to neutron irradiation of fluences in excess of 10^{18} n/cm². What is the cause for this? What can we do to lessen the decrease in T_c and $J_c(H)$? These questions are of paramount scientific interest as far as our understanding of the A-15 compounds are concerned and enter into the design options of fusion systems. Thus the group strongly urges that ERDA continue to support experimental and theoretical efforts in this area.

7.0 Electronic Materials

High sensitivity detectors and high speed electronic elements utilizing the quantum interference nature of superconductivity have widespread applicability. These tunnel junctions and weak link Josephson devices would demonstrate improved reliability and could be used in connection with closed cycle refrigerators if higher T_c and d-band materials (for example Nb or A-15 materials) were used. We recommend a materials effort directed toward the understanding and fabrication of devices of these materials. This would involve studying and understanding the oxidation processes of harder materials and the fabrication of weak links and tunnel junctions in a reliable way.

8.0 Nonsuperconducting Materials (Problems and Interfaces)

The group recognizes that the technological exploitation of superconductivity requires the low temperature behavior of nonsuperconducting components be studied and understood. Here we have reference to: radiation damage in metals and insulators, dielectric properties, mechanical properties, thermal transport phenomena, etc. Problems of interfacing nonsuperconducting and superconducting materials (i.e. proximity effect) must be addressed.

2. Materials Synthesis/Process/Characterization

Recent use of newly developed techniques have led to advances in preparing non-equilibrium phases some of which have interesting and/or improved superconducting properties. It is the consensus of the group that BES should strongly support efforts to develop new methods and improve existing methods of preparing new materials or processing known materials for particular applications. These include chemical deposition (CVD), physical vapor deposition (PVD), precipitation growth from a non-aqueous solution, epitaxial growth, ion implantation, high pressure-high temperature synthesis, radiation enhanced diffusion, powder metallurgy a la Tsuei and others.

Developing new methods of preparation and processing without at the same time developing truly adequate characterization facilities would indeed be shortsighted. It is a common complaint of materials scientists that the cost of characterizing their samples, in order to relate physical parameters to observed superconducting properties, is a major concern. It is strongly recommended that ERDA support the acquisition of capital equipment to allow ongoing programs to better characterize their samples.

3. Summary

This report condenses two days of discussions into nine briefly described task

areas. The panel regards all nine areas to be of importance and worthy of support by the Division of Basic Energy Sciences. At the concluding session of the workshop, the panel members were presented with a matrix scheme listing these areas and were asked to rank them along two independent lines (1) technological importance and (2) scientific interest. Results of this rating are noted in the section headings.

Epilogue

During the course of these two and one-half day discussions it became quite apparent that there exists a deep, genuine, and unusual concern about the escalating cost of materials characterizations. Service charges are such that many materials scientists are unable to take advantage of state-of-the-art techniques let alone to develop advanced techniques. What is drastically required is funds for capital equipment to allow facilities to be expanded and developed.

APPENDIX I

A15	Strukturbericht notation for the cubic B-tungsten phase.
B1	Strukturbericht notation for the cubic NaCl phase.
H_c	Thermodynamical critical magnetic field.
H_{c1}	Lower critical magnetic field.
H_{c2}	Upper critical magnetic field.
J_c	Critical current density.
K	Temperature, kelvin scale.
T	Magnetic field in tesla ($T=10,000$ gauss).
T_c	Superconducting transition temperature in zero magnetic field.

TYPE-II SUPERCONDUCTIVITY

Study Group Members:

John R. Clem, Chairman
 Simon Foner
 Edward J. Kramer
 D. M. Kroeger
 James M. Turner

A. Introduction

The applications of type-II superconducting materials to major energy technologies involve large systems which operate at both high and low fields. Generation and conversion of electrical energy requires large-volume, high-field superconducting solenoids for fusion devices, superconducting generators and motors, MHD generators, and magnetic energy storage systems for peak shaving. Upgrading of the Fermilab accelerator with the Doubler would not have been economically feasible without type-II superconductors, nor would the numerous bubble chamber magnets that have been constructed for basic high energy physics research. Applications of large-volume superconducting magnets to high-speed transportation are being developed largely in Europe and Japan, and applications of magnetic filtration to sewage treatment and ore beneficiation are feasible. Electric power transmission over large distances can be made with superconducting ac or dc cables operating at relatively low magnetic fields. Other applications of type-II superconducting materials will occur in geophysical exploration and medicine. In all large-scale applications, the type-II superconducting material will be the key component in a composite conductor, and its primary function will be to carry a large electrical current. Although superconducting multifilamentary composite conductors are commercially available, the properties of such conductors have not been fully optimized. To realize the full potential of type-II superconductivity in energy-related applications, a vigorous research program is required.

The technologically most important properties of type-II superconducting materials are critical current density J_c ; upper critical field H_{c2} ; critical temperature T_c ; ac losses; capability of formation in a composite and ease of fabrication; ductility; mechanical, electrical, and thermal stability; and susceptibility to radiation damage. Because the most interesting open fundamental questions in this research area involve all the above properties, there is little conflict between the desire to answer such questions and the need to solve practical problems. Fundamental advances are likely to lead quickly to more effective use of superconducting materials in major energy technologies.

In Section B we discuss, in order of priority, those open areas of basic research that we feel to be currently of greatest importance in the field of type-II superconductivity. At the first level of priority we place research leading to an improved understanding of the fundamental aspects of the critical current density J_c and flux pinning. At a second level of priority we place basic research on (a) losses, which are intimately connected with J_c , (b) composite superconductors, and (c) mechanical properties of type-II superconductors, with roughly equal emphasis. At a third level of priority we place research on H_{c2} and T_c . Several other topics, not included in these priority areas, also should be supported, as discussed in the final paragraph.

B. Priority Research Areas

1. Critical Current Density J_c and Flux Pinning

The primary goal here should be to understand flux pinning in superconductors. With such understanding one could predict the ultimate J_c obtainable in practical materials and have a guide to the microstructural manipulations necessary to achieve this J_c . There are two parts to this problem: to determine the elementary pinning force f_p between a single lattice defect (pin) and the flux-line lattice (FLL) and to sum the various f_p 's with proper statistics to arrive at the total pinning force and thus J_c . The summation problem is the more difficult of the two parts, because it involves taking account of the elastic and plastic deformations of the FLL caused by the pins. Recent advances in small angle neutron scattering, which allow one to obtain direct information on FLL structure and elasticity, should be exploited, as should new theoretical methods for computing FLL elastic constants. Other experimental techniques (e.g. decoration) for examining the FLL structure and the flux distribution on a microscopic scale should be developed. Flux-flow noise experiments also have potential to give insight into this problem. Both first principles theories and phenomenological models should be pursued. Computer modeling experiments, which have solved analogous problems in metal plasticity, also should be encouraged.

Experiments on flux pinning in model systems offer the most important source of information. For example, measurements of J_c in bicrystals and materials with controlled grain boundary structures have just become available. Experiments on regular arrays of pinning defects, e.g., regular hole arrays produced by electron lithography/ion etching methods in films, give both a direct measure of f_p (with no summation complications) at certain fields and well-defined tests of summation theories at other fields. Radiation damage techniques either in combination with lithographic masking or to produce void lattices may be useful in producing model flux-pinning structures. It should be emphasized that results on model pinning systems in low-field, low-pinning superconductors, e.g., granular Al films, are expected to be highly relevant to high-field, high-pinning superconductors.

The stability of superconductors to flux jumps and current-induced breakdown is an important problem for which there is also incomplete fundamental understanding. To date, technical solutions of this problem have involved fabrication of multifilamentary superconductor-copper composites, reduction of the superconducting filament size, and prevention of conductor motion. Research on fundamental instability mechanisms should be funded, but at a lower priority than the flux-pinning research above.

2. Losses

Encouragement should be given to research seeking a fundamental understanding of energy loss mechanisms in type-II superconductors. Low losses are critically important to several energy-related applications of superconductivity, including ac superconducting cables for electric power transmission and pulsed magnets for magnetic fusion. Experimental tests of critical state model calculations of ac losses are needed. Such research should examine the influence of surface morphology and composition, which recently have been observed to affect strongly the ac losses of Nb_3Sn and Nb_3Ge and the cavity breakdown fields of type-II alloys. Work should be done to determine whether such effects are best described in terms of

enhanced bulk pinning near the surfaces, Bean-Livingston barriers, surface superheating fields, or high values of the lower critical field H_{c1} . Work should be carried out to develop new models for those cases in which the critical state approach cannot successfully account for the measured ac losses. As an example, research should be done to understand the ac losses produced when vortex displacements are small by comparison with the penetration depth or the range of the elementary interaction force between vortices and pinning sites. Attention also should be given to methods of calculating losses when the flux entering the specimen is spatially inhomogeneous. Superconductors containing nonparallel vortices or helical vortices of different pitch recently have been found to have smaller ac losses as well as larger dc critical currents. These results are not understood, but it has been suggested that vortex instabilities and flux cutting play important roles. Research should be carried out to understand this puzzling behavior.

3. Composite Superconductors

Conductors for high-current applications are invariably composite conductors, consisting of superconducting filaments or layers embedded in a normal matrix in order to achieve thermal and electrical stability. To optimize the properties of composite superconductors, investigations of critical currents and ac losses should be supported along with research on conductor stability. An improved microscopic theory of the proximity effect needs to be developed for application to such systems, and superconducting-normal-superconducting tunneling experiments should be carried out in support of this work. Various methods for composite and ribbon fabrication, such as directional solidification, powder metallurgy, and melt spinning, should be developed, and the investigation of new techniques should be encouraged. Additional research should be carried out on the effects of radiation upon composite superconductors. Because conventional insulators used in conjunction with cryogenic and superconducting structures are much more susceptible to radiation damage than the superconducting materials, the effects of radiation damage on insulators at low temperatures should be pursued.

4. Mechanical Properties

One of the primary limitations anticipated in the performance of large, high-field magnets is the sensitivity of the critical parameters (J_c , T_c , and H_{c2}) of the conductors to mechanical strain. At present, multifilamentary composite conductors containing an inherently brittle A-15 structure superconductor often exhibit serious degradation of J_c for tensile strains as small as 0.2 to 0.5%. These strains are smaller than those expected from handling, winding, and energizing the magnet. For relatively small strains, a portion of the J_c -degradation may be recovered when the load is removed. Effects of stress upon T_c have been reported, and in some cases J_c is increased by small strains, suggesting that at least a portion of the effect of stress upon J_c is not caused by simple cracking of the superconductor. Efforts should be made to understand these effects. Measurements of the mechanical properties and of the effects of strain upon the superconducting properties of composite conductors are needed. Careful analyses of the states of stress of the superconducting composite, for example, by x-ray lattice parameter measurements, should be made. These stresses may arise both from the externally applied stress and from differences in the thermal contraction of the various components of the composite. A search for new high-field superconductors which have low strain sensitivity should be pursued. In order to determine the fundamental mechanical as well as other properties, good single-crystal

superconductors must be grown. The interaction between the well-known lattice instability of A-15 materials, their mechanical properties, and their strain sensitivity should be investigated.

5. H_{c2} and T_c

In addition to increasing the field and temperature range over which a superconductor is useful, increasing H_{c2} and T_c also increases the flux pinning and corresponding J_c . Although theories for H_{c2} in type-II superconductors are adequate for semiquantitative predictions of $H_{c2}(T)$, band structure effects have not been included for some of the most interesting high- H_{c2} materials. High accuracy band calculations should be carried out in order to predict the anisotropy of H_{c2} for high-field superconductors. Measurements of $H_{c2}(T)$ and its anisotropy in selected cubic and noncubic single crystals should be extended for comparison with theory. Very few suitable single crystals exist, and an effort to grow clean well-characterized crystals should be supported. Current models suggest that high anisotropy of H_{c2} results in large flux pinning by grain boundaries. Often high-field superconductors are paramagnetically limited. Improvements in H_{c2} should be achievable by adding controlled impurities, which increase the resistivity or spin-orbit scattering of the material. Such studies should be made.

Radiation damage in type-II superconductors affects the critical properties (J_c , T_c , and H_{c2}). Controlled irradiation studies may be used as a tool in understanding the effects of crystallographic order and lattice defects on flux pinning (J_c), T_c , and H_{c2} .

6. Other Topics

The search for interesting new type-II superconducting materials should be continued, and the properties of such materials should be measured. Experiments on the flux-line lattice structure and H_{c2} of materials with reduced dimensionality, such as layer-structure or quasi-one-dimensional conductors, should be carried out in conjunction with the development of new theoretical approaches for such materials. A theory of time-dependent superconductivity valid throughout the mixed state needs to be developed for the calculation of various transport properties during vortex motion. It is likely that such a theory will evolve from related studies of non-equilibrium phenomena in superconductors.

UNDERSTANDING AND ATTAINING HIGH T_C 's

Study Group Members:

P. B. Allen, Chairman
W. Butler
D. H. Douglass
F. Y. Fradin
M. Strongin

A. Introduction - Our Present Status

Finding materials with higher superconducting transition temperatures, T_C 's, is an important long-range technological goal, and couples to the scientific problem of fundamental understanding of T_C 's. Improved understanding has already motivated advances in band theory, phonon spectroscopy, and in fact almost every area of solid state science. Coordination between theory and experiment has been quite close in this effort. Thus, a continued strong effort in understanding T_C can and should be justified both in terms of the beneficial impact on fundamental science, as well as in terms of increasing T_C .

I. Fundamental Understanding

Microscopic theory divides into two aspects: (1) explaining the coupling constants (λ , θ_D , μ^*) which determine T_C , and (2) understanding how T_C depends on these coupling constants. The latter problem is now well understood (except for questions of anisotropy, and the possibility of other mechanisms beside electron-phonon coupling). Our present understanding leads to optimism about prospects for higher T_C 's: if the coupling constant λ can be increased, T_C will go up. Tunneling spectroscopy in s-p metals has been instrumental in deriving and confirming these insights.

The first aspect, understanding the coupling constant λ , is a difficult and important problem. It is necessary first that the electronic band structure be well known. This has now been accomplished for d-band elements by combining computational theory and experiments such as deHaas-van Alphen effect.

The relation between band structure and λ has received much attention in the last five years, and is now nearly solved for d-band elements (with uncertainties of order 20% which translate into 40% uncertainties in T_C). More important, the chemical factors which influence trends in the periodic table have been identified. Unfortunately, this advanced state of understanding is confined to materials with $T_C < 10$ K.

II. Empirical Strategies

The majority of all binary alloys and compounds that can be prepared by standard metallurgical techniques has now been studied. By this method, T_C 's up to 20 K have been found. Although theoretical understanding of the systematics of λ is absent, helpful empirical rules (such as correlation between T_C and e/a ratio) have helped guide the search. Recently new methods of preparation (sputtering, ion implantation, evaporation) have been explored. Higher T_C 's (up to 23 K in Nb_3Ge) have been found in new metastable phases.

B. Recommendations-Low Risk

Our recommendations are divided into two categories: "Low Risk," and "High Risk." In the former category we can state with high confidence that continued work will lead to real gains; in the latter category the risks are greater, and so are the potential gains. The present, conservative section is divided again into "Fundamental" and "Empirical." These two avenues of research are mutually supportive and are equally deserving of support. Progress on fundamental aspects requires deeper study of materials that are already known, while the empirical approach is directed at finding and correlating properties of new materials.

I. Fundamental

The recent advances in understanding of the electron phonon interaction in d-band elements should be exploited to give a detailed theoretical treatment of anisotropy effects, phonon dispersion, screening effects, and transport. Simultaneously there should be continued experimental measurements of tunneling, neutron scattering, infrared spectroscopy, and transport coefficients.

Our understanding of the electron-phonon interaction in compounds lags behind that in the elements. Accurate, self-consistent energy band calculations are sorely needed for high T_c phases such as the A-15's. These calculations will require two things: larger computer budgets and, more important, Fermi surface measurements (such as deHaas-van Alphen effect or positron annihilation experiments).

Experimental measurements of $\alpha^2F(\omega)$ from tunneling and measurements of phonon dispersion relations and linewidths from inelastic neutron scattering on high T_c compounds are very important. Many of these experiments depend on the existence of either highly perfect or large single crystal samples that are difficult to prepare by conventional techniques.

Newer techniques in tunneling, neutron, and infrared spectroscopy need to be encouraged in order to bypass materials problems. (For example, neutron scattering measurements of phonon density of states in powdered samples of complex materials has recently been published for A-15 compounds and Chevrel phases.)

It appears that the problem of raising T_c is intimately tied to the problem of preventing lattice instabilities. Work aimed at understanding phase stability, both equilibrium and metastable, should be supported.

II. Empirical

Progress in attaining higher T_c 's is likely to come in the immediate future by an empirical approach focused on rather complex intermetallic compounds. Highest on the list of materials to be investigated are (a) binary compounds such as the A-15's that require either exotic preparation techniques or the addition of third elements in order to stabilize the phase, and (b) ternary phases such as the Chevrel phases (e.g., $PbMo_6S_8$), and the $X(RhB)_4$ compounds where X is of the rare-earth family of elements.

Predictive phenomenological theories are urgently needed to lend insight and direction to the experimental search for higher T_c and H_{c2} materials. Theories of a qualitative nature are also needed to establish a basis for understanding the

surprising superconducting and magnetic effects in the ternary phases.

Experimental approaches that should be emphasized in the study of these complex phases include (1) the use of sophisticated characterization tools to determine structure, degree of order, and purity (e.g. x-ray and neutron diffraction, EXAFS, ion backscattering microprobe analysis, etc. and (2) the use of bulk tools, e.g. susceptibility and heat capacity, and microscopic tools, e.g. nuclear magnetic resonance, Mossbauer effect, and polycrystalline inelastic neutron scattering to characterize the electronic density of states at the Fermi level and the vibrational modes.

Because of the importance of understanding and preventing the degradation of superconducting properties either in a radiation field (such as is present at a superconducting magnet for a fusion reactor) or under mechanical working, the general field of understanding damage in A-15 and other superconductors as it affects T_C should be pursued. It is important to emphasize that the damaged state must be characterized as to the atomistic arrangement of the defects. The effects of the disorder on the electron and phonon spectra should be studied in the damaged materials. The study of the damage state should also lend insights into the importance of crystalline perfection on controlling T_C in various families of superconducting materials. This information could lead to renewed interest in optimizing T_C by new preparation techniques in known superconducting compounds.

C. Recommendations-High Risk

In this section we briefly discuss some areas, which are out of the main stream of most research on T_C 's, but require understanding and hold the promise of higher T_C 's.

1. Other mechanisms - For many years Ginzburg, Little, Bardeen and their co-workers have suggested that it may be possible to achieve higher T_C 's by coupling electrons via an excitonic mechanism. This area has been controversial and the very question of whether the excitonic mechanism is theoretically possible remains unsettled. Recent advances in calculations of real systems make a more rigorous theoretical approach possible, and we suggest that an effort be made to determine the general feasibility of excitonic coupling. Experimental work in this area is tedious, and the large range of possible systems must be narrowed by difficult theoretical calculations for real systems. We feel a broad experimental program in this area is premature at this time, although some work is very desirable.
2. Exotic materials - Work on new quaternary systems has begun with studies of pseudo-ternary compounds but true quaternary compounds will be explored much later. One-dimensional systems and organic systems will play a major role in the search for excitonic superconductors.
3. Superconductivity and Magnetism - This old question has never been fully understood, and surprises have recently come in the area of new ternary systems.
4. Inhomogeneous Systems - This area includes problems involving surfaces, interfaces, proximity effects, and small particles. Fundamental questions of metals on semiconducting surfaces are crucial in the problem of excitonic superconductivity. With recent advances in the calculations of real surfaces, reliable estimates can probably be made about the

- strength of the excitonic mechanism.
5. Phase stability - Since T_C has no fundamental limit, the question of why materials do not, so far, display superconductivity at high temperatures remains the major problem. Some materials that by all empirical extrapolation should have a high T_C , turn out to be unstable. This relationship between T_C and stability may also play a role in the excitonic superconductor problem.

Priorities

Low Risk

1. Intuitive chemical search and discovery of high T_C compounds.
2. Establishment of empirical systematics of electron and phonon behavior in new ternary and stabilized binary superconducting phases.
3. Tunneling and inelastic neutron spectroscopy on known high T_C compounds.
4. Production of good single crystals of high T_C compounds.
5. Fermi surface measurements and band calculations of high T_C compounds.
6. Phenomenological theory of T_C in intermetallic compounds.
7. Phenomenological theory of phase stability.
8. Experimental measurements of disorder in high T_C compounds.
9. Improved theory of H_{C2} .

High Risk

1. Possibility of excitonic superconductivity.
2. Inhomogeneous systems.
3. Interrelationship of superconductivity and magnetism.
4. Exotic materials.

MATERIALS SCIENCES WORKSHOP ON

PHASE TRANSFORMATIONS, STABILITY

AND MATERIALS INTERACTIONS

Held April 18 to 20, 1977 at Lawrence Berkeley Laboratory

Organizers

J. W. Morris, Jr., Lawrence Berkeley Laboratory
L. Brewer, Lawrence Berkeley Laboratory
J.R. Cost, ERDA, Division of Physical Research
P. Shewmon, The Ohio State University

Participants

H. Aaronson, Mich. Tech. Univ.	R. Landingham, LLL
A. Ardell, UCLA	R. McLean, ORNL
L. Brewer, LBL	J.W. Morris, Jr. LBL
J. Brophy, INCO	K. Natesan, ANL
J. Cahn, NBS	F. Nolfi, ANL
I. Carmichael, U. C. Berkeley	W. Owen, M.I.T.
R. Carpenter, ORNL	J. Phillips, Bell Labs.
R. Coble, M.I.T.	R. Perkins, Lockheed Palo Alto
J. Cost, ERDA	F. Pettit, Pratt and Whitney
I. Cutler, Univ. of Utah	R. Reed, NBS, Boulder
L. Darken, Penn. State Univ.	R. Richman, EPRI
D. de Fontaine, UCLA	A. Searcy, LBL
J. DeVan, ORNL	R. Sekerka, Carnegie-Mellon
R. Dillon, Battelle NW	R. Schwoebel, Sandia
K. Drumheller, Battelle NW	D. Shannon, Battelle NW
J. Economy, IBM	P. Shewmon, Ohio State
J. Elliot, M.I.T.	D. Shirley, LBL
A. Goldberg, LLL	R. Staehle, Ohio State
L. Ianniello, ERDA	R. Swendsen, BNL
R. Jaffee, EPRI	D. Thomas, Westinghouse
B. Kear, Pratt and Whitney	G. Thomas, LBL
D. Keefer, Idaho Nat'l Lab.	J. Verhoeven, Ames Lab.
K. Kinsman, Ford Sci. Lab.	D. Vermilyea, General Electric

I. WORKSHOP SCOPE AND PRIORITIES:

The materials sciences program workshop addressing basic research needs and priorities in the areas of Phase Transformations, Stability, and Materials Interactions was held at the Lawrence Berkeley Laboratory, April 18-20, 1977. The forty-two participants included representatives of ERDA laboratories, universities, and industrial research organizations. The participants spanned a range of research interests and competence from highly fundamental theory to applied materials development.

To consider the status of basic research and the choice of priorities for future research in the area of phase transformations, stability, and materials interactions the workshop was organized as follows. The first day was devoted to a survey of ERDA mission needs for research in the workshop area. For the remainder of the workshop the study groups were reorganized along technical lines. The reports and recommendations of both the ERDA mission and technical area study groups are included in the following. Highlights of the research recommendations may be summarized under three headings: Thermodynamics, Phase Transformations, and Corrosion and Environmental Interactions:

A. Thermodynamics: Virtually all participants in the workshop were deeply concerned by the current status of thermodynamic research and by the demise of the groups which had previously taken on the important task of providing critical compilations of thermodynamic data. The problem is made particularly acute by the increasing interest of ERDA mission groups in thermodynamically complex systems and non-equilibrium situations for which neither the theory nor the data are well developed. The workshop participants felt that the Division of Physical Research should move actively to revivify research in this important area. Four tasks were singled out for particular emphasis: (1) classical thermodynamics including high quality calorimetric measurements and equilibrium measurements of surface and interface properties; (2) thermodynamics of gaseous, liquid, and solid solutions emphasizing the interaction of theory and experiment and paying special attention to the complex solutions of interest to ERDA; (3) non-classical thermodynamics emphasizing new theoretical developments in irreversible processes and inhomogeneous materials; (4) critical evaluations and compilations of the relevant thermodynamic data.

B. Phase Transformations: The participants were on the whole enthusiastic about the status of research in this area. They felt that basic research in phase transformations has the momentum of a decade of significant accomplishment in problems ranging from fundamental theory and experiment to application in such exciting new areas as alloy design, glassy metals, and laser processing. Given the rapid current development of new theoretical tools, useful computer simulation techniques, and precise experimental devices for high resolution studies the participants felt that research in this area is entering a particularly productive period which, assuming the continuation of a reasonable level of support, should prove unusually fruitful in results of value both to fundamental science and to engineering practice. Specific areas for research emphasis include: (1) theoretical studies, particularly those at the interface between physics and materials science; (2) research on solidification and crystal growth with emphasis on fundamental interactions across interfaces, the

control of structure and microstructure during solidification, and the technologically important problem of welding; (3) precipitation reactions in the solid state emphasizing the role of interfaces in defects in precipitation processes, the control of precipitation processes, and chemical stability during long time exposure to high temperature, to aggressive environments, or to radiation fields; (4) martensitic transformations in solids with particular emphasis on the nucleation of martensite and on the influence of mechanical deformation.

C. Corrosion and Environmental Attack: The current status of research on materials interactions is conditioned by the historical fact that this area has not received the basic research emphasis given other important scientific problems and by the trend for ERDA mission groups to establish a growing variety of relevant materials needs. As a result, while the participants were pleased at the recent rate of research progress, they emphasized that the current level of research in this area is not adequate to provide needed basic research support for the complex of ERDA needs. The Division of Physical Research should encourage a substantial growth in research on the related problems of corrosion and environmental attack including: (1) research on the environments of particular interest to ERDA considering species adsorption and scale formation of exposed materials surfaces and their influence in inhibiting chemical interactions; (2) the formation, integrity, and retention of natural protective films on engineering materials on exposure to aggressive environments including particularly the nature of flaws or imperfections which may act as short circuit diffusion paths allowing accelerated substrate attack; (3) modification of the substrate due to chemical interaction across the interface including the ingestion of deleterious species such as hydrogen, the leeching of useful alloying elements, and associated long term chemical and microstructural changes; (4) the development of protective coating schemes for engineering materials subjected to particularly severe environments including research on coating materials, deposition and adhesion, and interfacial integrity during long time exposure.

New ventures in fossil, geothermal, solar and advanced nuclear energy production will require major materials improvements and sophisticated handling of new chemistries. In the area of high temperatures stability and corrosion ERDA faces increasing problems with an inadequate technical base. In thermodynamic research and data compilation, the effort is shrinking at a time when growth is badly needed. In phase transformations research recent advances offer the opportunity for significant new contributions to energy science and technology.

II. STUDY GROUP REPORTS - ERDA MISSION NEEDS

II-1 Energy Conservation

Chairman: K. Kinsman

Members: L. Brewer W. Owen
 J. Economy G. Thomas
 R. Landingham D. Vermilyea

This sector represents a collection of activity that is related in a general way by the intended result of direct energy savings. As a group, we have chosen to address only selected activities, those of which we are aware and that have program content relating to the topic of the workshop: phase transformation, stability and material interactions. Even so, the breadth of scientific issues encountered is large, reflecting the variety of engineering systems challenges.

Materials problems and basic research opportunities include metals, ceramics, and polymers. Research activity in the broad sense ought to be multidisciplinary. The consensus of the group was to emphasize the value (and expediency) of interaction among disciplines particularly with regard to technique development and application (and interpretation).

Pervasive problem areas were corrosion and environmental interaction (hostile), and phase transformations and phase stability. The first includes a range extending from "familiar" stress corrosion cracking phenomena on "conventional" materials to interactions of new corrosive media ("relevance pull") with a host of new and old materials and material systems. The challenges of hydrogen containment as currently recognized will become more severe in new power systems, requiring evaluation of new materials, (i.e. ceramics) against phenomena that are currently not understood. Phase stability and phase transformations in the broad sense provides a base upon which other "design" phenomena rely, i.e. mechanical behavior and durability, electrical properties, etc. With the trend to high temperatures in energy systems microstructural stability is paramount. Concomitantly, the emerging advantages of ceramics and polymers requires a reassessment of the fundamental understanding of phase relations in these "unfamiliar" systems. The status of useful sophistication among ceramics, metals, and polymers varies greatly. Thus, for example, in steels and aluminum alloys, basic research problems could involve the subtleties of (both chemical and physical) microstructure management to optimize physical properties. By contrast, in ceramics the challenges in many cases revolve around first-cut processing issues in the sense that material preparation is often a pacing item. Nevertheless, to meet the requirements for engineering application, fundamental knowledge of these same materials (i.e. structural ceramics and fiber composite matrices) must have virtually the same base as the more familiar systems. In many cases this base simply is not yet being developed.

The following list contains a summary of research opportunities based upon some of the principal engineering challenges in energy conservation. Some basic research areas are more clearly defined than others; this is not meant to imply priority but rather reflects the personality of the group.

Group Consensus of Systems Challenges and Research Opportunities

<u>System</u>	<u>Issues</u>
<u>Energy Storage</u>	
-Battery Systems (e.g. Na_xS_y , Li_xS_y)	Corrosion, Electrolyte Performance
Research Opportunities:	
•Material interaction with polysulfides (corrosion), sulfide corrosion chemistry as influenced by temperature, composition, purity, etc. •Solid electrolyte - (β-alumina) -Fundamentals of ion transport mechanisms as influenced by material microstructure, electric field, etc. -Structural stability (fracture mechanisms) as influenced by metal ion transport, impurities, electric field variables, etc. -Develop analytical techniques to permit spatial differentiation (identification) of phases - paramount to accurate studies of micro-structure development. -Fundamentals of sintering doped materials; microstructure control.	
-Stored Energy of Phase Transformations	Innovation
Research Opportunities:	
•The system Na_2SO_4 •Structurally reversible materials - martensitic "memory" alloys - fundamental understanding of microstructural mechanisms.	
-Hydrogen Storage	Environmental Interactions, Containment
Research Opportunities:	
•Hydrogen-materials interactions, hydride formation (influence on structurally significant properties), hydrogen attack, hydrogen transport - in both metals and <u>ceramics</u>.	
-Other Stored Chemical Energy (heat pipes, etc)	High Temperature Inter- actions
Research Opportunities:	
•Thermodynamics and Kinetics of chemical energy storage	
<u>Advanced Power Systems</u>	
-Turbines	Corrosion, Microstructural Stability
Research Opportunities:	
•Thermodynamics and kinetics of material-environment interactions •Microstructural stability (phase transformations of two phase composites (directionally solidified eutectics, eutectoids, etc.) •Structural ceramics (special effort to achieve scientific/technological currency)	

- Phase relations and phase transformations
- Diffusion (mass transport in sintering, etc.)
- Structural characterization and influence of structure upon properties
- Environment - material interactions
- New Engines (e.g. Stirling, Na heat engine) Environmental Interactions
Ceramic Membrane Development

Research Opportunities:

- Fundamentals of hydrogen-material interactions (as above)
- Ceramic material understanding (as above)
- Fuel Cells Microstructural Stability
Environmental Interactions

Research Opportunities:

- Stability of ceramics (as above)

Transportation

- Light weight materials Conservation of Alloying
Elements, Optimal
Structure-Property
Relationships, Environmental
Interactions, Phase Stability
and Transformation

Research Opportunities:

•Continual improvement in understanding of structure-property relationships in physical metallurgy with the tacit goal of optimizing properties (for applications which will have energy savings potential). For example, it is not enough to develop materials with high strength/weight ratios without giving consideration to attaining it along with properties (e.g. "formability") which make possible application in significant quantities and competitive cost.

•Role of alloying elements with consideration to replacing expensive or availability-limited elements with others. Influence of these changes upon time-temperature schedules (i.e. processing) to produce equivalent (or improved) properties. Systems analysis of whether the trade-offs really net an energy saving.

•Fiber reinforced polymers

-Stability of polymer matrix (co-polymer) materials and fiber-matrix interfaces

- Fuel Efficiency (catalysis) Particle Morphological
and Stability

Research Opportunities:

•Morphological stability of fine particle arrays. (Coarsening)
•Role of trace impurities (innate and those occurring in the use environment) upon particle stability

- Tribology Materials Interaction

Research Opportunities

- Fundamentals of friction and wear - influence of structure and environment upon the phenomenon. A basic systematic understanding is needed

- Stability of lubricants under high pressure and temperature

Chemistry of lubricant (degradation) stability

Insulation

Microstructural Stability,
Environmental Interaction

Research Opportunities:

- Stability of high temperature insulators, typically glasses and ceramics subjected to a range of environments.

- Devitrification of glasses

- Stability of high temperature fire brick. Development of ceramics for higher temperature applications. Hot metal/slag erosion and corrosion of materials

- Influence of environment in degradation of spectral reflectivity of low temperature thermal insulations

- Stability of interfaces in multicomponent insulation material

Recycling

Environmental Interactions

Research Opportunities:

- Systematics of complex chemistry and physics of retained extraction

II-2 Fossil Energy

Chairman: R. Jaffee

Members: J. Brophy R. Perkins
I. Cutler R. Staehle
B. Kear

The panel recommends that programming in fossil energy research supported by the Basic Energy Sciences Division of ERDA be confined to coal as the energy source. The nature of the research supported should be aimed at a better understanding of critical issues in the performance of metallic and refractory materials in coal conversion to clean fuels, coal combustion, and conversion from heat to power.

A. Coal Conversion and Combustion: The pressure vessel used for coal conversion to liquids and gases are currently designed by ASME codes and correlation with past experience without benefit of how a flaw in the vessels might grow to critical size in an aggressive environment containing H_2 and H_2S at elevated temperature and pressure. What is needed is a fracture mechanics analysis and supporting data on pressure vessel steels tested in metallurgical conditions of significance to the application and in coal conversion environments. Subcritical crack growth measurements under cyclic and steady loads, with particular attention to the threshold are particularly needed. The temperature range should embrace regimes where plane strain crack growth and creep-fatigue crack growth occur.

Coal liquifaction let-down valves and slurry pumps are subject to severe erosion-corrosion conditions. A predictive theory supported by data are needed on erosion of hard materials as a function of composition and microstructure to provide a rational basis for materials design. This effort should be coupled with parallel efforts in fluid dynamics and correlated with component design.

Low oxygen activity in the presence of multiple oxidants in coal gasification and fluidized bed combustion environments poses a very severe challenge to metallic materials such that operational regimes will be drastically curtailed and that recourse will have to be made to use ceramic materials. Information is needed on corrosion chemistry and short circuit diffusion paths in reaction products on metallic materials. Refractories also are subject to corrosion by slags and gaseous corrosive species, and an analogous body of corrosion chemistry information is needed. Erosion by particulate matter is less of a problem at low velocity and for small particle size, but should be studied over the ranges of interest, particularly those found in cyclone separators, similar to those suggested for let-down valves.

Fireside and steamside corrosion of conventional boiler superheater and reheater tubes will become a more severe problem as lower rank coals are utilized and when higher steam temperatures than 1000F (540°C) are generated. The corrosion reactions in both regimes need much better understanding if better boiler tube materials are to be developed. Also important will be the improvement of creep rupture properties of superheater tube materials to couple with improved corrosion behavior.

B. Heat/Power Conversion: The coal-fired steam plant consists of a boiler, steam turbine, condenser, and various auxiliary pumps and heaters. Improved materials technology for the steam power plant will pay great

dividends in terms of improved reliability and efficiency in the near term. ERDA is urged to direct substantial resources to research in steam plant materials. Some of the problems needing attention are: (1) stress corrosion and crack propagation in steels used for rotors and discs; (2) the effect of impurities condensed from contaminated steam on turbine blade fatigue and stress corrosion water droplet erosion of last stage blade materials; (3) thermal stresses and creep-fatigue interaction in high-pressure rotors, etc.

The corrosion of heat exchanges tubes in coal fired fluidized bed boilers is similar to corrosion of coal gasification internals, but is aggravated by corrosive deposits. Basic attention is needed for both. If the fluidized bed combustion is pressurized, the expander turbine will be subject to high temperature corrosion-erosion and fouling by high velocity particulate matter and alkali sulfates, even after hot gas cleanup. Combustion gas turbines fired with coal derived fuels also will be subject to combined erosion-corrosion. What is needed is an understanding of degradation mechanisms of turbine materials in this environment, which will provide a basis for designing improved materials.

Gas turbines of the closed cycle type with air, helium, or metal vapor as the working fluid, heated by combusted coal in a heat exchanger, are an alternative power conversion cycle. Corrosion is expected in the fireside of the heat exchanger. Corrosion by the metal vapor or by impurities in the helium working fluid needs fundamental attention, as this is another example of corrosion in low-oxygen environments where protective oxide scales are not formed.

Charge transport by electron emission or by arcing is important in coal-fired MHD ducts, and is a subject particularly needful of fundamental attention. Fuel cells utilize fossil fuels, which ultimately must be derived from coal. A current problem is instability of platinum catalysts. A future problem will be development of base metal catalysts.

II-3 Nuclear Fission

Chairman: D. Thomas

 Members: R. Carpenter P. Shewmon
 J. DeVan J. Verhoeven
 D. Keefer

The study group derived suggested research areas from a consideration of materials problems which exist in the several reactor systems currently utilized or being developed.

I. LMFBR

<u>Research Areas</u>	<u>Technological Concern</u>
•Diffusion in a temperature gradient	Fuel Stability (Mixed oxide or Mixed Carbide)
•Phase Stability	Fuel/Clad Interaction
•Radiation damage, swelling and radiation induced phase stability	" " "
•Diffusion	" " "
•Grain boundary penetration effects	" " "
•Short circuit diffusion	Primary circuit, alloy stability
•Fe-Ni-Cr Phase Diagram	" " "
•Phase relations in heat affected zone of welds	Phase stability in welding in primary circuit
•Phase relations in stainless steel castings	Pump and valve stability
•Interstitial diffusion in austenitic steels	Primary circuit carbon transport
•High temperature oxidation in steam atmosphere with and without a heat flux	Steam generator tube integrity
•Phase relations in ferritic steels	" " " "

II. HTGR

•Thermal gradient induced mass transport	"Amoeba" effect in fuel particles
•Internal oxidation of high temperature materials at low oxygen activities	Oxidation of critical metallic components in primary circuit
•Internal carburization of high temperature materials at low carbon activities	Internal carburization of critical metallic components in the primary circuit
•Stability of ordered structural alloys of the A_3B type under creep conditions	Advanced alloys for primary circuit applications

III. LWR

•Precipitation and segregation in stainless steels and Inconel in the sensitizing regions	Stress corrosion cracking in BWR primary loop environments and PWR secondary environments
•Relationship of microscale structural changes during deformation & fracture to the fracture mechanics of pressure vessel steels-irradiated and unirradiated	Pressure vessel integrity

II-4 Magnetic Fusion

Chairman: R. Reed

Members: A. Ardell F. Nolfi
J.W. Morris R. Swendsen
K. Natesan

The panel recommends that the currently projected materials requirements of magnetic fusion energy would be considerably assisted by the following fundamental research projects:

A. Irradiation of Alloys: The complex metallurgical problems associated with the construction of fusion reactor first walls and blankets requires a detailed understanding of the effects of irradiation on alloy stability. Phenomena such as irradiation induced non-equilibrium segregation, phase boundary shifts, defect-impurity interactions, and accelerated precipitation kinetics are presently not well understood, especially in the presence of the transmutation products helium and hydrogen.

B. Stability of Coatings During Irradiation: Reactor first walls may be constructed using protective, low-Z coatings. For these coatings, radiation-induced sputtering requires adequate characterization. Research considering ion size, energy and incident angle, as well as alloy chemistry, would supply much-needed background information. Also, assessment is needed of the effects of radiation-induced phenomena such as cavity formation and enhanced diffusion of coating-wall bond integrity.

C. Irradiation Studies of Organic Materials: Reactor electrical insulation and superconducting magnet electrical and thermal insulation requirements will require the use of organic films and composites. Studies of irradiation effects inorganic insulator materials are generally sparse, and at 4K (superconducting magnets) studies of these effects have apparently never been carried out. Fundamental studies, considering polymer types and temperature effects and directed toward radiation-insensitive material development, should be initiated.

D. Welding: The large magnetic forces generated from high-field magnets require very thick sections of structural alloys for containment. Weldability may well be a limiting parameter of the use of refractory metals for first walls. Basic research on welding has not been prominent. It is recommended that research be initiated to consider phase stability and grain boundary segregation of austenitic stainless steels and the role of impurities/solutes in refractory metal welding.

E. Martensitic Transformations: Superconducting magnets will probably require the use of structural alloys, such as austenitic stainless steels, that have possible martensitic transformations at cryogenic temperatures. Proper characterization of the role of deformation, welding-induced precipitation and chemical segregation, magnetic fields, and temperature on martensitic transformations in austenitic stainless steels would assist in alloy selection and welding procedure selection.

F. Liquid Lithium Characterization: Currently, liquid lithium is the leading candidate for the coolant and breeding materials in fusion reactors. Basic information on the thermodynamics and kinetics of interstitial migration in high magnetic fields is needed. Studies are

needed on interactions between lithium interstitial elements and structural alloys and on corrosion rates of structural materials in lithium environments as a function of temperature, alloy chemistry, and lithium purity.

G. Metallurgy of Superconductors: In the quest to obtain useable NbTi and Nb₃Sn superconducting wires and cables, most research and development has concentrated on the maximization of the critical current as a function of magnetic field. Surprisingly, there has not been characterization of the phase stability and deformation modes of these alloys at low temperatures.

These recommended projects are not necessarily listed in a priority order and are not all inclusive.

II-5 Solar Energy

Chairman: R. Richman

Members: J. Cahn A. Searcy
 K. Drumheller R. Sekerka
 J. Phillips

The field of solar energy is so new that the problems have not yet been defined or even identified, in contrast to a more mature technology such as nuclear fission. However, the study group agreed that the direct conversion of light (or heat) to electricity probably offers the best opportunities for supporting basic research. Following is a list, largely by program, of solar-related research topics pertinent to this workshop.

I. Solar Heating and CoolingA. Phase Separation and Devitrification

- Most soda-lime glasses are two-phase on a microscale. Structures might be tailored by heat-treatment, selective leaching, etc.
- Stability at temperatures higher than the present 300°-400°F for cover glass

- Glass solders for device fabrication

- Polymers

B. UV-Induced Degradation of Glasses and Polymers

- Reflectivity and transmittance

- Electrical properties

- Mechanical properties

C. Surface Preparation

- Thermally processed layers, as by laser glazing. Rapid solidification on surfaces of non-metallics; structure of surface transformations

- Diffusion produced coatings; the moving-boundary problem

- Chemically produced coatings, such as dark conversion coatings on solar absorbers. Also, techniques will be needed for property predictions and lifetime projections.

II. Direct Conversion

Research on this topic will be necessary to achieve inexpensive photovoltaics and thermovoltaics.

A. Liquid-Solid-Gas Interfaces

- Dihedral angles in non-equilibrium situations is a basic underlying topic about which almost nothing is known.

- Refers mostly to silicon now, but will apply to whole field of inexpensive strip semiconductors.

B. Growth Morphologies in Anisotropic Circumstances

- Inexpensive wafer materials from the melt

- Structure of thin layers grown by reaction between solid substances; e.e., Si/transition-metal reactions.

C. Epitaxial Growth

- Is thin-film science likely to be the foundation for cheap, extended converters?

- Can bring defective bulk material into specification only where it is needed, i.e., at the surface.

- Liquid-phase epitaxy

D. General Interactions

- Purity; definitive information about limits in silicon and other semiconductors.

- Dopant effects
- Metallurgical structure

III. Solar Thermal

A. Diffusion in Thermal Gradients

- Carriers
- Impurities
- Interface stability
- Thermal cycling; two phases may be in equilibrium at T_1 , but excursions to T_2 may cause microstructural instability.

B. Thermal Storage

- Latent heat.
- Cyclic degradation of media that rely upon phase-change
- Peritectics offer advantages but they have not been studied much, certainly in metallurgical systems.
- Cyclic growth of crystals from the storage-medium melt.

IV. General Topics

A. Accelerated Testing

- A crucial issue; since we cannot afford 20-year tests, we must be able to predict all aspects of stability in order to make lifetime projections.

- Time/temperature parameters for extrapolation

B. Corrosion

- Interaction of materials with low-temperature ocean water, intermediate-temperature organic working fluids, and high-temperature gases.

C. Fatigue

- Mechanical, as in wind devices
- Thermal, as in central-cavity receivers.

II-6 Geothermal

Chairman: A. Goldberg

Members: I. Carmichael F. Pettit
L. Darken D. Shannon
R. Dillon

The geothermal energy conversion systems considered for identification of areas of needed research are based on hydrothermal reservoirs, vapor reservoirs, hot rocks and lava beds. The problem areas identified are listed as follows:

A. Scale Formation: Scale deposition buildup, caused by a temperature drop or by flashing, can rapidly decrease flow capacity to unacceptable values. Entrapped particles downstream from flashing can cause serious erosion problems. Scale has been shown to both decrease and increase corrosion. Information on the thermodynamics of scaling from aqueous geothermal systems and the kinetics of scale formation must be obtained over a range of pressures, temperatures and pH values. One must also obtain basic information on the influence of hydrodynamic conditions on the morphology of scale deposition. Synergism between scale deposition and corrosion must be studied.

B. Materials Behavior: The geothermal resources will present aggressive environments to various degrees depending upon both the particular reservoir and the location within any given energy conversion system, e.g., well casing, surface piping, heat exchangers, turbine system, valves, pumps and the effluent treatment and discharge system. Behavior of materials in these various environments is virtually unknown and this must be examined with respect to stress corrosion cracking, corrosion fatigue, erosion/corrosion and other forms of failure and wastage.

C. Improved Performance: Basic research must be performed which could lead to better materials systems and cost effectiveness. The effect of alloy additions in simple Fe-base systems on corrosion resistance for low cost piping and plant materials should be studied. The potential use of coatings, liners, or claddings with low cost structural steels must be considered by studying the interaction of candidate coating, liner or cladding materials with the geothermal environments. Research should be performed which isolates the effects of erosion from corrosion and thereby identifies which materials are most suited to resist wastage by either one of both of these mechanisms.

D. Lava Beds: Lava beds are now mainly of geological interest, but their potential must not be overlooked. Temperatures are of the order of 1200 to 1300°C. Materials which are now being developed for MHD and coal gasifier internals should be studied for their interactions with lava compositions in this temperature range.

II-7 Environment and Safety

Chairman: R. L. Schwoebel

Members: H. Aaronson D. deFontaine
R. Coble J. Elliot
J. Cost R. McLean

Environmental and safety concerns represent important driving forces for the selection and development of various alternatives in energy generation. A perceptive ranking of such alternatives in terms of environmental and safety efforts is a complex task requiring the interdisciplinary efforts of experts in several fields.

The two principal areas discussed by this subcommittee were the environmental and safety problems associated with the large scale utilization of fossil fuels, particularly coal, and the disposition of fission products and transuranic nuclide wastes associated with nuclear reactors. Our recommendations for research in support of these two areas are as follows:

A. Coal Utilization: Concepts for the beneficiation of coals prior to combustion or conversion should be pursued to reduce sulfur, trace impurities such as arsenic, cadmium, mercury, and other elements detrimental to eco-systems. There is also a need for definitive characterization of the chemical evolution of sulfur and nitrogen bearing compounds, and identification of the most important species in terms of health effects. This is particularly true in the case of coal gasification and liquification processes which are thought to produce organic fragments that evolve into carcinogenic and mutagenic species.

There is a critical need to accumulate selected thermodynamic data to establish predictive performance and failure models for pressure vessels, etc. This would include phase diagram determinations, inter-diffusion data, surface and interfacial energies, and boundary diffusion parameters.

B. Nuclear Reaction Operations: Biofouling of reactor cooling equipment continues to be a problem which significantly impacts the ecology surrounding water cooled power reactors. This phenomena apparently depends on several parameters including the surface morphology and composition of cooling systems and further study is required.

A principal problem in the development of nuclear power is the safe disposition of radioactive wastes associated with the fuel cycle. Several long lived nuclides are extremely toxic and effective isolation is required for extended intervals. Although vitreous waste forms have been under development for many years, there is still a need for definitive characterization of these waste forms with regard to physical and chemical stability. This would include microscopic studies of nuclide chemistry, homogeneity, effects of transmutation and radiation damage, and identification of significant processes associated with devitrification and interactions with the disposal environment. We also recommend the pursuit of alternative crystalline waste forms selected on the basis of known or predicted stability. This would require the study and modeling of the chemical and physical stability of particularly transuranic compounds of high radiation fields.

II. STUDY GROUP REPORTS - TECHNICAL AREA RESEARCH PRIORITIES

III-1 Thermodynamics

Chairmen: L. F. Darken
J. F. Elliot

Members: L. Brewer R. Schwoebel
J. Economy J. Verhoeven
F. Nolfi

We noted first the current dismal level of support for thermodynamic investigations, in fact the termination of many. We deplore the general lack of interest even in presumable informed quarters - even in the University communities. In strong contrast to this attitude we note the essentially universal permeation of thermodynamics into the physical sciences and technologies. In particular all the "tutorial speakers" for the other areas of this Workshop made explicit or implicit reference to the use of thermodynamics in their presentations - reminiscent of the famous quotation from G. N. Lewis on "the broad highway of thermodynamics" (1).

Our study group stressed the need for support agencies to seek out and support: (1) the relatively few scientists capable of advanced thermodynamic thinking (including those outstanding in modern physics); (2) outstanding, well-equipped experimentalists in the field. Otherwise, these scientists drift to other fields with almost irretrievable loss.

General areas where we feel strong support is needed are:

A. "Classical Thermodynamics": There is a critical need for high quality (a) calorimetric measurements and, (b) equilibrium measurements including surface and interface properties (related to catalysis wetting combustion and corrosion phenomena).

B. Thermodynamics of Solutions: Gaseous (including ions), liquid and solid. Models should be built to facilitate the interaction of theory and experiment (methodology). Special attention should be paid to elements, oxides, halides, sulfides, polysulfides, sulphates and aqueous solutions at high temperature and pressure.

C. Now-Classical Thermodynamics: Efforts should continue to be made to push thermodynamics to its limits. Areas here include irreversible thermodynamics, quasi-equilibria (as for systems subject to high radiation flux), systems in high magnetic fields, stressed solids, high gradients of various sorts, defect structures, glasses, polymers, and multiple adsorption phenomena.

D. Critical Evaluations and Compilations: Our group felt it a matter of the utmost urgency to re-institute the critical evaluations and compilations of thermodynamic data so that thermodynamic information may be readily available to those who need it.

We feel that Alvin Weinberg's criteria of technological, scientific and social merit are more than fulfilled by these areas of thermodynamic research.

The appended table summarizes present and contemplated needs for new thermodynamic data on materials species and phases which are critical to the successful development of energy systems.

(1) G. N. Lewis and M. Randall, Thermodynamics, 1st edition, preface, McGraw-Hill, N.Y., 1923.

Summary Chart: Areas Where Thermodynamic Information is Needed and Kind of Information Desired

System	Thermo. Prop.	Solutions	Surface Phenomena	Phase Stability
*(N) Fossil Energy	Complex Spec. Complex Comp. Polycyclic Comp. (V,VI)**	Coal Slags Liquid Coal Polycyclic Comp. (V,VI)	Conversion (V,VI)	Structural Materials (Phase Trans. and Stability) (II, III)
(N) Energy Conservation	Compounds, e.g., (V,VI) Si_3N_4 , SiC , Na_xS_y	Alkali Poly. Sulfides (V,VI)	Friction and wear (V,VI)	Waste processing structural materials; polymers
(M) Energy Storage	Electrolytes (V) Fluids	-----	Catalytic effects	-----
(M) Fission Energy	Actinide Comp. V.P. of Fission Prod. Cmpds.	H.T. Aqueous soln. (V,VI)	-----	Struct. Materials (IV); Fuel stability
(L) Geothermal	Complex Sulfides (V)	High Temp. Aq. Soln. (V)	-----	-----
(L) Magnetic Fusion	Ion Properties at high T. and Mag. fields	Alkali Metals (V,VI)	Sputtering (VI) surface phenomena	Metals, Ceramics; Org. Materials
(N) Environment and Safety	Gaseous species in atm. and combust. gases	Aqueous ionic species	Atmospheric part. matter (combustion gases)	Actinide cmpds (storage)
(L) Solar	Prop. of high temperature liquids	-----	Absorbtivities and photocatalysis	Struct. Materials in sunlight

* Term interest, N=near, M=medium, L=long

** Areas of study-group Discussion: II-Solid.+ H.R., III-Ppt. and Coarsening, IV-Mart. Trans and Crit. Phenomenon, V-Corrosion, VI-Environmental Attack.

III-2 Solidification and Homogeneous Transformations

Chairmen: R. Coble
B. Kear

Members: J. Cahn R. Reed
K. Drumheller R. Sekerka
R. Jaffee

The prospects for significant advances in understanding in these areas are related to new or advanced tools or techniques for the conduct of experimental programs. Rapid solidifications by atomizing liquids into gases, and laser or electron-beam melting of surfaces on crystals which then self-quench, provide the possibilities of sample purification, and of model testing, and generation of data on epitaxial relations on re-growth, the growth vectors in high temperature gradients, and non-equilibrium segregation of components. With the theories now available these studies will permit determination of the anisotropy of the atom attachment kinetics during solidification. The theory applies to simple systems; studies of the influences of 3rd (or more) components on these phenomena are needed for the next step in understanding more complex systems. The cellular: dendritic transition can also be addressed using high cooling rate experiments. Metastable phases, easily produced, can also be studied more intensively because of different composition ranges that can be converted to: glasses or metastable crystalline phases. The glass transition itself is not fully understood for metals, ceramics, or polymers and deserves intensified effort. Decomposition of glassy or metastable crystalline phases have been observed to evolve through sequences of metastable phases prior to formation of equilibrium phases. Studies of these evolutions are needed to deduce why the sequence appears. Thermodynamic data and chemical diffusivities in these multicomponent systems will be required for basic testing of the applicability of nucleation/spinodal, etc. models.

Texture generation in unidirectional solidification is appreciated for all classes of materials. Polymers may be further "textured" to produce chain alignment by controlled shear in fabrication. Metals, ceramics, and polymers should be studied for texture development due to re-crystallization, and/or growth, under variable temperature and stress gradients imposed during annealing (in the solid state).

Tri-junctions in float-zone growth of Si (e.g) show non-equilibrium wetting angles (at the solid liquid gas junctions). These as well as moving solid I, solid II, liquid junction morphologies should be studied because of their importance in shape control of solidified materials, and potential insight to be gained from this phenomenon that is not understood.

Basic studies of reactions across interfaces are needed particularly for slag, melt interactions, and the process of grain growth. Polymer to metal/ceramic attachments presents further complexity because of the variable chain orientations which can be controlled (parallel/perpendicular to the surfaces) with important consequences for lubrication versus bonding characteristics, respectively.

Finite element analysis techniques now available should be applied to the moving boundary problem, to thick-plate welding, to determine how the heat affected zone might be altered as a function of the variables, number of passes, power and feed rate. Hot tearing should similarly be

attacked with elastic and plastic modeling of the stress fields generated.

High resolution instrumentation must be applied to the structure determinations of interfaces and grain boundaries, and to the chemistry of each for proper characterization of these features in order to understand their mobilities and the reactions which may take place across them. Fundamental work is needed on plasma-materials interactions, but may now be used empirically for refining purposes. Boundary growing experiments and solid faceting at liquid interfaces can now be used to deduce interface energies and their anisotropies; liquid crystals add anisotropy from the liquid components in polymeric systems as well.

Basic data needed to support these efforts are on thermodynamics and transport in non-metallic crystals and liquids, the structure of interfaces, liquids and glasses, chemical diffusivities in multicomponent liquids and solids, interface energies and their anisotropy, and interface diffusivities.

III-3 Precipitation and Coarsening Phenomena

Chairmen: A. Ardell
G. Thomas

Members: H. Aaronson R. Carpenter
J. Brophy K. Kinsman
I. Carmichael D. Thomas

The study group concentrated its efforts on two broad areas of research:

- A. Precipitation in general, including homogeneous and heterogeneous nucleation, growth, discontinuous or cellular precipitation, and coarsening;
- B. Irradiation effects, including the effects of neutron and charged-particle irradiation on several of the phenomena cited in (A) and phenomena that appear to be unique to the irradiation environment, such as irradiation-induced segregation and associated precipitation phenomena. In discussing these topics the group attempted to highlight those areas in which basic research was needed, and to provide a loose assessment of the extent of the effort required. These are summarized below.

A. Precipitation:

1. Nucleation: Homogeneous nucleation theory has never been tested in solid systems by direct measurement. Since the formalism serves as a basis for heterogeneous nucleation theory as well, an effort to test the theory should be made. Although the measurements are difficult, a relatively small effort would suffice to provide the necessary data on nucleation rates and incubation times as a function of undercooling.

Heterogeneous nucleation is in particularly bad shape with regard to the theory of nucleation on dislocations. A moderate effort should be made to develop an appropriate theory incorporating elasticity theory and precipitate morphology in an attempt to rationalize existing observations.

2. Growth: What is needed here is knowledge of the detailed structure of interphase interfaces so that growth kinetics could be compared to the predictions of various models as a test of theory. A moderate effort, involving the application of high resolution electron microscopy and analytical techniques, should be supported.

3. Discontinuous Precipitation: The major problem in this area is to provide a definitive explanation for the known effects that third elements have on the suppression of this reaction. This has important consequences on mechanical behavior. A small but continuing effort should be supported.

4. Coarsening: An explanation of the resistance to coarsening in certain alloys (e.g. θ' in Al-Cu alloys) is worth pursuing because of its implications in high-temperature microstructural stability of alloys. Other problems, such as the role of strain energy, also remain unsolved and a small to moderate effort is definitely worthwhile in this area.

B. Irradiation Effects:

1. Parallel Studies: The need was expressed for studies on the effect of irradiation on phenomena, such as particle coarsening, to be conducted in parallel with studies on identical alloys in the absence of an irradiation environment. In view of the large number of variables and potential alloys involved, a large effort would be required to get the job done.

2. Unique Effects: Recently discovered phenomena, such as irradiation-induced segregation to free surfaces and precipitation in otherwise stable solid solutions, are as yet poorly understood. A large effort, both theoretical (e.g. the thermodynamics of systems containing large excess amounts of point defects) and experimental, is clearly necessary to elevate our present level of understanding.

C. General Concerns:

In addition to the research areas cited above, the study group was particularly cognizant of the lack of ancillary data available to properly interpret experimental results. Conventional data on solution thermodynamics, diffusion rates, interfacial energies, single crystal elastic constants of solid solutions and binding energies between solute (and solvent) atoms and point defects are sorely needed.

New methods of materials characterization have been, and are being, developed which should be brought to bear on the problems cited. Indeed, recent advances in high resolution electron microscopy, electron energy loss spectroscopy and X-ray analysis, will eventually become indispensable in solving the current and future problems.

Finally, the study group emphasized that the problems cited should not be viewed only in their own light, but that they have important implications and applications in alloy design and behavior.

III-4 Martensitic Transformations and Critical Phenomena

Chairmen: J.W. Morris, Jr.
W. Owen

Members: D. de Fontaine
J. Phillips
R. Swendsen

The subjects of martensitic transformations and critical phenomena fall in a vital area of current research activity which is alive with many important new ideas. Recent progress in this area has been stimulated by the development of a variety of new theoretical approaches. These include techniques in statistical mechanics, such as renormalization group theory, cluster variation methods, and Green's function techniques, tools in solid state physics, such as pseudo-potential theory which permits the estimation of thermodynamic functions, and powerful new numerical techniques, particularly computer simulation techniques which permit detailed studies of the behavior of simple systems through pseudo experiments carried out in the computer. Recent theoretical progress has been paralleled by major advances in experimental devices & methods. These include ultra high resolution microscopy, the application of dynamical diffraction theory to the interpretation of electron microscope images, the study of dynamical effects on neutron diffraction, synchrotron radiation, the study of defects by diffuse intensity measurements (x-rays and neutrons), and a variety of other tools and techniques.

The research topics of major current interest include: soft mode transformations, ordering-clustering phenomena, amorphous materials, micro-domains, defect stabilization of unstable structures, phase instabilities (compositional lattice, electronic and magnetic) and precursor phenomena (including pre-martensitic precursors) and fluctuations. In each of these subjects exciting advances are being made in physics, in metallurgy, and in materials engineering. Progress in fundamental physics is indicated by the rapidity with which new and probative ideas are being introduced in each of these research topics. Progress in metallurgy is indicated not only by the rapid growth in understanding of these phenomena and the increasing recognition of their importance but also in the manner of which these various phenomena are being integrated into a more unified theory of phase transformations. Progress in materials engineering is indicated by the quickness with which these new research ideas have been adapted to interpret important aspects of the behavior of engineering materials and to create new engineering materials of unusual and important properties.

Given its perception of the current state of research in the areas of martensitic transformations and critical phenomena the highest priority recommendation of this study group is that ERDA maintain levels of support and encouragement to sustain scientific momentum in this important research. Specific research topics which should receive emphasis in theory, experiment, and applications areas include the following:

A. Theoretical Research: While a wide variety of theoretical investigations could have a significant impact, those which should receive greatest emphasis were, the study group felt, those which focus on problems at the interface between fundamental physics and materials science. These include, in particular, (a) dynamical studies which theoretically model

systems in real time yielding new information on the kinetics of phase transformations; (b) theoretical studies which include the effects of elastic interactions on phase transformations permitting better understanding of transformations in real solids; (c) theoretical work on the role of defects in solids including, in particular, the role of dislocations and other defects on the occurrence and kinetics of martensitic transformations. It is felt that in many cases the best theoretical route to follow in these investigations blends sound fundamental theory with computer simulation studies to monitor the details of phase transformations in model systems. It is important in this context that the Division of Physical Research insure the availability of the facilities and funds needed for large computer simulation studies.

B. Experimental Studies: The experimental studies of highest scientific priority are those which utilize the high resolution available in powerful new research tools to conduct detailed studies of phase transformation phenomena, particularly where these may be examined in situ in real time. Specific investigations having particularly high priority include the following: (a) high resolution transmission electron microscopy studies of the initial stages of phase transformations and of the structure of critical defects, including surfaces, which participate in the nucleation phase of the transformation; (b) in situ experiments using TEM and other high resolution techniques which follow the progress of transformations in real time with particular emphasis on critical fluctuations, precursor phenomena, and the features controlling transformation kinetics; (c) high resolution studies using well defined model systems, particularly those in which experimental results and theoretical studies can be directly matched for critical evaluation of the theories.

C. Applications Oriented Research: The importance of critical phenomena to materials science lies mainly in the domain of electronic and magnetic materials which are discussed in a separate workshop. The understanding of martensitic transformations, however, is directly relevant to the design of structural materials, in particular alloy steels, and properly falls in the domain of this workshop. Recent research has led to the identification of several new facets of the martensite transformation which may be of considerable significance to the performance of energy systems. These should be the subject of high priority research. They include: (a) the nucleation of martensite in steel with particular emphasis on nucleation at low temperatures under conditions of stress or electromagnetic fields of the sort which may be encountered in cryogenic devices; (b) the retention of austenite in the interstices of martensite plates or in the boundaries of martensite lathes which may not only have a significant effect on the mechanical properties of steel but may also contribute to embrittlement phenomena in ways that are only now coming to be understood; (c) the reversibility of the martensite transformation on thermal cycling, a problem which is important in the advanced processing of a variety of steels including both austenitic steels and high strength martensitic steels for advanced applications; (d) other in depth studies of the relation between the martensite transformation, the structure of the resulting martensite, and the mechanical properties of the martensitic steel.

III-5 Corrosion

Chairmen: R. Staehle
R. Dillon

Members: J. DeVan D. Shannon
A. Goldberg D. Vermilyea
D. Keefer

The primary objective of work in corrosion studies is to inhibit or retard degradation of substrates by chemical-mechanical influence of environments. This inhibition is accomplished primarily by modifying the environment, the substrate, the stress-time wave, and the geometry. Seven component areas can be identified where fundamental work should be undertaken. Underlying these component areas are the areas of thermodynamics and equipment application. Finally, there are five important logistical considerations; equipment, talent, interaction with designer, interdisciplinary interaction and financial resources.

The mechanical part of the environment includes both the initiation and propagation of cracking, but within a framework of the mechanical parameters of cyclic frequency, wear stress, stress ratio, wave shape and non-conformity or randomness of load cycle. In general, SCC and CF should be at either end of the mechanical continuum with phenomena of creep, fracture, and fatigue as affected by environments key parts of this set. This mechanical part also includes the thermal fatigue phenomenon of fracture mechanics analyses.

The thermodynamic underpinning should include aqueous solutions especially concentrated ones and at temperatures above room temperature. Other important environments with dissolved species are steam, molten salts, and liquid metals. Properties of complex protective oxides and solutes (C in Fe) in metals are also important.

The seven component areas with priorities are:

A. Protective Films: Structure, composition, reactivity, nucleation and growth, alloy influence, Soret effect, transport of electronic and ionic defects, epitaxy electropolishing films.

B. Substrate: Grain boundary composition including segregation and precipitation, slip including grain boundary deformation, coplanarity, surface interaction, mass transport, surface energies, matrix structure.

C. Hydrogen-Metal: Entry (poison effects), defect interaction hydrides, void stabilization, dislocation motion, M-M vs M-H bonds, thermal and stress gradient diffusion.

D. Film Free Dissolution: Alloy effects, enrichment, ionized or non-ionized dissolution.

E. Adsorption Effects: Inhibition, fracture.

F. Cathodic Reduction Processes: H^+ , O_2 , Anion, Location of reaction, mass transport.

G. Fluid-Surface Boundary: Mass transport, double layer.

III-6 Environmental Attack

Chairmen: A. Searcy
I. Cutler

Members: J. Cost R. Perkins
R. Landingham F. Pettit
R. McLean P. Shewmon
K. Nateson

We have distilled from our discussion two short lists of areas in which we judge that an increase in basic research effort could be particularly helpful to efforts to improve resistance of materials to attack in the high temperature environments of the energy utilization programs. Most high temperature environmental problems overlap those addressed by the corrosion panel, but we decided that we need not consider attack by aqueous solutions or the influence of mechanical stress. Each of our two lists is arranged in decending order of priority on the basis of our collective judgement of the interaction of two factors: (a) the benefit that a successful basic research program could provide to energy programs; (b) the probability of significant success for a basic research study in each given area.

A. Thermodynamic Studies:

1. Phase equilibria and activities should be studied for oxide-sulfide, oxide-carbide, oxide-halide, and oxide-oxide (including sulfate) systems. Mixtures of such phases are encountered in the processing of hydrocarbons at high temperatures, but little thermodynamic information is available. Particular emphasis should be given to determination of liquidus temperatures and the variation of solid and liquid phase boundary compositions with temperature.
2. Theoretical models for extrapolation of measured thermodynamic data for inorganic systems should be developed so that realistic predictions and interpretations of behavior in multicomponent systems can be made from data for systems of fewer components.
3. Devices for quickly and inexpensively monitoring the thermodynamic activities of sulfur and of carbon in high temperature systems should be developed if possible.

B. Kinetic Studies:

1. Chemical attacks through coatings and scales appear usually to proceed much more rapidly than can be accounted for by bulk diffusion. Diffusion along grain boundaries and along interfaces in complex scales and the mechanisms of reaction in complex systems (especially O + S + metals or binary alloys; O + C + metals or binary alloys) are important subjects for increased basic research. Because the systems are complex it is essential that these studies emphasize as complete characterization of the reaction parameters as possible. Thus, while the experimental thermodynamic investigations that we recommend require mainly that well-known experimental techniques be applied to little known systems, effective kinetic studies for complex reactions systems require that a broader range of experimental techniques be applied than have been applied in most past solid state reaction studies.
2. Corrosion of refractory oxides, and selected nitrides, carbides, oxy-nitrides and oxycarbides by the gases and liquids characteristic of

high temperature energy systems should be investigated. Little information is yet available, but serious environmental attack problems are almost certain to be encountered.

3. Studies of mechanisms of erosion of oxides and metals by solid particles should be augmented.

4. If programs that give real promise of increasing our fundamental understanding of mechanisms of adhesion of scales on structural metals and alloys are identified, they should be supported. The prediction and control of adhesion is one of the most important problems, not just in reducing environmental attack, but in all of Materials Science, but really useful basic research in this general area is hard to devise.

MATERIALS SCIENCES WORKSHOP ON

DEFECTS, DIFFUSION AND RADIATION EFFECTS

Held April 27 to 29, 1977 at Oak Ridge National Laboratory

Organizers

F. W. Young, Jr., Oak Ridge National Laboratory
 J. R. Cost, ERDA, Division of Physical Research
 A. S. Nowick, Columbia University
 J. O. Stiegler, Oak Ridge National Laboratory

Participants

R. W. Balluffi, Cornell Univ.	R. A. Johnson, Univ. of Virginia
H. Birnbaum, Univ. of Illinois	W. G. Johnston, GE R&D Lab.
R. S. Blewer, Sandia Lab.	F. A. Kroger, Univ. of S. Calif.
T. H. Blewitt, Argonne Nat'l Lab.	D. Lazarus, Univ. of Illinois
E. E. Bloom, EPRI	G. C. Libowitz, Allied Chemical Corp.
W. L. Brown, Bell Telephone Lab.	A. S. Nowick, Columbia Univ.
O. N. Carlson, Iowa State Univ.	T. C. Reuther, Jr., ERDA, Mag. Fusion
Y. Chen, Oak Ridge Nat'l Lab.	M. T. Robinson, Oak Ridge Nat'l Lab.
F. W. Clinard, Jr., Los Alamos Sci. Lab.	B. R. Rossing, Westinghouse R&D
C. R. Cooley, ERDA, Nucl. Fuel Cycle & Prod.	H. Rupprecht, IBM Corp.
J. R. Cost, ERDA, Physical Research	J. Schultz, Univ. of Delaware
J. H. Crawford, Univ. of North Carolina	W. A. Sibley, Oklahoma State Univ.
M. A. Dayananda, Purdue Univ.	R. W. Siegel, Argonne Nat'l Lab.
L. DeVries, Univ. of Utah	J. O. Stiegler, Oak Ridge Nat'l Lab.
G. J. Dienes, Brookhaven Nat'l Lab.	J. L. Straalsund, Hanford Engr. Dev.
R. Donnelly, Oak Ridge Nat'l Lab.	J. D. Walton, Georgia Tech.
L. Eyring, Arizona State Univ.	H. Wiedersich, Argonne Nat'l Lab.
A. N. Goland, Brookhaven Nat'l Lab.	M. C. Wittels, ERDA, Physical Research
P. S. Ho, IBM Research Center	W. Williams, Univ. of Illinois
B. Holt, Lawrence Livermore Lab.	W. D. Wilson, Sandia, Livermore
R. A. Huggins, Stanford Univ.	F. W. Young, Jr., Oak Ridge Nat'l Lab.

SCOPE

Defects, Diffusion and Radiation Effects were considered for all types of materials. This subject area overlaps that of many of the other Workshops and therefore the scope was limited as follows. Dislocations and grain boundaries were considered only as they related to other defects; consideration was given to radiation effects in semiconductors, but not to semiconductor physics; radiation effects in superconductors were considered only peripherally, as were radiation effects on surfaces; impurities were considered to be defects; solid state chemical reactions which involve defects and diffusion were not considered in detail.

The workshop was first divided into seven study groups, one for each of the energy technologies. Each group heard a presentation of the needs of that technology by the technology briefer, then after discussion prepared a report of the needs of that technology with emphasis on this area of Materials Sciences. These seven reports were presented and discussed in plenary session, and are included in this Report.

The workshop was then divided according to scientific interest into six study groups (Atomic Transport in Metals and Alloys; Atomic Transport in Ionic Materials, Semiconductors and Polymers; Defect and Impurity Centers in Transparent Ionic Materials, Glasses and Semiconductors; Defects in Non-Stoichiometric Compounds; Radiation Effects in Metals; Gases in Solids), and they identified the basic research which should be done in their area to answer the needs of the energy technologies as determined by the first set of study groups. They prepared reports, including priorities, which were presented and discussed in plenary session and are included in this Report. Finally the Workshop met in plenary session for a general discussion of priorities, special equipment and institutional needs, which are summarized below.

PRIORITIES

All study groups found that research on defects and diffusion is essential for solutions of the many materials problems of all the energy technologies. For fission and fusion, radiation effects are of vital concern. Detailed priorities are given in the reports of each of the six study groups into which the subject matter of the present workshop was subdivided. The present section provides a composite listing of the major priorities of the entire workshop, selected by the organizers because of their outstanding importance scientifically and/or technologically. Most of these items consistently recur in the study group reports.

Priority I

- More complex materials. - There is a great need to extend the understanding of defects previously achieved for certain simple materials (e.g. Cu, Si, NaCl) to materials more closely related to those used in energy technologies, including complex crystal structures, polycrystalline materials, ternary solutions, hydrides, Al₅ compounds and multiphase materials. Such materials must be carefully prepared and characterized, however.
- Behavior under adverse conditions. - We must improve our understanding of the behavior of materials under severe conditions of operation, particularly under very intense irradiation and exposure to corrosive gases and liquids, often in combination with high stress or temperature. Included are questions of phase and compositional stability in these environments.
- Defect interactions. - The study of point defect interactions, including defect-defect, defect-solute, defect-phonon and defect-cluster interactions should be strongly supported. Special attention is required for the study of defect ordering, microdomains and extended defects in crystals in which the total defect concentration is high.

- Interfaces. - There is a strong need for further study of both internal and external interfaces and the processes taking place there, including behavior of defects, mass transport and chemical reactions at interfaces.
- Transport under driving forces. - The study of mass transport under various driving forces, such as chemical and temperature gradients, electric fields, and stress gradients, should be strongly supported.
- Gases in metals. - The behavior of hydrogen and its isotopes, of He, and other interstitial solutes in metals, especially the trapping of these atoms at other solutes and defects, and the mechanisms of bubble formation and coalescence are of utmost importance.

Priority II

- Theory. - New theoretical techniques such as more elaborate computer simulations and improved interaction potentials should be strongly encouraged. Of special interest is the simulation of high energy displacement cascades.
- Radiation damage. - Fundamental studies of radiation damage in basic materials, including defect production, defect interactions and annealing behavior, should be continued. Such studies have already produced great benefits, both scientifically and technologically, and can be expected to continue to do so. ERDA has primary responsibility for this research area.
- Sputtering. - The mechanisms of sputtering and related studies of erosion, blistering and gas re-emission deserve special attention.
- New experimental techniques. - The development of new experimental techniques and the exploitation of recently developed techniques (e.g. high resolution and scanning electron microscopy, Auger and other electron spectroscopic methods, positron annihilation, diffuse x-ray and neutron scattering) play an important role in the advancement of all materials sciences.

INSTITUTIONAL ISSUES

As the research on Defects, Diffusion and Radiation Effects shifts to the more complex systems and more extreme environments, more sophisticated research tools such as an x-ray synchrotron source, a MeV electron microscope or more intense irradiation sources will be required. For such research, cooperative projects and users groups will become more pervasive, in contrast to the simpler equipment used for many of the researches in this area in the past. It was noted, however, that much of the needed research could be accomplished on a relatively small scale, and thus was suited for University research students.

REPORTS OF TECHNOLOGY STUDY GROUPS

FOSSIL FUELS

W. S. Williams, O. N. Carlson, B. Rossing, J. Schultz, H. Wiedersich

Fossil fuels continue to represent the major energy source for the U.S. economy. However, severe materials limitations for use of coal in MHD generators and in conversion of coal to gas and liquid fuels continue to plague the industry and frustrate the projections of even three years ago.

Fossil Fuel Technologies and Materials Problems

Magnetohydrodynamics (MHD) Generator - In this coal-based technology, combustion gas is seeded with easily-ionized potassium and expanded through a nozzle to make a high-velocity, conducting plasma that passes through a high magnetic field and produces an electric current by virtue of the Lorentz force. The problems of corrosion by potassium and coal slag and others are still limiting the lifetime of all major components of the MHD device--combustor, generator, air heater and heat-recovery chamber. The coal slag is composed of alumino-silicates containing oxides of iron, calcium, magnesium, etc., with the proportions depending on the origin of the coal. A materials problem common to all coal-based technology, erosion by hard particles, also plagues the generator and air heater sections of the MHD device. The generator section also exhibits several materials' problems of a unique nature for fossil fuel technologies, but found in other generating systems--current blockage by insulators and current in sharp temperature gradients. Candidate electrode materials are zirconia-ceria solid solutions and doped lanthanum chromite. Phase instability and vaporization are problems, however.

Coal Gasification - Although low BTU gas can be made from coal by the well-known Lurgi process, enrichment with additional hydrogen is required for turning coal into pipeline-quality fuel. Gasification reactors, as enormous, high-pressure high-temperature chambers, present serious erosion and mechanical problems, but in addition the hydrogenation must be catalyzed by materials not subject to chemical poisoning by C, S, and CO. Similar erosion and corrosion problems are met in proposed in-situ gasification of coal and shale.

Coal-Liquefaction - The required temperatures are lower than for gasification, so the materials problems are correspondingly somewhat less severe, but the familiar ones of corrosion and erosion are present. The diffusion of sulfur and carbon into the metal walls of the reaction vessel to form precipitates that weaken the structure is a serious issue, which may be met only by introducing a coating or diffusion barrier.

Petroleum Recovery - Recent failures of North Sea drilling rigs have underlined the importance of salt-water corrosion.

Petroleum Refining - Selectivity and stability of cracking catalysts are concerns of the industry: agglomeration and sintering of dispersed catalysts and alteration of alloy composition in time can reduce the activity.

Fossil Fuel Extraction - Improved methods and materials for rapid drilling and excavation for coal, oil, and gas are needed, but the focus is on the mechanical properties of the materials rather than on defects or diffusion.

Relation to Defects, Diffusion, and Radiation

Corrosion - A recurrent theme in this review is the importance of corrosion. We include here both condensed phases (e.g., slag) and gas phase (e.g., O₂, H₂) interactions. Although chemical reactions determine the corrosion products, the penetration of the critical atomic species into the material is governed by diffusion. For example, the formation of sulfides in steel piping of a coal gasification vessel is controlled in part by the rate of diffusion of S into the steel.

From the great body of knowledge about mechanisms of diffusion in solids, the design of diffusion barriers should be possible. Similar problems have been faced in DOD projects and in other industrial processes. One need is to apply intelligently the models and theories of solid-state physics to these matters. The prospect is aided by advances in surface analysis that allow high-resolution mapping of diffusion profiles.

Erosion - The other major theme is erosion, including gross removal of chunks of material by high-velocity particles, and liquid-phase erosion by chemical action and cavitation. However, the former is primarily a problem in fracture and the latter in chemistry and make only indirect contact with this study of defects and diffusion.

Catalytic Activity - Defects appear to be involved in the effectiveness of catalysts (e.g., the Mg^{++} vacancy on the cube corner of MgO , where the oxygen is in the form of O^- , binds hydrogen; tungsten carbide in the form of W_6C_{30} can react H_2 and O_2 to make H_2O , but the pure form, WC , cannot). In view of the importance of catalysis to fossil fuel conservation, increased attention to the role of defects in catalysis would complement the heavy activity in surface analysis and perhaps lead to more general understanding of the electronic structure of active sites. Application of the lore and methods of defect physics would be profitable here. Another aspect of defects in catalysis is the way in which poisons affect the activity. The low concentrations required again point to defects as the sites. Catalysts that are not so affected might be developed from more information on the electronic structure of the defect site. Practical catalysts are dispersed in the form of atomic clusters. Such systems tend to agglomerate and sinter, reducing the effectiveness of the catalyst. Atomic diffusion processes are involved.

Compositional Stability - Time-dependent compositional changes in alloy catalysts and in refractory compounds have been cited as problems in fossil fuel technologies. These changes are related to the relative diffusion rates of multicomponent systems. Fundamental studies of the relations among crystal structure, electronic structure (i.e., bonding), defect structure and atomic mobility in these complex systems are needed.

Electrical Conductivity - Although identified as important for MHD, the conductivity requirement is for electronic rather than ionic transport, so defects and diffusion are involved only in a negative sense.

General Conclusions

In a recent comprehensive review of U.S. programs on the behavior of metals in coal-fossil energy systems, twenty-nine separate efforts, including ones funded by non-ERDA sources, were identified. No comparable survey of ceramic programs has yet been made, but the number is surely much smaller. Since a common theme in this review of fossil fuel/materials problems is the need for better information on high-temperature ceramics, we urge more boldness on the part of solid-state physicists and chemists in joining their colleagues in metallurgy, ceramics and polymers to study complex materials and the role of defects in controlling properties. Just as semiconductor physics moved into electrical engineering, so defect physics in insulators can move into ceramic engineering, and contribute conceptual models, theoretical methods and sophisticated instrumentation for advances in the science of high-temperature ceramics on which the successful operation of many technologies--especially those built on fossil fuels--depend.

NUCLEAR ENERGY

J. L. Straalsund, T. Blewitt, E. E. Bloom, N. A. Dayananda, L. Eyring, and J. O. Stiegler

The technology experience of the working group members is mostly related to LMFBFR core materials. Although other reactor systems were considered, there may be significant problem areas related to LWR, HWR, HTGR, and other nuclear systems which are not addressed by this report.

Problem areas associated with nuclear power facilities were classified either as "core problems" which involve the expendable structural materials and fuels in the high flux zone of the reactor core, or "plant problems" which involve all materials outside of the core. Typically plant components are designed to last the life of the facility, about 40 years.

Major materials problems that are associated with plant components are stress corrosion, response to cyclic loads, fracture toughness, friction and wear and mass transport. The potential for stress corrosion must be considered in essentially all plant components. Response to cyclic loads is particularly important to piping, which is subjected to large thermal stress during shutdowns. The manner in which the material deforms in response to cyclic loading conditions can lead to "ratchetting" and subsequent failure. Design must consider low and high cycle fatigue. An accurate understanding of radiation effects on fracture toughness is important to the safety of pressure vessels. Fracture toughness also plays an important role in the safety analysis of large piping. Defects and diffusion may play an important role in many of the friction and wear problems associated with valves and pumps. Decarburization and subsequent reduction in strength affects the life of ferritic steels used in the sodium/steam heat exchangers in LMFBFRs because the carbon tends to transport through the sodium to austenitic stainless steel portions of the loop which have a higher affinity for carbon. Mass transport mechanisms of a similar nature can occur in the helium loops for HTGRs and GCFRs, depending upon the impurity levels in the helium.

In contrast to plant components, core components are considered expendable and replaced in one to three year periods. Plant fuel costs are strongly dependent upon the core lifetime. LMFBFR core lives appear to be limited by one of the following mechanisms. (1) Flux and temperature gradients in the core result in bowing of sodium coolant channels induced by gradients in the swelling, or void formation phenomena, which is both temperature and flux dependent. These bending distortions become large enough to limit core life unless they are relaxed by irradiation creep, a phenomenon similar to swelling. (2) Excessive bulging of the hexagonal flow channels will occur in response to the sodium coolant pressure if irradiation creep rates are too high. (3) Mechanical or stress rupture failure of the fuel pin cladding occurs as a result of fission gas pressure and possibly fuel-clad mechanical interaction. Mechanical failure of cladding is also an important consideration for thermal moderated plants. Materials phenomena which must be considered in the evaluation of the above phenomena are discussed below.

Chemical interaction between the fuel and cladding may be an explanation for the fact that the mechanical properties of cladding samples taken from the fuel column region of the fuel pins are often more severely degraded than samples irradiated under similar conditions but in the absence of the fuel. Clad-coolant interactions must be contended with in sodium, helium, and water-cooled reactors.

Phase stability during irradiation must be investigated because the changes in microstructure and matrix composition associated with irradiation-induced precipitation can have a dramatic effect on swelling, irradiation creep and mechanical properties. No means are presently available to predict how irradiation will modify the thermodynamics and kinetics associated with precipitation and redistribution.

Alloy additions as well as changes in base composition have a strong effect on the swelling behavior. Explanation of these compositional effects would be highly beneficial to alloy development efforts.

The effects of irradiation on fracture and ductility are particularly important because the major impairment in stress rupture life during irradiation is due to embrittlement. Relatively new modes of failure, such as channel fracture or extremely localized shear, have been observed in studies involving high fluence irradiations, but are not understood.

Mechanistic understanding of irradiation creep is needed for guidance in developing engineering correlations and extrapolations, as well as for alloy development.

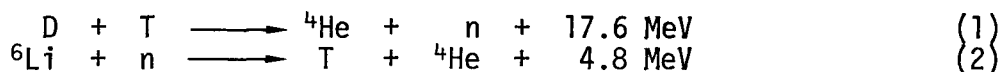
Research areas which were considered important by the working group, but to have lower priority than the ones described above, are defect migration in thermal gradients and in multicomponent systems, development of simulation techniques, and characterization of swelling and creep of fuel. Defect migration in the presence of thermal gradients is considered important because of the relatively high thermal gradients in cladding, whereas diffusion in multicomponent systems should be studied in order to improve our understanding of mass transport as well as for understanding swelling in complex alloys. Simulation techniques need to be developed for mechanical properties studies, and further fundamental work on existing simulation techniques would establish the conditions under which such techniques are valid. Fuel swelling and creep mechanisms are important because they may affect the mechanical loading on the cladding.

Recent changes in national policy may result in increased emphasis on HTGRs, and consequently a need for studies of mass transport in helium loops and studies of irradiation effects in graphite. However, the need for LMFBRS may not be reduced if it is feasible to operate these machines economically on a uranium-thorium cycle. The new concept of accelerator breeders involves very high energy neutrons and charged particles. If this concept is pursued, fundamental research will be required on the effects of the high energy neutron bombardment and associated transmutation products.

FUSION ENERGY

M. T. Robinson, F. W. Clinard, Jr., J. R. Cost, G. J. Dienes, W. G. Johnston, T. C. Reuther, Jr., and W. G. Wilson

As presently conceived, fusion systems will generate energy through the nuclear reactions



thus consuming deuterium and lithium. Systems operating on other fuels were not discussed. The fusion reaction (1) will take place in a plasma. About 20 percent of the energy released is carried by the product alpha particles (3.5 MeV); the remaining 80 percent is carried from the plasma by the product neutrons (14.1 MeV). These neutrons must be moderated, multiplied, and absorbed in a lithium-containing breeder region, where reaction (2) takes place. The product tritium must be separated from the breeder materials and returned to the plasma.

The plasma will be confined either magnetically or inertially. The inertial confinement systems were discussed only briefly in this Workshop. They would operate by using laser or electron beams to heat a solid pellet to the required temperatures and are characterized by an extremely short cycle ($\sim 10^{-9}$ sec) frequently repeated (~ 1 sec). Magnetically confined systems would use (probably superconducting) magnetic fields of several possible configurations. The plasma may be heated by the injection of beams of neutral particles. The cycle times

could be moderately short (10^{-1} sec pulses at 10 sec intervals in theta pinch systems) or rather long (10^2 sec "burn" at 2×10^2 sec intervals in some tokamaks).

The so-called "first wall" separates the plasma chamber from other portions of a fusion reactor (heat exchange fluids, breeder region, etc.). It is exposed to intense fluxes of 14.1 MeV neutrons coming from the plasma; of moderated neutrons coming from outer parts of the reactor with an energy spectrum resembling that in a fast fission reactor; of alpha particles of energies up to 3.5 MeV, the actual spectrum depending on the degree of thermalization of the fusion product He in the plasma; of neutron plasma particles (D and T) produced by charge exchange having energies around 30 keV or more, depending on reactor design; and of electromagnetic radiation from the plasma. The neutron fluxes are comparable to those in high power fission reactors.

Several major problem areas have been identified and related research needs outlined. The following general points underlie all considerations of fusion materials problems: (a) No facilities currently exist for radiation effects testing which possess the correct neutron energy spectrum and intensity, nor are such facilities likely to become available in advance of operating thermonuclear systems. Thus, testing must be based on fission reactor irradiations, ion irradiations, and low intensity, small volume high energy neutron sources. Such test programs require a substantial theoretical input to allow for scaling among the various facilities and from these to real fusion reactor conditions. (b) Nuclear transmutations are far more prevalent in 14 MeV neutron exposures than in fission systems. Increased production of He, H and metallic transmutation products is perhaps the most important difference in fusion systems, as compared to fission reactors. (c) The stress environment in fusion reactors is very complex. There are substantial thermal gradients at the first wall. The cyclic nature of the stresses could prove to be of crucial importance. The structural elements must support the pressure of the atmosphere and great magnetic stresses as well. (d) The particle fluxes in the system are not necessarily uniform. Regions distant from the plasma (magnet components, for instance) may experience substantial inhomogeneities because of penetrations such as neutral beam injectors, plasma diagnostic probes, and the like.

The following list of problems was developed during the Workshop. These are all concerned with problems of defects, diffusion, and radiation effects in complex materials.

1. Damage production - (a) The morphology of displacement cascades as functions of neutron and primary recoil spectra (b) Intracascade collapse: problems concerned with short time ($\sim 10^{-6}$ sec) annealing and free defect production (c) Methodology for damage analysis in insulators.
2. Alloy stability under irradiation - (a) Diffusion in complex irradiated alloys such as the stainless steels, other Fe-Cr-Ni alloys, and reactive refractory alloys of V, Ti, etc. (b) Alloy thermodynamics during irradiation (c) Alloy kinetics during irradiation (d) Transmutation effects.
3. Mechanical properties during irradiation - (a) Helium and hydrogen effects (embrittlement, etc.) (b) Crack propagation: leaks through the first wall may be a life-limiting problem (c) Effects of cyclic stresses.
4. Plasma-wall interaction problems - (a) Sputtering and plasma reflux (b) Defect structures near surfaces.
5. Special materials problems - (a) Insulators (b) Magnet materials (superconductors, organic insulators) (c) Tritium handling materials (d) Graphite for moderator or first wall protection (e) Laser optics.
6. Experimental methodology - The need is clear for a multiplicity of observations to be carried out on common well-characterized sets of materials to reduce uncertainties in results caused by variability in composition and preconditioning.

ENVIRONMENT AND SAFETY

W. A. Sibley, H. Birnbaum, Y. Chen, C. R. Cooley, J. R. Cost

The purpose of this report is to outline those ways in which radiation effects, diffusion or impurities in materials affect the safety and environmental features of energy production and use in our society.

I. Power Systems

A. Nuclear

1. Waste Disposal

- a. Processing Equipment: Radiation effects on the processing equipment range from contamination to equipment failure because of brittle fracture. For glass encapsulation the ceramic melters have materials problems ranging from electrodes (SnO_2 , Inconels, etc.) to refractory ceramics walls.
- b. Containment:
 - i) Glass or Ceramic Incapsulation: The problem of incapsulating radiation waste for disposal is a major one. Very little basic science data is available to predict the radiation and temperature effects on glass, glass ceramic or ceramic waste forms. A systematic investigation of the influence of the severe environmental conditions expected in nuclear waste storage on the properties of simple and complex glass compositions is sorely needed.
 - ii) Storage Environment: The storage environment could be the sea bed, salt, shale or granite. The reliability of the container will be affected by the temperature (25°C to perhaps 150°C), the pH of the surroundings, the pressure (up to 2500 psi) and the corrosiveness of the environment.
 - iii) Kinetics: Long-term basic research on the kinetics of glass reactions and phase transitions, including redox effects, transmutations, valence changes and stress effects should be supported.

2. Reactor Container Vessels

- a. Radiation and diffusion effects can result in swelling or brittle fracture of reactor vessels and welds. A strong effort needs to be continued on the influence of radiation dose, flux and temperature dependence of materials. New materials should be developed which are more radiation resistant. Non-destructive materials evaluation techniques are also needed.
- b. Window systems can be important and diffusion and radiation effects can adversely affect the strength of windows thus creating a safety problem.

B. Non-Nuclear Systems

1. Pollution and Radiation Hazards: In systems which burn coal both sulfur and heavy metals such as Hg, As and U are a problem. Therefore, it is necessary that filters or precipitators be developed to effectively extract sulfur and heavy metals from the output of these reactors. For instance, as much as 40,000 tons of coal per day may be processed in some gasification plants. This will be a tremendous strain on the filter or "clean-up" systems. Also, how will the waste products be stored?
2. Container Vessels for Coal Conversion: Liquefaction Process Type. There are three types of liquefaction processes - hydroliquefaction, extraction and pyrolysis. In each of these processes high temperatures, corrosive poisonous gases and high pressures lead to safety and environment problems. It is extremely important that research on the corrosive effects of hydrogen sulfide, syn-gas, etc., on reactor vessels, and the effects of erosion, high pressures and temperatures on these materials be increased. At temperatures of 200°C to 500°C and pressures of 200-1000 psi, hydrogen sulfide, hydrogen gas, and chloride concentrations in the range of 100 parts per million with a companion moisture content in the range of 1.5% can attack severely many of

the materials which will be involved. In fact since the reactor can be 200 ft high and weigh 105 tons it can be a rocket if there is severe materials failure.

II. Transport of Energy

Energy is at present transported as a liquid, both gas and oil. In the future hydrogen gas will most likely be transported through pipelines. Whatever the form of transport corrosion, hydrogen diffusion and hydrogen embrittlement of welds will be a problem.

III. Transportation Systems

In transportation systems the environment is affected primarily by automotive emissions. At present catalytic converters are used to keep the atmosphere clean. Catalytic converters are expensive and can be compromised by impurities. More research on catalysts is needed.

Since gaseous hydrogen can be obtained from solar processes, it is conceivable that hydrogen will be used as a fuel as petroleum stocks are exhausted. This means considerable research must be done on the safety of liquid hydrogen containers and transport lines.

Alkali metal batteries also can be hazardous. Research is necessary on impact containment and corrosion effects.

IV. Research Needs

- A. Kinetics and thermodynamics of phase changes in glasses.
- B. Corrosion and erosion of oxides and metals in hostile environments (temperature, pressure, oxidation and reduction atmospheres, radiation, stress, etc.).
- C. Hydrogen diffusion and embrittlement.
- D. New techniques for evaluation and early warning of material failures. Non-destructive evaluation techniques must be improved.
- E. New types of catalytic converters.
- F. Improved neutron and ionizing radiation dosimeters.

CONSERVATION AND STORAGE

R. A. Huggins, R. Donnelly, A. N. Goland, R. A. Johnson, G. C. Libowitz and A. S. Nowick

The general technology area under the responsibility of ERDA's Assistant Administration for Conservation, which we have considered to delineate the scope of our overview, is very broad. It includes conservation activities related to communities, buildings and urban waste. Within this arena we have pointed out only the matter of the radiation-induced decomposition of polymeric materials, which may be important in limiting the life of inexpensive solar-thermal collectors. Likewise, we focussed upon only two problems related to electric energy systems, the defect-sensitivity of the magnetic properties of the new class of very hard permanent magnet materials, which provide an opportunity to increase the efficiency of some types of electric motors, and the current evidence of the importance of structural defects and variable stoichiometry upon the behavior of superconductors.

The other areas of ERDA's energy conservation concern received more attention, and it was found that there are a number of research topics related to defects, diffusion and radiation effects that involve the interests of more than one of them. A few will be mentioned. Conservation via the use of alternate fuels, especially coal, and more efficient combustion and vehicular propulsion could be aided by research in high temperature corrosion of both metals and ceramics, and in the influence of defects on high temperature structural ceramics and catalysts. Improved efficiency by the use of electrochemical combustion in

fuel cells, as well as energy storage by means of new types of batteries will both be greatly influenced by the development of new solid electrolytes, mixed ionic-electronic conductors, sulfide corrosion-resistant metals and catalysts. The effective utilization of hydrogen will be accelerated by progress in the development of hydrides for storage, and photoelectrolysis for more efficient generation by electrolysis. Likewise, energy conservation in industrial electrolytic processes could be improved by further advances in certain types of catalysts.

Because of the interrelationships between these research activities and the various areas of conservation technology, the results of our evaluation are presented briefly below, arranged according to research activity, but indicating related potential technological areas.

Materials Science Problems in Defects, Diffusion and Radiation Effects as Related to Conservation and Storage

High Temperature Corrosion - Mechanisms, kinetics, defect behavior: Metals-gases containing sulfur, molten alkali metal sulfides; oxide ceramics - alkali metal oxides, transition metal (e.g. vanadium) oxides

relevant to: Coal gasification, coal combustion, residual oil combustion, industrial heat exchangers (e.g. recuperators), elevated temperature battery systems.

High Temperature Structural Ceramics - e.g. Si_3N_4 , SiC , Sialons: defects, diffusion, influence of doping and stoichiometry on mechanical properties and resistance to oxidation

relevant to: Advanced heat engines (e.g. gas turbines) high temperature heat exchangers

Solid Electrolytes - Ionic conductors: oxide ion, proton, alkali metal ion conductors; principles underlying behavior; search for, design, develop new materials; emphasize ionic conductivity, lower temperature operation, thermodynamic stability

relevant to: Batteries, fuel cells, electrochemical sensors (e.g. oxygen in gas streams)

Mixed Ionic-Electronic Conductors - Solid solution electrodes: oxide, halide ion, proton, alkali metal ion conductors; principles underlying behavior; search for, design, develop new materials; emphasize stoichiometry range, diffusion

relevant to: Batteries - electrodes, fuel cells - electrodes, catalysts, hydrogen storage

Hydrides

Ternary intermetallic compounds, oxides, sulfides: principle underlying behavior; search for, design, develop new materials; emphasize stoichiometry range, thermodynamics, diffusion

relevant to: Hydrogen storage, fuel cells - electrodes, catalysts

Catalysts

Effects of defects and stoichiometry on mechanisms and kinetics; emphasis on non-metals; use of new experimental techniques

relevant to: Coal gasification, industrial electrolytic processes (e.g. chlorine production), fuel cells

Photoelectrolysis Phenomena and Materials - Effects of defects, doping on kinetics; photocatalysis principles

relevant to: Hydrogen generation, other electrolytic processes

Permanent Magnet Alloys (e.g., SmCo_5) - Effects of defects, stoichiometry

relevant to: More efficient electric motors

Superconductors - Influence of defects and stoichiometry on superconductivity relevant to: Energy transmission, possible energy storage devices

Radiation Effects on Polymers - Degradation of polymers in sunlight: problem in solar-thermal systems; deliberate degradation may assist polymer recycling

Hydrogen-Metal Interactions - Mechanisms, fundamentals: embrittlement, stress-corrosion

Special Problem - Experimental facilities and methods for work at very high temperatures in controlled atmospheres

SOLAR ENERGY

W. L. Brown, R. S. Blewer, P. S. Ho, F. A. Kroger, H. Rupprecht, J. D. Walton

Dividing this technology into its main components: Thermal, Photo-electric, Ocean, Biomass and Wind, we recognize material problems involving defects, diffusion or radiation effects that represent real limitations to technological development in all five. In Biomass systems, defects are involved through catalysts which may be essential to production of desired and product fuels. In wind systems, defects are controlling in large mechanical components that fail through material fatigue or fracture. In these two cases, the problems seem to fall naturally into workshops on surfaces and engineering materials, respectively, and they will not be considered further here. The other three are discussed below.

Thermal

Thermal systems can be divided into three groups depending on the level of solar concentration and hence the effective working temperature: flat plate collection ($\sim 100^\circ\text{C}$), one dimensional concentration ($200\text{--}300^\circ\text{C}$) and two dimensional concentrations ($\geq 500^\circ\text{C}$). Flat plate collectors, used for space or hot water heat, must be very inexpensive. Hence utilization of plastic "greenhouse" covers instead of glass (for cost and weight reduction) is attractive. However, defect generation in plastic by solar UV limits the optical and mechanical life of these materials. Transparent plastics may also be used as Fresnel lenses in concentrators for higher temperature systems and plastics even more generally may be important as structural members or mirror forms for light weight heliostats. UV degradation of plastics must be studied to reach an understanding of defect production, trapping and recombination processes with the goal of gaining material control and longer life.

One dimensional concentration systems (for example by parabolic trough reflectors) are critically dependent on greenhouse efficiency because the energy receiving tube at the line focus of the parabola is relatively open to radiant energy loss. Multilayer selective coatings on the receiver provide a valuable means of manipulating the visible absorptivity and infrared emissivity. The mechanical and optical stability of such coatings at $200\text{--}300^\circ\text{C}$, however, is limited by interfacial diffusion and reaction which are governed by defects in the polycrystalline films and their interfaces. Corrosion, another defect and diffusion limited interface problem, will also be important here both at the interface to the working fluid and to the atmosphere. Much better understanding and control of these interface defect processes is essential for commercially viable systems.

Two dimensional concentration systems, for example those involving a field of heliostats directing sunlight to a central receiver at the top of a tower, are capable of producing very high working fluid temperatures ($\geq 500^\circ\text{C}$), and are attractive for efficient electric power generation and perhaps for direction utilization of thermal energy in some chemical processes. Material properties of the solar receiver now become critical. High strength, high temperature ceramics

and metals are important material candidates, for example SiC, Si₃N₄ and Al₂O₃, high nickel alloys and possibly refractory metals. The mechanical failure modes of these materials under thermal cycling at high temperature (and often high pressure) in an oxidizing atmosphere require serious study. Although these materials may be used inside insulated receiver cavities which reduce the requirements on emissivity, controlling the transparency of such materials could be valuable in optimizing the coupling of the solar energy to the heated fluid. The color of these materials is largely due to defects, either structural or impurity.

The primary heliostat reflectors in high temperature systems do not seem to present critical materials problems at present, unless a need to achieve the ultimate in reflectivity drives the system toward antireflective coatings, or unless plastic backed front surface reflectors are used which require protective coating. The temperature at these reflectors is ambient. However, to reduce the requirements on precision heliostat systems by permitting a poorer focus of the sunlight on a tower, secondary reflectors can be used around the tower top to scoop in fringe power. Such reflectors will experience high thermal flux, multi-coated surfaces will be important and their stability against diffusion, reaction and corrosion will be limiting.

Photovoltaic

Photovoltaic system designs are moving in two main parallel paths. If very inexpensive and reasonably efficient (>10%) photovoltaic elements can be developed they may be usable without concentration. On the other hand, by concentration, the required active area is reduced, and more expensive elements may be used if they can operate efficiently, particularly at higher temperatures. Material preparation techniques other than those conventionally used in production of single crystals are essential in the first approach. Crystal growth itself and the electrical and optical properties of the materials formed are strongly defect influenced. Polycrystalline Si, GaAs, InP, CdTe and CdS films and amorphous Si films (with or without hydrogen), for example, may be prepared by evaporation, sputtering, chemical vapor deposition or electrochemical deposition techniques amenable to large area processing. The quality of these materials is still relatively poor. Optimizing growth conditions and the properties of the films produced is a major research and development effort which requires much better understanding of the effects due to grain boundaries which dominate these materials.

More sophisticated photovoltaic cells may involve single crystal GaAs-AlAs or CdS-InP heterojunctions formed by liquid or vapor phase epitaxy. Such materials are attractive for higher temperature, concentrated sun applications. However, the long term performance of these devices (particularly at higher operating temperatures) will be limited by interfacial diffusion and reactions between metal contacting layers, passivating surface films and the semiconducting layers themselves. These processes are invariably defect controlled and are highly dependent on the microstructure of the films involved. A concentrated materials research effort will be required to gain control of these interface phenomena.

Ocean

Ocean energy systems of many types are being considered utilizing waves or tidal motion or thermal gradients. For the first two, materials problems seem largely to involve mechanical strength and corrosion resistance. Thermal gradient systems, however, are critically influenced by biological organisms that foul the heat conducting surfaces. Diffusion controlled release of antifouling chemicals over long operating life is a demanding requirement of the materials involved.

GEOHERMAL ENERGY

R. W. Siegel, J. H. Crawford, L. DeVries, B. Holt, D. Lazarus, F. W. Young, Jr.

Geothermal energy appears to be a viable energy source for at least partial fulfillment of future U.S. needs. Hot, dry or wet, steam beds can supply only ~0.1% of present U.S. energy consumption. However, relatively shallow (depth < 4 km) hot water sources could conservatively yield on order 1-10% of present U.S. energy consumption, and deeper (depth < 10 km) dry hot-rock areas, if efficiently tapped, could yield effectively unlimited energy supplies, since the energy equivalent, in the form of heat, of $\sim 2 \times 10^{11}$ barrels of oil per year flows upward to the earth's surface.

Serious materials problems stand in the way of full utilization of these vast energy reserves. Deep drilling of wells with bottom-hole pressures up to 10^4 psi and temperatures up to $\sim 300^\circ\text{C}$ will place severe requirements on the variety of materials which comprise a drilling system. These requirements are further exacerbated by the highly corrosive nature of the geothermal reservoir fluids. Once tapped, these hot corrosive brines, with impurity contents which can be as high as 25% by weight, will be a source of continuous problems related to the fouling of various elements of geothermal systems such as well casings, heat exchangers and turbines. This fouling will take the form of scale formation (build-up of polymeric SiO_2 , CaCO_3 , etc.), corrosion (stress corrosion cracking) and erosion (impact and cavitation). Furthermore, environmental concerns will require adequate waste disposal for excess H_2S , ammonia, etc., which comprise the effluent of geothermal wells.

Shorter term materials problems in presently conceived geothermal systems and related research topics are as follows: Scaling - polymerization of SiO_2 ; scale adhesion mechanisms; nucleation and growth of scales; filtering of scale forming agents, Corrosion - stress corrosion cracking; hydrogen embrittlement; diffusion of corrosive agents through scale; fatigue corrosion, Erosion - Impact erosion; cavitation erosion, Wastes - Handling of H_2S , ammonia, salts and heavy metals, Drilling Materials (including bits, bearings, packers, seals, lubricants, muds and cements) - Bearing steels with greater fracture toughness; elastomer seals for high temperature operation; suitable drilling muds for high temperature, high pressure operating for cooling, pressure balance and rock-chip removal; mud additives for reduction of rock fracture energy; high pressure and temperature lubricants; hydrofracture fluids.

Longer range materials related problems will surely be associated with developing new concepts for tapping geothermal resources. Since the major cost in establishing a deep geothermal well is involved in the drilling, if heat sources in the 4-10 km depth range are to be widely utilized, new drilling techniques will be sought. These might include, among others, plasma, electron-beam, laser, ultrasonic, chemical and spallation drilling, and each will have its own set of materials problems. The efficient use of high temperature heat available from molten lava in volcanos will require development of materials compatible with this hostile environment. On the other hand, the efficient use of low temperature heat for space heating and agriculture will require research into efficient heat transfer from low-grade energy via heat pipes and pumps, possibly utilizing thermo-electric devices. Finally, the problem of materials reclamation and separation of constituents from geothermal effluent will be of importance in both the environmental and energy conservation areas. For example, deleterious gases (e.g. H_2S) and heavy metals (e.g. Pb, Hg) will necessarily have to be safely disposed of, while possible valuable elements (e.g. Mn, Mg, Li) and potential fertilizers (e.g. ammonia, phosphates) might well be economically extracted from geothermal fluids.

REPORTS OF SCIENTIFIC STUDY GROUPS

ATOMIC TRANSPORT IN METALS AND ALLOYS

R. W. Balluffi, M. A. Dayananda, P. S. Ho, R. A. Johnson, R. W. Siegel

Phenomena which involve atomic transport in metals and alloys are of importance in almost all areas of energy technology. Although much work has been done, there are many aspects of transport in metals and alloys about which more must be known to understand and solve the problems of future energy systems. In some cases the basic mechanisms which are involved have not even been identified. In the following we define the scope of the field by outline and indicate relevant connections between the phenomena and the energy technologies. We then identify priority areas and make recommendations regarding equipment and facility needs.

Scope of the Field

- A. Defect Properties
 - A.1. Intrinsic point defect properties
 - A.2. Interactions between defects (point defect-point defect), (point defect-dislocation), (point defect-grain boundary or interphase boundary)
 - A.3. Creation and destruction
 - A.3.1. Thermal
 - A.3.2. Irradiation
 - A.3.3. Plastic deformation
 - A.3.4. Chemical reaction
 - B. Atomic Mechanisms
 - B.1. Lattice diffusion (elemental solids, dilute solutions, concentrated solutions, compounds)
 - B.2. Dislocation "pipe" diffusion
 - B.3. Grain boundary diffusion
 - B.4. Interphase boundary diffusion
 - B.5. Surface diffusion
 - B.6. Diffusion in amorphous alloys
 - B.7. Diffusion in liquids
 - C. Driving Forces
 - C.1. Tracer gradient (self-diffusion)
 - C.2. Chemical concentration gradient
 - C.3. Electric field gradient
 - C.4. Thermal gradient
 - C.5. Applied and internal stresses
 - C.6. Coupled defect flux
 - C.7. Capillarity
 - C.8. Radiation induced defect gradient
 - C.9. Radiation induced defect migration
- A. Defect Properties
- A.1. Intrinsic defect properties include formation and migration energies and entropies of vacancy and interstitial defects and their clusters. While the basic diffusion mechanisms are known in some simple crystal lattice cases, they are unknown in more complex lattice systems and in the important short circuit paths. A quantitative knowledge of these fundamental defect properties is necessary to the realistic modeling and understanding of complex energy systems undergoing diffusive processes such as fission and fusion reactors, solar energy devices, etc. For example, the modeling being used to attack the problem of the swelling behavior of fuel cladding materials in fission reactors requires a detailed knowledge of the processes of atomic transport. Recent successes in the study of the effect of solute atom segregation on cladding swelling have depended upon our knowledge of the migration of vacancies and interstitials as well as the interaction of solute atoms with these intrinsic defects. Further effective work with engineering alloy systems for both fission and fusion reactors demands the availability of knowledge of these parameters. As far as lattice defects are concerned, we have relatively good information for fcc metals. However, comparable information is largely missing for the bcc and hcp metals important to higher-temperature applications in future energy systems such as the first wall of the fusion reactor.

In addition, we know very little about point defect properties and behavior in superconducting compounds (e.g., V_3Si , Nb_3Sn , etc.) which will be used in fusion reactors, electricity generation and for energy transport. Also, more must be learned about the intermetallic compounds which form in the diffusion zone between metals and semiconductors in the devices used in solar photovoltaic systems.

A.2. Particularly important interaction phenomena involve binding between like defects leading to the formation of simple clusters, and between vacancies or interstitials and solute atoms leading to more complicated clusters. Studies of the former phenomena will lead to an understanding of the void formation in reactor materials, while studies of the latter will improve our understanding and control of solute atom redistribution in alloys in service in energy systems (e.g., fission and fusion reactors and solar devices). The forces which exist between point defects and line (dislocations) and planar (grain boundaries) defects, and the pinning effects which can result, should be further studied in terms of their effects upon the mechanical properties of metals and alloys.

A.3. Thermal processes of creation and destruction of defects include the action of dislocations, grain boundaries and interfaces as thermally activated sources and sinks. In many cases the efficiencies with which these entities operate control the rate of important kinetic processes such as the growth of voids and gas filled bubbles in reactor materials. Unfortunately, these efficiencies are often unknown. The production of defects by plastic deformation is important, for example, in determining the low temperature electrical resistivity of composite metal-superconductor devices and the lattice perfection of solar device material. Relatively little is known about the detailed nature of the production of point defects by plastic deformation. Point defects can also be produced by chemical reactions at metal/oxide interfaces during oxidation, and by non-stoichiometry in compounds. These phenomena, also with defect-solute interactions, produce important effects regarding the long term stability of coatings in energy devices, e.g., those subjected to corrosion attack.

B. Atomic Mechanisms

B.1. - B.7. Included in this category are the types of diffusion which occur in crystalline lattices and along various short-circuits in crystalline solids as well as in amorphous solids and in liquids. The current state of affairs in these different types of diffusion in these different materials, is indicated by the matrix type diagram shown below. A matrix of this type exists for each type of driving force enumerated in Section C. Here we only consider self-diffusion under a tracer gradient since this diffusion situation has been the most studied and has yielded the most useful information for application to the engineering use of materials. For this reason, the use of tracer diffusion studies, along with complementary studies of atomic defect properties, should continue to receive high priority. We indicate the approximate level of current knowledge ("extensive" or "small") about each diffusion situation and note that only lattice diffusion in elemental solids and dilute solutions is relatively well understood. Our knowledge of additional important situations, such as lattice diffusion in concentrated alloys and short circuit diffusion, is relatively unsatisfactory and incomplete.

C. Driving Forces

C.1. - C.9. This category includes diffusion under different driving forces such as exist in the materials used in the many aspects of energy technology. Much work will be required to bring our understanding of the phenomena related to these driving forces to a satisfactory operational level. In the case of electromigration, for example, our knowledge of the coupling between the electron current and the atomic current, particularly at grain boundaries or surfaces, is inadequate.

In thermal migration, which will be important in the first wall materials in a fusion reactor, work is needed on the coupling of the thermal current and the atom current. Further, under stress conditions (Herring-Nabarro creep, Weertman creep, defect-drift situations) the boundary conditions at interfaces are affected, and the diffusivity also becomes anisotropic. Induced diffusion due to the presence of a coupled defect flux has been shown to be important in causing the redistribution of solute elements and in drastically affecting the swelling behavior of alloys under irradiation with neutrons. More theory is needed to understand these phenomena.

Material Type Type of Diffusion	Elemental Solid	Dilute Solution	Concentrated Solution	Compound
lattice	extensive	extensive	small*	small*
dislocation	small*	small*		
grain boundary	small*	small		
interphase boundary			small*	
surface	small*	*		
amorphous solid				
liquid	small			

Priorities

High priority should be given to items A.1. and A.2. In general, many powerful tools including:

tracer techniques
microanalytical equipment
EM(High voltage, high resolution, scanning transmission)
resistivity measurements
x-ray, neutron, electron scattering (synchrotron radiation, high intensity sources)

calorimetry
dilatometry
surface techniques (Auger, LEED, SAM)
Mössbauer spectroscopy
ion-beam spectroscopy
FIM-atom probe
positron annihilation spectroscopy

are now available for experimental studies in these areas. It is necessary to have these techniques available to the research community. Also recent theoretical developments in the areas of electron theory and lattice statics and dynamics of atomic defects show considerable promise for the future and deserve support. High priority should also be given to those categories starred in the matrix given above in B. Finally, high priority should be given to diffusion under the technologically important driving forces C.2, C.5, C.6, C.8 and C.9.

ATOMIC TRANSPORT IN IONIC SOLIDS, SEMICONDUCTORS, AND POLYMERS

D. Lazarus, L. DeVries, G. J. Dienes, R. A. Huggins, B. R. Rossing, H. Rupprecht, J. Schultz

The classes of materials encompassed by the three categories included in this panel review are ubiquitous in nearly all energy systems, and their uses span the range from electrical and thermal insulators to conductors, from protective layers to selective sieves, from minor components to major structural members, from reactor fuels to the major components in electronic circuits. In all these functions the major utility and limitations of the materials are frequently governed largely by the rates of atomic transport. Yet, except for the simplest ionic solids (chiefly alkali and silver halides) and monocrystalline silicon and germanium, there exists an enormous paucity of precise diffusion data and verified theoretical models on which to base even first-approximation design calculations. We strongly recommend a two-pronged basic scientific program to remedy these deficiencies, one segment of which is to furnish needed information for immediate use in current and contemplated energy systems, and the second to supply long-term baseline scientific knowledge.

The purpose of the scientific program is to elucidate quantitative, atomic mechanisms responsible for mass (and sometimes charge) transport in these materials to optimize their practical use under a wide range of environmental conditions. This means, of course, careful experimentation utilizing optimal modern techniques where possible, radiotracer and isotope effect measurements, studies over wide range of both temperature and hydrostatic pressure, together with measurements of concomittant properties such as electrical conductivity, creep, etc. A parallel theoretical study is, of course, essential.

It is impossible in this brief report to anticipate all possible fruitful approaches and areas of research, nor can we hope to discuss even those mentioned in any detail. All the fields suggested are characterized by a present nearly complete lack of precise data and theory, and are "priority" problem areas. We have identified seven major areas of immediate energy relevance - the first four of which we would place in the "high priority" category - and five areas of basic scientific importance:

Energy-relevant areas of basic research

- I. Transport under extreme non-equilibrium conditions.
- II. Transport in polycomponent solids.
- III. Transport in anisotropic solids.
- IV. Combined ionic and electronic charge transport.
- V. Transport along surfaces, interfaces, and dislocations.
- VI. Transport in non-crystalline solids.
- VII. Transport in "special" materials.

General basic science areas

1. Electronic configurations: "ionicity" to "covalency".
2. Defect-defect interactions.
3. Defect superlattices.
4. Basic atom transport studies in organic and inorganic polymers.
5. Defect production by particle and electromagnetic radiation.

We may subdivide each of the Roman-numbered research areas further to indicate the contemplated scope of the studies and, in some cases, the relevance to energy programs, if this is not obvious.

- I. Transport under extreme non-equilibrium conditions.

There are essentially no current data or theoretical models to characterize this important area in which the defect population and/or mobility may depart strongly from equilibrium values resulting in major changes in transport

properties and, frequently, formation of internal voids, cracks, and dislocation loops by precipitation of excess defects. We can identify five major causes of departures from equilibrium, each meriting independent study:

A. Electric fields, with or without large electronic currents (electromigration). Models are needed to optimize the lifetime and utility of, e.g., integrated circuits, photovoltaic devices, and photoelectrolytic devices.

B. Temperature gradients (thermomigration). Models are needed to optimize performance of, e.g., MHD materials, reactor fuels, and first walls in fusion reactors.

C. Irradiation effects. Models are needed to quantify a wide variety of important problems areas, including fuel migration and swelling in reactors, mobility of accelerator-implanted ions, effects of ultra-violet on polymers, effect of recombination radiation on defect production and precipitation in light-emitting diodes, and motion of fission products and transmutants (e.g. ^4He , ^3H) in reactor fuels and clads.

D. Stress gradients. Models are needed to understand phenomena associated with both externally-imposed stresses (e.g., wear, abrasion, erosion) and internal stresses (e.g., stress corrosion cracking, crack and craze propagation, loops, precipitates, voids).

E. Chemical potential gradients. Models are needed for a wide variety of uses, e.g., osmotic membranes, molecular sieves, batteries and fuel cells, chemical corrosion, ion implantation, and p-n junctions in semiconductor devices.

II. Transport in polycrystalline solids.

Practically all current data and models are restricted to the simplest binary ionic solids or monatomic semiconductors, in which a single diffusion mechanism is identifiable. Many important devices rely on utilization of more complex solids in which co-diffusion of several species by different mechanisms may be possible. As examples of such uses: thermoelectric materials, light-emitting diodes, solar cells (e.g., $\text{CdS} - \text{Cu}_2\text{S}$), ferroelectrics, laser materials.

III. Transport in anisotropic solids.

Current data are chiefly restricted to cubic solids in which diffusion is completely isotropic, or in solids (bct, hcp, etc.) in which there is marginal anisotropy. Nearly no data or models are available for highly anisotropic solids in which diffusion is effectively one-dimensional (e.g., some solid electrolytes, some polymers, $(\text{SN})_x$, polydiacetylene), or two-dimensional (e.g., some solid electrolytes, layer compounds - including intercalated impurities - and battery electrodes).

IV. Combined ionic and electronic charge transport.

There has been little concern with understanding the interaction between individual electrical transport mechanisms and the importance of traps, with a view to optimizing the combined electrical behavior. In fact all combinations are of considerable practical importance:

A. Low σ_e , low σ_i : in insulators;

B. Low σ_e , high σ_i : in solid electrolytes and electrochemical sensors;

C. High σ_e , low σ_i : in MHD electrodes;

D. High σ_e , high σ_i : in battery and fuel cell electrodes.

In addition, such processes are important in

E. Corrosion through oxide films;

F. Free radical motion in polymers, giving rise to chain reactions.

V. Transport along surfaces, interfaces, and dislocations.

Such studies are important for understanding, e.g., diffusion of metals on non-metallic surfaces (to reduce particle coarsening in catalysis), impurity diffusion down grain boundaries and interphase boundaries (corrosion, cracking, etc.), epitaxy (semiconductors), precipitation and phase separation (stabilization of small-grain structures).

VI. Transport in non-crystalline solids.

There is nearly a complete lack of data or models for such materials. Obviously important cases include: helium diffusion in glass; hydrogen diffusion in amorphous silicon; surface hardening of glasses by diffusive treatment; transport in amorphous semiconductors; diffusion and trapping in submicroscopic, stabilized defect structures such as controlled pores in polymers and cage structures in aluminosilicates; solvent and impurity transport through crazes in glassy polymers; mass transport through slag layers (MHD, coal gasification) or scale layers (geothermal systems).

VII. Transport in "special" materials.

These include: Si_3N_4 ; SiC ; BN ; metal sulphides; various hydrides; various geological minerals.

As a final note, it appears that little in the way of new major facilities is required to make major headway in the recommended program. We recommend general support for facilities to provide precise structural determinations (neutron diffraction, EXAFS, etc.), precise chemical compositions on a microscopic scale, and, of course, for preparation of precisely characterized special materials of interest. In addition, work would be aided by development of special apparatus capable of operating at extremely high temperatures (1000-2000°C), by providing knowledge of surface topology (electron microscopes), local atomic configurations and mobility (NMR), and microscopic atomic transport (ion probes, etc.).

Summary

There is a great lack of precise data and atomistic models regarding atomic transport in all but the simplest ionic solids, semiconductors, and polymers, and basic scientific information is lacking for nearly all current and contemplated energy-related uses of these materials. We recommend a major expansion of research in these materials.

DEFECTS AND IMPURITY CENTERS IN TRANSPARENT IONIC MATERIALS, GLASSES AND SEMICONDUCTORS

J. H. Crawford, W. L. Brown, Y. Chen, F. W. Clinard, W. A. Sibley

Defects and impurities have striking effects upon the behavior of semiconductors and transparent insulators, largely determining their optical, electrical and mechanical properties. In a very real sense this sensitivity to lattice imperfections is the basis of the semiconductor industry with its profound impact upon modern life and commerce via electronics and digital computers. Other familiar examples include TV screen phosphors, photochromic spectacles and window glass, solid-state lasers and radiation dosimeters. On the negative side, defects often limit useful service life or even suitability of this class of materials in many applications, particularly in certain adverse environments that may be demanded by energy technologies. These include high temperature, nuclear radiation, continuous electrical stress and mechanical cycling, factors which both introduce defects and promote their interaction.

In this section attention is focussed primarily upon defect research directed toward explaining the influence of "centers", i.e. atomic scale lattice imperfections, upon electrical and optical properties. Particular emphasis is given studies of defects created by energetic radiation. Many experimental probes which take advantage of the optical and dielectric transparency of these materials have been developed to permit direct examination of a given defect's electronic and physical structure. Connection of defect structures with their experimental consequences is often made possible or conclusive through theoretical models which predict energy level structures, formation energies, motion energies, etc. Recently developed computational techniques have resulted in a great improvement in these structural

predictions. During the process of "identification" of a defect or a class of defects, their useful or deleterious potentialities often become evident. These studies also suggest what probe or probes are most useful for assaying the different defect concentrations and monitoring solid-state "chemical" interactions in which they are involved.

Transparent Crystalline Materials

Although much research effort has been devoted to defects and impurity centers in simple crystals such as alkali-halides, attention has begun to shift to more complex systems such as perovskites, fluorites, spinels, rutiles and hexagonal crystals which are more closely related to materials with technological potential. These are the types of crystal structures which are most likely to find application in fission and fusion reactors, MHD generators, host structures for catalysts, lasers, etc. Now that suitable high purity specimens of these crystal types are becoming available, a strong effort in this direction using a wide variety of experimental tools and theoretical approaches is essential. Techniques such as high-voltage electron microscopy and diffuse x-ray scattering are needed to expose the extent of defect clustering and dislocation-loop formation that results from high fluences of energetic radiation. The thermal annealing of these complex defects should be explored in refractory oxides to ascertain the basis of void formation and swelling.

The main task, however, is identification of the intrinsic point defects in these more complex crystal structures so that interactions can be studied to the same degree of confidence as is possible for the alkali halides. Also important are the interactions of defects with lattice vibrations of the host crystal and local modes associated with defect structures themselves. Hence, attention should be given infra-red spectroscopy, Raman scattering, vibronic transitions and low temperature thermal conductivity methods which have been fruitful in revealing defect-lattice interactions in simple cubic structures. Recent theoretical and experimental progress in dynamic Jahn-Teller relaxations should also be exploited in these more complex structures. Another phenomenon showing promise is the breaking of selection rules for intraband transitions by defect-impurity interactions, e.g., F-center - Mn^{2+} interactions in $KMgF_3$ lead to a 10^4 increase in the transition probability.

A careful assessment of the dimensional electrical stability of refractory insulators in adverse environments is needed. This points up the importance of determining the motion energies of cation and anion vacancies in their various charge states since complex and extended defects causing deleterious property changes result from interactions of these elemental point defects. The charge state of a defect has a profound influence on its activation energy of motion, and has important consequences for lattice expansion. Substantial outward relaxation around electron-capture defects occurs when the trapped electrons are removed. This effect, diminishes with increasing covalent binding. Although there has been considerable work in the past on quartz, its covalent bonding has frustrated efforts to understand aging and radiation effects. The availability of highly purified quartz crystals is necessary for the solution of this problem.

Glass

Because of its low cost and the ease with which it can be fabricated into components, glass holds promise for a wide variety of applications in energy conversion and waste disposal. However, there are a number of basic questions that need addressing. Although it is known that fused silica and silicate glasses of various compositions contract during exposure to energetic particles and photons, the degree of contraction is sensitive to composition and there are glasses which are known to expand. Indeed the dimensional stability is known to be affected by several physical processes; e.g. enhanced ordering of SiO_4 tetrahedra, network

interruption, gas retention, etc., which act in opposition or in concert to produce the net effect. These processes need study particularly as a function of temperature. Other questions include the effect of radiation on the devitrification temperature, its influence on creep stress relaxation, fracture resistance and mechanical strength. These questions need to be tackled systematically and from a basic point of view. Emphasis should be given those experimental probes effective for revealing network modification during radiation and annealing.

Semiconductors

Experimental probes for defect research in semiconductors are much the same as for transparent materials suitably adjusted for the smaller band gap of the former. Electron spin resonance and polarized absorption studies should be continued on compound semiconductors. Deep level spectroscopy, involving capacitance measurements as a function of biasing potential, is capable of revealing the position of deep acceptor and donor levels of defects and impurities. This tool has yet to be exploited fully.

From an energy conversion perspective a host of new problems mainly centered upon interfaces has emerged. Polycrystalline silicon and amorphous silicon present an enormous challenge to the defect scientist. Grain boundaries not only serve as defect sources and sinks, they are defects themselves albeit of an extended type. Empirical means of coping with some of these problems, e.g. blocking of grain boundaries with phosphorous or hydrogen in the case of polycrystalline silicon, have improved device performance. However, these problems need serious attention from a basic approach to achieve long range solutions.

Extended Defects

The time is ripe for pushing defect investigations into the area of dislocation, stacking faults, shear-plane precipitates, grain boundaries and interfaces. All of these are lumped together under the term extended defects since they involve one or two dimensions. Their systematic study in non-metals should have important consequences for many technological problems. Although new experimental tools will be needed, existing ones can be used with profit. An example is the delineation of slip bands and slip systems in freshly deformed alkaline earth oxides by ultra-violet excitation of luminescence from defects created by the deformation process. There is a strong need for research on problems associated with grain boundaries and grain growth in fabrication of ceramic components for high temperature applications.

Priorities

- Extend investigation of the physical properties of point defects to more complex systems which are directly related to materials of present or potential application to energy technologies.
- Give emphasis to studies of the interaction between phonons and defect centers and the influence of lattice distortions on the electronic (optical) characteristics of point defects in insulators.
- Explore systematically the influence of adverse environments (thermal, radiation, high electrical stress) on the dimensional, chemical and electrical stability of refractory nonmetals.
- Much more attention to defect structures as they affect glasses, amorphous semiconductors, surfaces, etc. In particular, time is ripe to push investigations on extended defects.

DEFECTS IN NONSTOICHIOMETRIC COMPOUNDS

G. C. Libowitz, L. Eyring, F. A. Kroger, A. S. Nowick, W. S. Williams

Before discussing the recommendations of this study group the term "nonstoichiometric compounds" should be clarified because all compounds have variable compositions on the basis of thermodynamic principles. A nonstoichiometric compound is usually considered to be one which exhibits easily detectable deviations from the stoichiometric composition and therefore one which will have a relatively high intrinsic concentration of defects. However, since there is no clear-cut quantitative definition of the term, nonstoichiometric compounds may also include normally "stoichiometric" compounds which become nonstoichiometric under severe conditions of temperature, pressure, radiation field, or impurity contents.

Suggestions for further basic research are discussed under nine general areas, and their relevance to specific energy technologies are identified.

I. Characterization of Defects

The properties and behavior of nonstoichiometric compounds strongly depend upon the nature and concentration of the defects associated with the nonstoichiometry. Therefore, it is extremely important that the defects be completely characterized from a fundamental standpoint. Such characterization would include identifying the nature and structure of the defects and their modes of interaction which lead to clustering and ordering. The defects may be simple point defects, complexes, or extended long range configurations such as crystallographic shear planes or microdomains. Combined use of many techniques including measurements of transport, optical, magnetic, and thermodynamic properties, as well as microscopy, diffraction and scattering techniques must be brought to bear on solving these problems in compounds of both fundamental and technological importance. Of special interest in characterizing extended defects is the use of high resolution and scanning transmission electron microscopy. Also, new experimental techniques for identifying and characterizing defects must be sought.

Particular emphasis should be placed on ternary and multicomponent compounds which have been the subject of relatively few studies to date. Some examples of such compounds are perovskites (used in catalysis), transition metal oxide "bronzes" (possible new electrode materials), nitrides and carbides (for high temperature structural applications) and selected intermetallic compounds.

II. Stability of Ceramics

Many ceramic materials for high temperature applications are nonstoichiometric or become so under severe conditions of operation. Investigations of the conditions which cause dissociation and phase transitions of ceramic materials are needed. These include temperature, temperature gradients, high level radiation and electric fields, variation of thermodynamic activities of the constituents, and composition gradients. The effects of cycling these variables are also important. The development of techniques for measuring and working at temperatures in excess of 2000°C in both oxidizing and reducing atmospheres must be developed.

Instability is a major problem in MHD electrodes (ternary oxides are of particular interest here), alternative fuels for fission reactors (uranium carbides and nitrides, thorium compounds) and ceramic insulators for fusion reactors, particularly the effect of high neutron fluences on materials such as Al_2O_3 .

III. Atomic Transport Processes

The relationships between deviation from stoichiometry and defect microstructures on the one hand and diffusion, high temperature creep, and radiation induced creep on the other hand should be studied. The role of extended defects on mass transport processes is very unclear and requires further investigation.

Such studies would be important in understanding sintering in nuclear fuel elements (e.g. UO_2), radiation-induced creep in electrical insulators for fusion

reactors, and the kinetics of hydride formation and dissociation in hydrogen storage systems. Also, atomic transport data would be useful in determining the extent of ionic mobility in electronically conducting solid solution electrodes, and in designing photovoltaic systems in which interdiffusion between components is minimized.

Since diffusion through oxide, sulfide, carbide (etc.) films is frequently the controlling factor in gaseous corrosion of metals (e.g. oxidation, sulfidization), information on diffusion of ionic or atomic species (usually via defects) through such nonstoichiometric compounds would be of special importance in all systems utilizing metals at elevated temperatures in oxidizing or corrosive atmospheres.

IV. Catalysis by Nonstoichiometric Compounds

The influence of the defects associated with nonstoichiometry on the catalytic activity of nonstoichiometric compounds has been the subject of a great many investigations in the past with only a moderate degree of success in explaining the fundamental relationships. However, in view of the recent availability of new surface (or near-surface) techniques such as X-ray photoelectron spectroscopy, Auger spectroscopy, scanning electron microscopy, etc., it is highly desirable that basic research in this area be continued. Of particular interest in such studies is the relative importance of point vs extended defects. The application of new, more powerful theoretical treatments emerging in this area also should be encouraged.

Catalysis is important in coal gasification (for both the Fischer-Tropsch process and the Shift reaction); in particular there is a need for improved catalysts which are resistant to sulfur poisoning. New catalysts are also required for thermochemical reactions for thermal energy storage and hydrogen generation, and in the development of industrial processes which are less energy intensive than existing ones (e.g. in electrolytic chlorine production).

V. Opto-Electronic Materials for Solar Conversion

A fundamental scientific approach to finding new materials for solar conversion is recommended. It is very likely that many such materials will be nonstoichiometric compounds whose relevant properties are dependent on defect structure. Included in this category would be materials which absorb at low wavelengths and reflect at higher wavelengths for use in solar collectors (e.g. HfC), and compound semiconductors for photovoltaic cells and photoelectrolysis (e.g. ternary chalcogenides and oxides).

VI. Intermetallic Compound-Hydrogen Interactions

New intermetallic compounds are needed for storing hydrogen since none of the known binary metal hydrides meets the requirements for efficient storage. At present, there is no reliable way of predicting the reactivity of an intermetallic compound with hydrogen from a knowledge of the behavior of the constituent metals. Both an intermetallic compound and its resulting hydride will usually exhibit wide deviations in stoichiometry. Investigations of the effect of nonstoichiometry of an intermetallic compound on its reactivity with hydrogen as well as of relationships between nonstoichiometry of the hydride and its properties could contribute greatly to finding efficient new hydrogen storage materials.

VII. Chemical Hysteresis

Cycling of an independent variable such as temperature or pressure of one component of a nonstoichiometric compound frequently results in chemical hysteresis, which is characterized by a different sequence of metastable states in each branch of the cycle. Although several models to explain these effects have been proposed, a complete understanding of the phenomenon, which appears to violate thermodynamic principles, has not been achieved.

Processes involving compounds which exhibit chemical hysteresis and which include cycling of an appropriate variable may be detrimentally affected by such hysteresis effects. Examples include ceramics which are subject to temperature cycling in industrial heat engines and recuperators, and hydrogen storage materials which undergo pressure cycling.

VIII. Effects of Nonstoichiometry in Superconducting Compounds

In A15 structures, stoichiometry appears to play a large role in determining superconducting critical temperatures and fields, but this aspect of superconductivity is poorly understood and requires further evaluation. High T_C and H_C superconductors are important in fusion and MHD reactors, for magnetic storage of electrical energy in superconducting inductors, and for power transmission and generation.

IX. Hard Ceramic Materials

The variation of mechanical properties (such as microhardness and fracture toughness) with composition and defect structure of hard ceramic materials should be studied. The results would be important in obtaining new materials for drills in geothermal applications.

Priorities

Although all the areas discussed here are important to one or more energy technologies, the first six should be given priority over the latter three. The decisions on priority were reached on the basis of three considerations: (1) the degree to which a particular research area pervaded several energy technologies (2) the importance of the particular energy technology problems related to that area of research and (3) the likelihood that technological problems would be solved in a reasonable time span as a result of the research.

RADIATION EFFECTS IN METALS

A. N. Goland, T. H. Blewitt, E. E. Bloom, W. G. Johnston, T. C. Reuther, M. T. Robinson, J. O. Stiegler, J. L. Straalsund and H. Wiedersich

The fission and fusion energy technologies benefit most from basic investigations of radiation damage in metals. The diversity of materials which require investigation and the fact that related research is carried on in many laboratories creates requirements for the availability of well-characterized research materials, including those metals and alloys most likely to be allied with energy technologies. The study group recognized the distinction between the basic research which has been performed on simple metals, and the needs of the fission and fusion technologies for an understanding of radiation-damage phenomena in engineering materials. While basic investigations using the latter may yet be too difficult, studies utilizing more complex materials, e.g., binary and ternary alloys should be initiated. Such research would serve to identify important parameters controlling the behavior of alloys.

The evolution of radiation damage can be described as a sequence of events starting with the initial transfer of energy to a lattice atom by an incident particle. The branching cascade of subsequent displacement events terminates in the so-called primary damage state, by which time defect clustering or migration from the vicinity of the cascade have occurred. New experimental methods and more extensive use of existing ones are needed to help establish the nature of the primary damage state. Such techniques as FIM, and small-angle and diffuse scattering of x-rays and neutrons are examples of experimental tools that are not yet in wide use in the United States. There is a possibility that theoretical results will outrun experimental capabilities if additional emphasis on the latter is not forthcoming. There is a need to develop techniques for computer simulation of high-energy cascades with special emphasis on the capability to

follow the cascade development beyond times of $\sim 10^{-6}$ sec. Descriptions of defect properties which govern the evolution of the cascade must take into account the influence of the locally high defect density in the cascade. Another complication arises when the cascade occurs near a surface, and this aspect of the computations also requires attention. Concurrently, experiments should be devised which can detect the number of free point defects that escape cascades. It is important to know the spatial distribution and configuration of the defects resulting from a cascade and to develop methods of predicting which configurations will collapse into dislocation loops at a later time.

In order to achieve their program goals, the fission and fusion materials programs will utilize a variety of radiation sources. These sources produce different primary knock-on spectra, and experiments designed to determine the energy dependence of cascade structure will therefore be very important. Computational techniques will be required to describe cascade development over a range of energies extending to several MeV and to consider the interaction of these cascades with preexisting defects in a variety of materials.

At temperatures where thermally-activated defect migration can occur, a damage microstructure nucleates and grows. This microstructural evolution is affected by a number of variables including impurities, gaseous and other transmutation products, prior microstructure, damage production rate and cascade structure. The combination of high temperatures and radiation has elevated the question of phase and compositional stability under these conditions to primary importance. Correlation of the results of ion-bombardment experiments with companion neutron irradiations requires a knowledge of the thermal stability of phases, structures and compositions which conventional metallurgy has not provided. In the presence of defects the thermodynamics of alloys can be altered and nonequilibrium phenomena can carry the system into previously inaccessible regions of the phase diagram. From a fundamental viewpoint, the creation and migration of point defects lower kinetic barriers and foster enhanced diffusion and nucleation. Most importantly for the development of microstructures, it causes composition redistribution by the cascade dissolution of defect clusters and the coupling of solute migration and defect migration. This can come about through the formation of mixed dumbbell interstitials, solute dumbbells and vacancy-solute complexes. It is most important that the migration mechanisms and energies of these fundamental defects be calculated and measured. Equally important to a description of segregation are the related binding energies of vacancies and interstitials to solutes. Measurement of these parameters should begin. Although swelling and the void phenomenon are receiving adequate attention both theoretically and experimentally, it is possible that correlations with new variables may be discovered. One example of this is the recent evidence that the diffusion coefficients of major constituents of some alloys are correlated with swelling.

It is difficult to separate microstructural development from its effect on the mechanical behavior of metals. Again the questions of phase and composition stability arise. Fracture can be influenced by radiation-induced segregation to grain boundaries and by high temperature He embrittlement. Much of the large effort on fracture relies heavily upon continuum mechanics and phenomenological variables. Fundamental research combining the methods of micromechanics with irradiation should be pursued more vigorously. It is also essential to devise experiments which will provide a basic understanding of irradiation creep mechanisms at high temperatures, and it should be recognized that possibly different mechanisms will occur at temperatures below $0.3 T_M$ during long-term exposure to neutrons.

The foregoing comments relate to processes in the bulk solid. However, equally important phenomena take place at surfaces. In particular sputtering, blistering and erosion may be critical to the operation of a fusion reactor. Poisoning of the plasma by sputtering of first wall alloys and low-Z compounds may well be a critical radiation-damage effect. Sputtering yields, charge states and angular distributions should be measured using ions of masses and energies typical of the first-wall environment. Events at the surface and in the bulk may interact, and this is a possibility which warrants study. For example, surface defects arising from blistering and erosion may influence bulk mechanical behavior. Conversely, microstructural evolution in the bulk may alter the composition near the surface, causing changes in the species of sputtered ions. Recognition that the surface is a large defect which may influence the primary damage state to some depth is important. Methods of introducing real surfaces into computer modeling need to be investigated and incorporated into existing programs.

The changing design of fusion reactors makes an assessment of the importance of radiation damage to high-field superconductors difficult. Penetrations for neutron-beam injection and diagnostic devices may cause the superconductors to be subjected to flux inhomogeneities which could reduce their critical currents drastically. As a result of research into this problem, it is recognized that the properties of superconductors such as the A-15 compounds depend critically upon their defect structure. Consequently radiation damage is currently a means of introducing defects in a controlled manner. This effort should be supported until it is determined whether it can lead to the creation of high T_c superconductors. The effects of radiation on the insulation surrounding the superconducting wires should not be overlooked.

A wide range of radiation sources will have to be employed. Some will adequately simulate environmental conditions anticipated in a fusion or fission reactor. In other cases the available sources do not match the required operating conditions, but their use is necessary in order to pursue a meaningful radiation damage program in the U.S. New ideas for neutron sources should be encouraged and supported.

Another aspect of the radiation damage program is the need for implementation or exploitation of relatively recent experimental techniques. Ion-beam methods of altering the near-surface properties of materials should be strongly supported. Such techniques can produce alloys unattainable through conventional metallurgical processes and may even conserve scarce mineral resources. Microanalysis using energetic charged particles continues to develop and should be supported. FIM, X-ray diffuse scattering, small-angle neutron scattering, positron annihilation and the Mössbauer effect are examples of other techniques whose value has been demonstrated, but which are not all generally available in this country. The application of these tools by a number of laboratories should be supported, and the development of new techniques should be encouraged.

In summary, radiation-effects research has entered a new era in which more emphasis must be placed upon the behavior of more complex materials than were previously investigated. Most of the important parameters having to do with the progression from damage cascade to final microstructural evolution have been identified, but not measured. Measurements must be made and continuously compared with computer models and rate-theory calculations. Tradeoffs will have to be made between the need to isolate variables through the investigation of simple systems and the necessity to furnish required data to developing energy technologies. The final link which relates defect microstructures to materials properties and behavior is weak and should be strengthened. This is evident, for example, in the case of irradiation creep.

Priorities

- Develop understanding of formation and migration and interactions of complex defects; relationship to phase and compositional stability under irradiation.
- Experiments and theory to develop understanding of irradiation-induced creep.
- Computer modeling of high energy cascades, radiation dynamics in complex materials, and low-energy, light-ion sputtering.
- Broader application of existing experimental techniques; development of new ones.
- Mechanisms of fracture in irradiated materials, especially the nucleation and growth of grain boundary cracks.
- Use radiation to help understand the ways in which defects control the properties of A-15 compounds.
- Sputtering experiments and studies of erosion, blistering, and gas re-emission.

GASES IN SOLIDS

H. Birnbaum, R. S. Blewer, O. N. Carlson, J. R. Cost, B. Holt, W. D. Wilson

I. Scope

We have defined "gases" to encompass H, He, O, N, C, S and P, all of which are believed to occupy interstitial sites in most metals. We generally make no attempt to specify the solid in which the interstitial behavior is of interest as the preferable host will depend on the investigative technique as well as the detailed interest of the investigator.

II. Research Areas.

A.1. Mechanical Properties - A major area of opportunity is the effect of gases on the mechanical properties and fracture of solids. Efforts in this area should be directed towards understanding the mechanisms of embrittlement due to the presence of the above gaseous species. Embrittlement due to these species should be considered as both a high and low temperature fracture mechanism. Embrittlement studies in radiation environments should be carried out. Particular attention should be directed towards fractures associated with welds due to these active species. In addition to transgranular failure, certain active species such as S and P appear to be associated with grain boundary fractures (temper embrittlement). Understanding these phenomena requires that the effects of H and the other active species on atomic bonding be understood. This aspect of the problem appears to be an area in which theoretical studies are promising.

Embrittlement due to tritium has the additional complication of the presence of ^3He due to T decay. Inert gas embrittlement appears to be due to the formation and coalescence of gas bubbles. Since the gas is generally the product of transmutation reactions or results from a flux of ^4He such as in the fusion reactor environments, the mechanisms of fracture should be studied in situations which combine high inert gas concentrations with irradiation. The kinetics of bubble formation and coalescence should be investigated.

Many material failures in the presence of aggressive liquid environments can be ascribed to stress corrosion cracking, which appears to be related to hydrogen embrittlement in certain alloys. The mechanism of this failure mode should be investigated.

The low ductility failure modes discussed above are of great significance in energy systems where high fugacities of gases containing the active species are present. These include fission and fusion reactors, fossil fuel systems such as coal gasification and liquification plants, geothermal systems and energy transport systems. In coal gasification plants gases containing S can result in sulfidization failures.

Non-destructive evaluation methods are needed for detecting cracks and predicting failures. Research in this area based on new scientific principles should be encouraged.

In addition to the low ductility failures discussed above, coal gasification and liquification systems which operate at elevated temperatures in high hydrogen fugacity atmospheres experience failures from "hydrogen attack". This results from reaction of hydrogen with second phase carbides and nitrides. The thermodynamics and kinetics of these reactions should be studied.

Little is known about the effects of interstitial solutes and their compounds on high temperature mechanical properties such as creep and cyclic fatigue, particularly in the presence of a high defect production rate due to irradiation. Under these conditions high solute interstitial mobility and changes in the stability of second phase compounds must be considered. Investigations of the phase equilibria and kinetics of dispersion or precipitation hardening in complex alloy systems and the attendant strengthening mechanisms should be made.

Increased use of polymers in energy systems will require understanding and control of their environmentally induced fracture. In many cases these are similar to those observed in metals. Embrittlement by cavitation, crazing and "inert gas" (such as N_2) embrittlement all require additional attention.

A.2. Priorities - Mechanisms of hydrogen embrittlement, stress corrosion cracking, inert gas embrittlement and kinetics of dispersion hardening.

B.1. Gas-Solid Interface Processes - Since many of the energy systems operate under conditions where solids are in contact with a gaseous atmosphere having high fugacities of H, O or S, the transfer of these solutes across the interface is of prime importance. Many of the fracture processes listed above are rate controlled by transfer across gas-solid interfaces. Hydride formation kinetics are often controlled by interface reactions. These studies are particularly timely due to the availability of new experimental techniques for surface studies. The dissociation mechanisms of H_2 at surfaces and the effects of adsorbed species such as H_2S , SO_2 and CO should be examined. The role of oxides in these processes appear to be of great significance.

Tritium permeation presents the special problem of the effect of β irradiation on the surface processes and this is of importance in tritium containment problems.

B.2. Priorities - The studies of the mechanisms of H_2 , H_2S and SO_2 dissociation and transfer across solid surfaces and the effects of adsorbed molecular species on these mechanisms.

C.1. Mobility of Interstitial Solutes - The mobility of interstitial solutes such as H and He are of great importance in hydrogen and helium embrittlement, hydride energy storage, and tritium containment. These problems are of scientific significance as well, because quantum effects may be of importance. New experimental techniques as well as opportunities for significant advances in theory make this area of great interest. Helium diffusion should be measured in a variety of systems and under conditions of high radiation fluxes. Both H and He mobility appear to be extremely sensitive to trapping at solutes and defects. For H it appears possible to influence the diffusivity and possibly the hydrogen embrittlement processes by solute additions. He mobility is of primary significance in reactor environments. The effects of stress, thermal and defect gradients are also expected to be of great interest.

C.2. Priorities - Effects of trapping on H and He diffusion.

D.1. Hydride Research - Hydrides (and tritides) are of interest for energy storage systems and tritium fuel storage. These systems are also of great scientific interest as they offer opportunities to study interstitial effects on the phonon properties of solids, phase transitions controlled by interstitial ordering

interactions, and solute effects on crystal bonding. The studies of hydride crystal chemistry should encompass inter-metallic, as well as non-metallic compounds. The basic understanding of the factors which determine the metal-hydrogen ratios should result. Studies of the thermodynamics and kinetics of hydriding and dehydriding is another promising area and one which has important consequences for use in storage systems.

E.1. Gradient Effects on Second Phase Thermodynamics and Kinetics - The thermodynamics and kinetics of second-phase compounds related to gases in solids should be sensitive to gradients of temperature, stress and radiation produced defects. Migration of inert gas bubbles and reversion and re-precipitation of hydrides, oxides, etc., should be investigated.

E.2. Priorities - The studies encompassed by E.1.

F.1. Electronic and Optical Properties - Available data indicate that H significantly improves the semiconducting properties of amorphous Si, but gaseous impurities in semiconductors generally adversely affect the efficiency of devices. The effect of H on the properties of superionic conductors is expected to be significant. For the development of ceramics with appropriate optical properties for thermal solar energy systems, interstitial solute effects on these properties should be studied. The mechanical properties of ceramics may also be affected by the incorporation of reactive gases during sintering processes.

The studies of amorphous metals are a new area of research which hold promise in a variety of energy systems. The effects of reactive gases on the properties of these materials should be examined.

G.1. Equipment Recommended - Many of the investigations discussed above require the ability to analyze the gas distribution in solids on a submicron scale and to determine the composition and structure of second phases. Two instruments are important for this work: (a) Scanning Transmission Electron Microscope with capabilities for elemental analysis; (b) Secondary Ion Mass Spectrometer Ion Probe. The fracture mechanism studies would be greatly aided by the availability of high voltage transmission electron microscope facilities. Improved neutron scattering facilities would be useful for a wide variety of studies of light element behavior.

MATERIALS SCIENCES WORKSHOP ON

ENGINEERING MATERIALS SCIENCE

Held May 2 to 4, 1977 at Oak Ridge National Laboratory

Organizers

C. J. McHargue, Oak Ridge National Laboratory
J. R. Cost, ERDA, Division of Physical Research
C. A. Wert, University of Illinois

Participants

T. Alfrey, Dow Chemical Co.	R. W. McClung, ORNL
B. R. Appleton, ORNL	C. J. McHargue, ORNL
H. Berger, Nat'l Bureau of Standards	R. D. Nelson, Pacific Northwest Lab.
J. R. Blevins, ERDA, Oak Ridge	F. A. Nichols, ANL
H. K. Bowen, MIT	W. D. Nix, Stanford University
A. D. Brailsford, Ford Motor Co.	R. M. Pelloux, MIT
O. Buck, Rockwell Science Center	J. Perona, Univ. of Tennessee
J. V. Cathcart, ORNL	F. S. Pettit, Pratt & Whitney
A. H. Clauer, BMI	L. W. Roberts, LLL
J. R. Cost, ERDA, Physical Research	W. F. Savage, Rensselaer Poly. Inst.
H. E. Frankel, ERDA, Fossil Energy	J. T. Spruiell, Univ. of Tennessee
H. L. Fraser, Univ. of Illinois	E. A. Stern, Univ. of Washington
D. H. Gurinsky, BNL	V. J. Tennery, ORNL
S. Hecker, Los Alamos Sci. Lab.	A.P.L. Turner, ANL
L. C. Ianniello, ERDA, Physical Res.	F. L. Vook, Sandia Labs.
D. Keiser, EG&G Idaho	J. L. Walter, General Electric
W. D. Kingery, MIT	M. S. Wechsler, Ames Laboratory
J. M. Khan, LLL	R. W. Weeks, ANL
D. L. Kummer, McDonnell-Douglas	C. Wert, Univ. of Illinois
A. Levy, Lawrence Berkeley Lab.	S. Wiederhorn, Nat'l Bureau of Standards
J. J. Loferski, Brown Univ.	F. Witmer, ERDA, Environmental Control
H. L. Marcus, Univ. of Texas	

SCOPE

The Workshop on Engineering Materials Sciences encompassed three areas: engineering materials, engineering physics, and engineering chemistry. It focused on the necessity of establishing a scientific base for technology requirements which use complex materials in complex systems or environments.

WORKSHOP PRIORITIES

Within the priority groups, subjects are listed by workshop recommendations, not by rank order.

Priority One

Nondestructive Evaluation. Improvement must be made in understanding the interaction of probing energy (e.g., ultrasonic, electromagnetic) with structural materials and in quantitative detection and characterization of flaws. This research area impacts many energy systems. To systematically improve resolution and reliability of measurements, studies are required on the interaction of the probe with surface and internal interfaces, sources of internally generated signals, and imaging techniques and pattern recognition. A large gap exists between detectability of "flaws" and the ability to use this information in design application.

Materials Characterization. Studies to quantify high spatial resolution and surface sensitive chemical and phase analysis are included in priority one. All study groups of this workshop identified surface sensitive problems.

Constitutive Relationships should be based on microstructure and complex loading tests. Because of safety and environmental considerations and the large capital costs of new energy systems, detailed structural feasibility studies must be made. Current constitutive equations do not account for many of the complex mechanical phenomena to be encountered.

Creep-Fatigue-Environment Interactions include effects of environment, temperature, stress or strain wave shape, hold-time, and combined deformation on crack initiation and growth. Such interactions may govern the life of complex structures.

Welding. Research in welding is urgently needed for the control of microstructure of fusion welds, prevention of embrittlement, use of minor elements to alter arc physics, specify post-weld heat treatments, and develop processes for joining complex materials. Of all methods of materials processing, welding is one most widely used yet least understood from a fundamental view.

Surfaces — Properties, Reactions, Modifications. Each of the five study groups identified some aspect of surface behavior as a critical problem in one or more energy applications. Specific topics include: Erosion, Wear, Corrosion-Enhanced Erosion, Sputtering Process Research, Coatings, Modification by Ion Implantation, Thin Films and Interfaces in Semiconductors, and Effect of Surface Reactions on Crack Initiation.

Ceramics for High Temperature Service. Research is required on most aspects of ceramics, e.g., the relation of the initial powder character to the finished solid product, novel fabrication processes, microstructural-property relationships. Design methods must take into account the need to use inherently brittle materials and the fact that for any specific application design alterations are required if ceramics are to be substituted for metals.

Polymers. Polymers represent a class of materials not adequately considered by the materials science community but deserves a concerted effort. The development of structure-property relationships to alter specific properties for particular applications has great potential payoff. Research on deformation processes, optical, thermal, elastic and dielectric properties were defined as critical areas for support. In view of industry's competence and large activity in the synthesis of polymers, this workshop concluded this aspect is not appropriate for support by the Division of Basic Energy Sciences.

Priority Two

Unconventional Materials and Process Research. Amorphous materials have recently become available but much of the effort to date has been on the production of such materials. They have unusual electrical and magnetic properties, strength and corrosion resistance. Studies on structure, property, and stability are suggested. Ion implantation and molecular beam deposition are processes whereby surface layers with unique properties may be produced. Advanced semiconductor, photovoltaic, and composite materials are included in this topic.

Fracture Analysis. Linear elastic fracture mechanics is widely used in design but is highly idealized relative to real materials. A critical need exists for improved understanding of fracture criteria in materials undergoing significant plastic deformation.

Stress Corrosion Cracking. A basic understanding of this process is still lacking although it is pervasive in most energy systems. Recent advances in microanalytical procedures may enable new approaches to be developed to obtain a mechanistic understanding.

Priority Three

Testing. Extrapolation of short-time or idealized test conditions to real systems cannot be accomplished with a high degree of confidence.

Surface Chemistry of Materials in Brines. Progress in geothermal energy utilization would be accelerated by understanding surface reactions of metals and polymers by concentrated brine solutions.

Hydrogen Embrittlement remains a significant problem in many systems in spite of a large amount of research conducted in the last twenty-five years.

Cementitious Materials. The setting and curing of cements is a highly complex chemical reaction and may occur over many years. Cements represent a class of materials used in large volumes and consumes large amounts of energy.

They are used in many energy conversion systems, e.g., prestressed concrete pressure vessel for high temperature gas-cooled reactors, waste management, geothermal installations, and coal gasification vessels. Modern methods of microanalysis of small volumes can determine the chemistry and physical arrangements of phases and relate these to physical, chemical and mechanical properties.

INTRODUCTION

Engineering Materials Sciences is a new budget activity for the Materials Sciences Program of the Division of Physical Research. It includes the sub-categories of Engineering Materials, Engineering Physics, and Engineering Chemistry. This activity encompasses complex physical phenomena in complex materials important to energy production, conversion, conservation, or use.

Much basic research has been conducted on simple materials under well-defined experimental conditions. In recent years, it has become apparent that although these experiments are necessary, a firm basis for predicting the long-term behavior of materials in real systems, and in some cases, the feasibility of advanced systems, requires studies of more complex materials and more complex test conditions. Thus, the research area of Engineering Materials Sciences has been proposed to provide the information necessary to form a base for ERDA technologies.

There are a number of reasons to conduct basic research. The one considered foremost in this workshop is the development of a scientific base from which applied research and engineering development can proceed in a logical and efficient manner. One must, however, always remember that many of our most important technologies have evolved from discoveries made in the pursuit of truth in nature without regard to a predicted use. A significant portion of fundamental or basic research is justified on the basis that history shows the rewards have been greater than the cost for undefined, but imaginative probing of the unknown.

In this study, we have focused on a reasonably well-defined set of problem areas but have also included an element of probing as defined above.

PROCEDURE

A three-day meeting was hosted by the Metals and Ceramics Division of Oak Ridge National Laboratory in Knoxville, Tennessee, May 2-4, 1977. Approximately seven hours were spent in discussion between the members of the workshop and the "Technology Briefers" (see list below) on Energy Sources and Energy Use and Conservation. Many of these briefers joined the workshop study groups for the balance of the meeting. The study groups spent nine hours discussing the technology briefings, state-of-the-art in their areas, and identifying the important problems in these areas. Another six hours were spent by the workshop members in discussing the preliminary and final reports of five study groups. Many study groups spent much more time than scheduled discussing the research needs and priorities.

Of the eight Technology Briefers, three were from USERDA, three were from ERDA contractor laboratories, one from a university, and one from an industrial

corporation. Thus, both in the briefings and in the study groups there was a representation of ERDA, ERDA contractor laboratories, the university community, and the industrial sector. The organizing committee believes this presented a balanced view of Engineering Materials Science.

The Technology Briefers were:

FOSSIL ENERGY:	Dr. Henry E. Frankel Division of Fossil Energy U.S. Energy Research & Development Administration Washington, D. C. 20545
SOLAR ENERGY:	Dr. J. R. Blevins Oak Ridge Operations Office U.S. Energy Research & Development Administration Oak Ridge, Tennessee 37830
GEO THERMAL:	Dr. J. Perona Department of Chemical & Metallurgical Engineering University of Tennessee Knoxville, Tennessee 37916
FISSION ENERGY:	Dr. R. W. Weeks Materials Science Division Argonne National Laboratory 9700 S. Cass Avenue Argonne, Illinois 60439
FUSION ENERGY:	Dr. D. L. Kummer McDonnell Douglas Astronautics Corp.-East Room E-457, P. O. Box 516 St. Louis, Missouri 63166
ENVIRONMENTAL CONTROL TECHNOLOGY:	Dr. Fred Witmer Division of Environmental Control Technology U.S. Energy Research & Development Administration Washington, D. C. 20545
WASTE MANAGEMENT:	Dr. R. D. Nelson Metallurgical Research Section Battelle-Pacific Northwest Laboratories Richland, Washington 99352
CONSERVATION:	Dr. V. J. Tennery Metals and Ceramics Division Oak Ridge National Laboratory P. O. Box X Oak Ridge, Tennessee 37830

GROUP I. NDE, MATERIALS CHARACTERIZATION AND TESTING

R. W. McClung, ORNL, Leader
 H. Berger, National Bureau of Standards
 O. Buck, Rockwell Science Center
 H. L. Fraser, University of Illinois
 H. L. Marcus, University of Texas
 S. Wiederhorn, National Bureau of Standards

Introduction

Improved service life and reliability of energy systems must be achieved despite the severe stresses and environments to which the diverse materials and components will be subjected. Research in nondestructive evaluation (NDE), materials characterization and testing will provide the knowledge and quantitative tools necessary to assess the integrity and character of materials and components which, coupled with other factors (e.g., design, materials selection, failure mechanisms), can lead to meaningful predictions of lifetime and failure. This goal is vital to reliable cost-effective energy systems. Before improvement in the longevity and reliability in performance of materials for use in energy systems can be accomplished, the materials must be thoroughly characterized and tested and subtle changes understood, particularly since long-term life prediction is normally based on short-term laboratory and system tests.

Scope

The scope of NDE, characterization and testing includes (1) the more traditional view of NDE (detection and analysis of mechanical discontinuities), (2) the nondestructive measurement of selected material properties that affect or may be correlated with serviceability (e.g., density, elastic properties, stress, electrical properties, homogeneity, et al.) as variations may be introduced during fabrication or service, (3) the macroscopic and microscopic evaluation of chemical, physical and mechanical properties of surfaces, thin layers and bulk materials (e.g., with electron microscopy, Auger or other types of spectroscopy), and (4) mechanical and proof testing to enhance knowledge of material performance and failure mechanisms.

The time of application for these technologies extends from in-laboratory evaluation and monitoring (e.g., during materials development and characterization), to manufacturing process control and product acceptance, to assessment of proper plant assembly, to in-service inspection and continuous monitoring to assure that the materials and components maintain the desired integrity (free from significant flaws or material degradation).

Evaluation Problems in Energy Systems

Most energy systems have some unique NDE and materials characterization problems because of the diversity in operating environment and materials requirements. These include requirements for both cryogenic and high temperature examination, superconductor evaluation, and evaluation of first wall damage in fusion systems, requirements for assessment of radiation damage (and examination in a radioactive environment) in fusion and fission systems, needs for examination of thick sections in fission and fossil systems, requirements for thin coating

evaluation in solar and fossil systems, and evaluation of high performance ceramics in fossil (e.g., MHD) and conservation (turbine) systems. However, many critical problems are common to most energy systems. For example, all equipment and plants are assembled from a variety of materials and components joined by a variety of methods such as welding, brazing, or bonding; thus, a common need exists for evaluating the joints for flaws, residual stress, etc. Corrosion and erosion are other generic problems in most systems, requiring an improved understanding of the mechanisms and quantitative measures of degree of degradation.

Needs for Research in NDE, Characterization and Testing

To effect a greater benefit and impact on improved energy systems, emphasis in our recommendations is directed primarily toward solutions to generic problems common to many systems. A current, chronic problem in NDE stems from the historical use of empirical approaches for detecting flaws. The quantitative ability for the analysis of a faulted condition has not been established. High priority has been placed on research to improve the understanding of the interaction of the probing energy (e.g., ultrasonic, electromagnetic) with structural materials for improvement of the quantitative measurement and characterization of flaws. This includes study of behavior both in the bulk and at interfaces, and in various microstructures. Measurements must be made as a function of varying parameters of both environment and probing energy. Improved methods of signal processing and of application of information theory should permit an improved understanding of the interaction of energy such as ultrasound and eddy currents with flaws (for quantitative characterization of type, size, shape, as well as orientation). A study should be initiated to develop high-sensitivity methods for characterizing flaws in ceramics and in embrittled materials. Investigations should be conducted to improve imaging techniques and to establish quantitative standards for NDE measurements.

Another area of high priority is for advancement and quantization of high spatial resolution and surface sensitive chemical and phase analysis instrumentation. Some of the most common, critical, materials-related problems in the energy systems are corrosion, stress corrosion, stress assisted corrosion, hydrogen embrittlement, radiation damage, process forming and joining-induced chemical segregation, creep, erosion, environmentally induced embrittlement, layered structure degradation, coatings degradation, concrete curing, and scaling. A common denominator in these problems is the need for detailed quantitative chemical and phase information about the surface, the bulk, and the gradients in chemistry through thin layers. Included in the required techniques are those that give elemental information, chemical state information, and gradient information. Ideally they would be nondestructive and, at least in certain cases, be ultimately adaptable for in situ usage in a non-ideal environment. In addition, the quantization and improvement of these tools is required for investigating real engineering materials. Examples of the types of instrumentation that need additional improvement and quantization are AES, SIMS, XPS, EXAFS, HREM, EDS, EELS, IMMA, and LANS. Equally important is the multiaxial mechanical testing of materials in a simulated hostile environment. The degradation of material under complex loading conditions in aggressive environments is a common problem in many of the energy systems. Testing capability for evaluating and simulating this type of loading environment should be established.

Other important generic needs are for NDE techniques to quantitatively assess materials properties (both pre- and post-service) such as residual stress (extremely important in all welded systems), density, homogeneity, strength and including those techniques by which direct or indirect (through correlation) analysis may be made of service-induced degradation such as chemical changes, incipient damage due to radiation, fatigue or other mechanisms, microstructural changes, or the many surface-related phenomena such as corrosion, erosion, wear, sputtering and blistering.

The successful application of nondestructive detection and analysis techniques for in situ examinations after periods of service and for continuous monitoring of structural or performance integrity will require research for implanted sensors, remotely controlled inspection devices and techniques that are resistant or immune to adverse environments of radiation, temperature and corrosive or erosive media or that can be utilized through intervening material.

Conclusion

Research in NDE in materials characterization and in testing is a high priority item in engineering materials science. Development of improved knowledge and technology for quantitative analysis of materials and components is necessary for assessment of component reliability and for prediction of service life of energy systems.

GROUP II. ENGINEERING DEFORMATION

R. M. Pelloux, MIT, Leader
 M. S. Wechsler, Iowa State University
 F. A. Nichols, Argonne National Laboratory
 W. D. Nix, Stanford University
 S. Hecker, Los Alamos Scientific Laboratory
 A. H. Clauer, Battelle Memorial Institute

Introduction

Within the purview of the Division of Physical Research there is a need for increased research on the mechanical properties of complex materials under conditions closely simulating those expected to be encountered in advanced energy technologies. This research should be basic in the sense that greater understanding of the pertinent mechanical phenomena is to be achieved but should be concerned with materials and phenomena of practical interest.

In the present study we attempt to identify the most pressing problems associated with deformation and fracture expected to be encountered in the energy systems.

Increasing importance of safety and environmental factors as well as large capital costs make necessary the detailed structural feasibility studies for many of the energy systems currently being considered. The present technology for making such studies is grossly inadequate. Materials property measurements under a variety of loading conditions (multiaxial, cyclic, high temperature) for a variety of structural materials are urgently needed. Constitutive equations that account realistically for the mechanical phenomena known to occur (inelastic, time dependent, high strains) must be developed. In conjunction with this work it will also be necessary to develop computational codes that are sufficiently flexible to account for the various materials properties.

Research Areas Recommended

The following specific research areas have been identified and some research guidelines are given:

1. Constitutive Relations. Realistic materials properties input for structural stress analysis codes is of great importance. To achieve this goal, we must measure mechanical properties under complex loads, and concurrently develop microstructurally based constitutive relations. Many structural materials (steels, stainless steels, superalloys, refractory and reactive metals, ceramics, polymers) should be examined. Multiaxial loading experiments should determine yield loci, hardening rules, stress-strain relations, including time- and temperature-dependence (cyclic, creep, strain-rate) pressure-dependence and large strain effects.

2. Creep-Fatigue-Environment Interactions. The critical areas for work in this specific research area concerns the effects of environment, temperature, stress or strain wave shape, hold-time, cyclic frequency on the life of a material or of a component; comparison of high temperature creep-fatigue damage concepts to creep-fatigue crack growth laws; study of the physical aspects of wave-shape damage to determine the specific microstructural and micromechanical factors involved in order to derive guidelines to design better alloys; the relative roles of creep damage and oxidation-corrosion damage during crack initiation and crack growth.

3. Fracture Analysis. Linear elastic fracture mechanics is widely used in design but is highly idealized with respect to the behavior of real structural materials. There is a critical need for developing improved understanding of fracture criteria with significant plastic deformation. Such studies include elastic/plastic/creep analyses of realistic cracks (with blunting) and multiaxial loading conditions. Especially critical is the use of reliable, mechanistically based constitutive relations as integral components of these analyses.

4. Effect of Radiation on Deformation and Fracture. Effort should be directed to achieve a better understanding of the mechanical behavior of engineering materials as affected by radiation environments applicable to fission and fusion reactors and to conditions possibly encountered in nuclear waste management and solar systems. The emphasis is to be on materials now used or projected to be used in energy technologies; examples are ferritic and stainless steels, refractory metals, and ceramics for first wall application in fusion reactors. The phenomena investigated will embrace complex loading conditions such as experienced in creep, fatigue, stress rupture, and brittle and ductile fracture under practical conditions.

5. Stress Corrosion Cracking. Stress corrosion cracking is pervasive in almost all energy systems, but a basic understanding is lacking. Studies aimed at developing mechanistic understanding are needed. These should include such things as Auger analysis of grain boundary segregation, in situ observations using environmental straining stages in the HVEM, and the use of ion implantation techniques both to determine mechanistic effects of alloying elements and to discover materials with high resistance. New techniques of monitoring initiation of failures in real structures should be developed, e.g., small angle neutron scattering (SANS).

6. Alteration of Mechanical Properties by Surface Treatments. There is increasing need to alter surfaces of structural materials exposed to hostile environments in order to modify their resistance to wear, erosion, corrosion and stress corrosion cracking. These modifications may be achieved by older methods such as carburizing and coating, or by newer methods such as laser processing and ion implantation. The surface modifications include changes in crystal structure, microstructure, surface composition and residual stresses. Research is badly needed to study the effects of these surface modifications on the surface sensitive deformation and failure mechanisms such as stress corrosion cracking, erosion, wear, and fatigue.

7. Structural Ceramics. Many of the emerging energy systems will use structural ceramics under conditions and in environments that have not yet been encountered. Attention should be focused not only on the high density ceramics such as Si_3N_4 or SiC expected to be used in ceramic engines but also on the low density ceramics or refractories that will be used for liners in fossil energy related industries such as coal gasification, incinerators, waste heat recuperators, waste management, etc. The properties of these materials depend on both environment and processing so that mechanical property studies must be conducted on carefully synthesized materials in various test environments. The application of fracture mechanics to ceramics has just begun and should be encouraged. Studies of high temperature creep and creep fracture are critically important to the successful development of ceramic engines.

TABLE I: A MATRIX OF ENGINEERING DEFORMATION AND FRACTURE PROBLEMS

Research Areas	Fusion	Solar	Geothermal	Fission	Fossil	Conservation	Environment Control	Waste Management
<u>Analysis & Life Prediction of Structures</u> (Multiaxial, cyclic, constitutive equation, codes) (Feasibility, safety, cost)	XXX	XX	X	XXX	XXX	X		X
<u>Mechanical Behavior</u> High temperature creep- and fatigue-environment interactions	XX			XXX	XX	XX		
Irradiation creep and embrittlement	XXX			XXX				X
Low stress-strain, long time				XX	xx			XXX
Inelastic fracture mechanics	XX		X	XX	XX	X		
Erosion-corrosion			XXX		XXX	XXX	XX	
Stress corrosion cracking		X	XX	XX	XX		XX	XX
Gaseous embrittlement (Hydrogen, helium, etc.)	XXX		XX	XX	XX		X	
Deformation processing	X	XX		X		X		

XXX - Critical problems; success or failure could hinge on their solution.

XX - Major problems.

X - Important problems.

GROUP III. MATERIALS PROCESSING

D. H. Gurinsky, BNL, Leader
 H. K. Bowen, MIT
 D. D. Keiser, EG&G Idaho, Inc.
 R. D. Nelson, Battelle-PNL
 W. F. Savage, RPI
 F. L. Vook, Sandia
 J. L. Walter, GE-Schenectady

I. Welding and Joining

Of all methods of materials processing, welding is one of the most widely used; yet from a fundamental point of view it remains one of the least understood. Fabricators are usually forced by expediency to establish welding procedures on a trial-and-error basis without the benefit of sound, scientifically based guidelines. Many structural failures are directly traceable to improperly made welds, and repairs of unnecessary weld defects often lead to delays and cost-overruns on critical projects.

The needs for higher quality welds, faster welding, and scientifically based methods require the establishment of a sound base built upon a coordinated research program. The following paragraphs summarize, in order of decreasing priority, five fruitful areas of basic welding research.

A. Control of the Microstructure of Fusion Welds

The microstructure and microsegregation in fusion welds can be modified by control of process variables and external environmental influences to provide:

1. Mechanical properties which more closely match those of the contiguous base material.
2. Significantly decreased sensitivity to general corrosion, pitting corrosion, and stress corrosion.
3. Minimization of swelling in nuclear applications.
4. Improved reliability through reduction in sensitivity to hot-cracking, porosity, and other common weld defects.

B. Prevention of Embrittlement

An improved understanding of the mechanisms involved in the following forms of embrittlement is essential:

1. Stress-relief cracking in low-alloy steels.
2. Strain-age-cracking in nickel-base superalloys.
3. Creep embrittlement in low-alloy steels.

4. Temper embrittlement in carbon and low-alloy steels.
5. Irradiation embrittlement in weldments.
6. Sigma-phase embrittlement in stainless steel.

C. Effect of Minor Elements on Arc Physics

Preliminary investigations have demonstrated that minor alloy additions (< 0.1 at. %) to either base metal or filler wire can cause variations in penetration of as much as 400%. If automated welding is to be a viable technique, an understanding of the mechanism responsible for this phenomenon is essential.

D. Advanced Joining Techniques

Two areas requiring improved fundamental understanding are:

1. Processes for joining heavy sections (4 in. and up) to provide reliable, high quality, and economical structures, such as out-of-vacuum electron beam and laser welding.
2. Processes for joining difficult-to-weld materials such as ceramics, superconductive alloys, refractory materials, and composites, ceramic to metals, ceramics to glass.

E. Post-Weld Treatments

With the massive reaction vessels to be constructed by the turn of the century, conventional stress-relieving practices will be impractical. Therefore, the fundamental aspects of other methods such as mechanical, acoustic and vibrational techniques should be investigated.

II. Deposition and Surface Modification Processes

A. Ion Implantation

Because of its potential wide-ranging applications to broad energy research and technology, ion implantation is a high priority area for DPR materials research funding. Ion implantation is a well-known substitute for diffusion in silicon single crystal devices; however, exciting new applications requires basic research on the near-surface modification of materials. Some promising areas include: the crystallization of glasses, the formation of erosion- and corrosion-resistant surfaces, the modification and study of catalysts, the controlled adhesion of thin-film contacts, the fixation of radioactive wastes by implantation, modification of fusion reactor first walls, the doping of compound semiconductors for solar cells, the ion simulation of long-term radiation damage, the controlled study of basic radiation damage processes from noting the partition of energy into ionization and atomic displacements, and the creation and doping of amorphous surface layers.

B. Sputtering Process Research

To expand sputtering capability to provide solutions for many energy-related materials or fabrication problems, the following research should be undertaken:

1. The influence of sputtering parameters on the properties of deposited alloys and ceramics;
2. Preparation and properties of coatings and free-standing materials (e.g., graded deposits, amorphous materials, and stoichiometric compounds);
3. Definition of the limits of technologies which contribute to high-rate sputtering, e.g., research on RF sputtering, plasma confinement, and large-scale depositions.

C. Coatings

Many of the materials to be used in energy applications may have all of the desired properties except that of being able to withstand the environment. Thus, some kind of protection may be provided to keep the surface of the material from being corroded or eroded; for example, high temperature alloys used in steam or gas turbines. Providing surface protection may allow operation at higher temperature to boost efficiency or may allow use of a less desirable but less expensive fuel to fire the turbine.

Other examples where coatings may help to alleviate surface damage are in the first wall of the fusion reactor and coal gasifiers and liquefiers. Coatings may be applied by ion implantation, chemical vapor deposition, sputtering, pack cementation, electroplating, electroless plating, plasma arc-spraying, and cladding. For all processes, problems such as adhesion to the substrate, compositional stability at high temperatures and control of grain structure of the coating need elucidating.

III. Particulate Processes

A. Research on Processing of Particulate Materials

A major portion of ceramic materials and some metals are processed from particulate starting materials. In the case of ceramics, many of the paradigms for reproducibly fabricating high-performance materials have not been established. In metal systems, rapidly quenched droplets when densified into a bulk material permit improved microstructure and properties because of metastable compositions or structures and because of very fine dendrite arm spacing. As an example of the kind of processing science needed to put particulate processing on sound footing we will consider the processing of a dense ceramic.

B. Powder Formation

The ideal powder which could result in a theoretically dense, polycrystalline ceramic by a sintering technique is: monodispersed (size less

0.5 μm), non-agglomerated, single phase and "pure" in composition, and has an equiaxed morphology. The science of producing such powders by vapor or liquid precipitation techniques has not been established.

C. Shaping/Forming

Research and analyses of the principles of injection molding, pressing and casting techniques are needed. For example, what are the flow properties of highly loaded polymeric carriers of the ceramic particulates and what are the effects of surface active additives?

D. Densification/Microstructure Control

Can bodies which contain greater than 25% voids be sintered to close tolerances and specified microstructures? Studies on grain boundaries, their mobility, near-boundary impurity distribution, etc., are required for microstructure control. "Grain boundary engineering" is of the utmost importance in ceramic processing and property control, but very few principles have been established. Incorporation of precipitation and phase transformations as an additional processing parameter has not been studied extensively.

E. Finishing

Basic research into the wear, grinding, cutting, and finishing of brittle materials is the final step in processing technology.

In each of the above areas, new experimental methods, theoretical models and controlled experimentation are needed; for example, laser-driven gas-phase reactions for fine particulate formations; sintering in a glow-discharge to increase sintering rates by tenfold; using a disappearing liquid-phase sintering additive; or use of hot-forged crystals to study intrinsic grain boundary behavior; design principles for materials having low inherent ductilities; substitution of ceramics for metals.

IV. Unconventional Materials and Process Research

A. Amorphous Materials and Processing

Amorphous metals and semiconductors are a new class of materials with new and interesting mechanical and physical properties. The processes for preparing these materials in useful form are relatively simple and (possibly) inherently less expensive than conventional processes for preparing material with similar properties.

Amorphous metals are prepared, for example, by rapid quenching from the melt, of alloys comprised generally of one or more metals with metalloids such as B, P, Si, C, Ge, etc., to provide a composition near a low-lying eutectic. The metalloids usually comprise about 20 at. % of the alloy.

Alloys based on iron or nickel-iron with phosphorus and boron as the metalloids have been prepared in ribbon form. Since the compositions may resemble well known, conventional soft magnetic alloys, e.g., Fe-Ni-P-B, Fe-Ni-B, or Fe-B, such materials might have magnetic properties approaching

those of the conventional alloys except for the fact that the amorphous alloys are noncrystalline. Early results indicate that some compositions of iron or nickel-base amorphous alloys have saturation flux densities sufficiently high that, coupled with the low coercive force and low electrical losses of the material, they may be used in distribution transformers with a subsequent reduction in core loss and a saving of electrical energy.

The simplicity of processing may also lead to reduced costs of electrical devices, compared to alloys prepared in the conventional manner. Continuous lengths of amorphous material are prepared by ejecting a stream of molten alloy onto a rapidly revolving surface. Continuous ribbons, the final shape of a material to be used in transformers, have been prepared at the rate of 5000 ft/min.

Alloy compositional studies may lead to the discovery of alloys with higher saturation flux density and with improved stability. There is little fundamental understanding of the compositional effects that allow one to quench an alloy to the metastable amorphous state and to keep it that way over a period of years at some ambient temperature. Fundamental understanding of the source of the magnetic behavior must also be gained to maximize the magnetic properties of such materials.

Laser processing of surfaces may also provide amorphous, or at least very fine grain surfaces, for corrosion and wear resistance or increased resistance to deformation and failure of many conventional alloys. It certainly provides a means of altering the surface properties.

B. Ion Implantation

Ion implantation is an exciting and versatile process to produce new and tailored materials for energy technologies. Two promising areas are: (1) the low-temperature production of metastable materials, and (2) the rapid production of specially tailored equilibrium phase for materials research.

1. Metastable Materials. As a research tool, ion implantation provides a controlled means of producing metastable materials. Additional work, however, is needed in order to understand the physical processes involved in the formation of these materials. Some examples of implanted metastable materials are: Hydrogen implantation into Pd-Cu has produced a superconductor with a transition temperature of 17 K. Implantation has been used to produce amorphous metal alloys and semiconductors.
2. Equilibrium Phases. Ion implantation provides a process to obtain quantitative information about equilibrium phases of intermetallic alloys. The preparation of intimate atomic mixtures by ion implantation allows the formation of phases which can be characterized by TEM and diffraction. The use of ion backscattering to continually, and nondestructively, monitor the depth distribution of implanted atoms permits sensitive determinations of phase diagrams and diffusion rates, thereby quantitatively giving the low temperature equilibrium and stability of alloys. The controlled

addition of minor elements by implantation can be used to investigate temper embrittlement and stress-corrosion-cracking resistant alloys, erosion and corrosion resistant materials, catalytic surfaces, and behavior of ceramic surfaces.

C. Molecular Beam Deposition

Controlled deposition from molecular beams has the potential to provide new materials with different lattices, compositions, and properties. Theoretical models and experimentation of these layered structures are needed before they can be applied in energy systems.

D. Composites

A thorough understanding of the manner in which properties of diverse materials can be combined to produce unique behavior may lead to major advances in structural materials. Material combinations include metal-polymers, metal-ceramics, polymer-ceramics, with either constituent being the matrix. There now are few principles on which to predict properties of a composite from those of its individual components.

V. Polymers

In view of industry's competence in the synthesis of polymers, DPR should not enter this aspect of polymer production. However, since marked improvements in properties can be obtained by special processing, a competent group should be selected to recommend what contribution DPR can make in this area. For example, improvements in the properties of polyethylene could lead to early acceptance in power cables to reduce dielectric losses.

TABLE II. MATERIALS PROCESSING

Technology	Fusion	Fission	Solar	Geothermal	Fossil	Conservation	Environment	Waste	Priority
Welding & Joining	XXX	XX	XX	X	XX	XXX	X	X	13
Deposition, Surface Modifications, Coatings	XXX		XXX	X	XX	XX	X		12
Particulate Process, Ceramics, Metals	X	X			XX	XX	X	X	8
Amorphous Materials			X			XX	X	X	5
Ion Implantation and Molecular Beam	X		X		XX	X	X	X	6
Polymers				X		XX	X		4

Priority Number - In order of increasing number.

XXX - Not possible with present technology.

XX - Vital for cost effectiveness, process life and safety.

X - Important but not essential to operation.

GROUP IV. EROSION, CORROSION, AND PROTECTION

J. V. Cathcart, ORNL, Leader
 T. Alfrey, Dow Chemical Co.
 H. E. Frankel, ERDA-Washington
 J. M. Khan, LLL
 A. Levy, LBL
 F. S. Pettit, Pratt & Whitney
 A.P.L. Turner, ANL

The technology reviews presented at the Workshop on Engineering Materials Science demonstrate that corrosion in its various aspects is a problem common to most systems. We perceive the role of Engineering Materials Science in attacking these problems to be that of moving beyond the study of corrosion in relatively simple systems to the characterization of phenomena in more complex engineering materials. What is needed is a sufficient understanding of the mechanistic details of such complex corrosion events to allow at least the prior evaluation of the corrosion resistance of any material in a given "real-world" environment.

I. Critical Problem Areas

The list of specific corrosion problems is almost endless, and we have attempted in this section to classify problem areas according to general type and priority of importance. We assign highest priority to research in the following area:

A. Combined Erosion-Corrosion Behavior at Elevated Temperatures

Of all the technologies reviewed we believe corrosion problems in coal conversion systems to be the most severe. Particularly difficult to solve are problems in which erosive processes continually destroy all or parts of an otherwise relatively protective scale. Such corrosion occurs in both oxide- and sulfide-forming environments. Another erosion-corrosion reaction type is that in which a liquid phase is formed on a structural component, thus introducing a variety of special corrosion problems, e.g., "hot" corrosion. A special area that deserves explicit attention is that of erosion, per se; there is a lack of fundamental understanding of the parameters necessary to characterize erosion. This deficiency must be remedied to ensure progress in elucidating combined erosion-corrosion phenomena.

The following three problem areas are assigned lesser priority but are still important.

1. Adhesion and Bonding Phenomena. Much greater use could be made of the protective coatings (polymers, ceramics, composite materials) if factors affecting the bonding of these coatings to other surfaces were better understood.
2. Surface Chemistry of Materials in Brine Solutions. Progress in geothermal energy generation requires solutions to the scaling problems encountered in concentrated brines. A better understanding of the surface chemistry of both alloys and polymeric or ceramic materials should help in solving this difficulty.

3. Effects of Radiation on Corrosion. Because of ERDA's unique testing facilities support should be given to studies of radiation effects on corrosion in fission and, probably, fusion reactors.

B. Recommended Approach to Engineering Materials Science Corrosion Research

Virtually any corroding system can be divided into three components or phases: the environment, the barrier layers, and the base material. Different events occur in each of these phases.

C. Environment

The composition of the environment determines to a large degree the thermodynamics of the process to be studied. It is the source of erosive particles. Fluid flow within the environment influences erosion and the composition of the fluid/solid boundary layer. The environment must be characterized and properly simulated in laboratory tests.

D. Barrier Layer

The barrier layer is the chief source of protection for the base material from the environment. Material transport processes within the layer frequently determine the kinetics of corrosion. This layer must be described in terms of its composition, defect structure, and morphology. Its mechanical and chemical properties determine its response to erosive interactions. Diffusion mechanisms in this layer must be understood, and its adhesion to the base material is critical.

E. Base Material

Corrosion processes can alter the dimensions of the base material, and diffusion processes within the base may change its mechanical and physical properties as well as its response to corrosive attack.

The overall corrosion process is determined not only by the events occurring in each of these three phases but also by the interaction among these events. For example, erosion can enormously influence corrosion, and the chemical and physical properties of the scale layer determine the extent of erosion. This type of interrelationship is particularly important in complex engineering materials. For this reason we urge that research programs be structured in such a way that the synergistic effects of the various processes can be analyzed.

Clearly, research should be centered on materials of technological interest. Only in this way will it be possible to identify many of the essential processes that occur in complex systems. Once these identifications have been made it becomes possible to sort out those problems requiring more fundamental study. Furthermore, the "integrated" understanding of the entire process should allow better and more uniform testing methods to be identified. The modeling efforts associated with the characterization of the processes may allow the development of predictive guidelines to be used in designing corrosion resistant materials; we are convinced, however, that this last goal can be reached only through close and continued interaction between the fundamental and applied researchers.

GROUP V. COMPLEX MATERIAL PHENOMENA

C. A. Wert, Univ. of Illinois, Leader
 R. B. Appleton, ORNL
 A. D. Brailsford, Ford
 W. D. Kingery, MIT
 J. J. Loferski, Brown Univ.
 L. W. Roberts, LLL
 J. T. Spruiell, Univ. of Tennessee
 E. A. Stern, Univ. of Washington

This group had the problem of identifying materials used in structures or devices which require complex arrangements of atoms in multicomponent alloys or compounds important in energy conversion or utilization. Because of the wide range of problems encountered, many candidate materials were identified on which basic work seems essential. Three major materials are listed along with several of secondary importance. Major problems are:

I. Thin Films and InterfacesA. The Problem

Many phenomena important in energy conversion systems occur at interfaces. Some of these phenomena are important in energy transfer from one medium to another; others are deleterious effects which degrade the operation of the system.

B. Opportunity

Because of continual improvements in methods of control of composition and physical arrangement of atoms at surfaces, in the near-surface region and in thin films, considerable improvements should be possible in development of structures and devices. Examples:

1. Thin Film Photovoltaic Cells. A large effort is being made in development of photovoltaic cells using single crystal silicon cells. It is not sure that the price of such cells can be brought down to acceptable levels (no more than \$500 per kw). Work should be conducted on other materials, especially on compound semiconductors. The following subjects should be examined:
 - (i) Fabrication, characterization and control of thin-film semiconductor devices of a wide range of materials;
 - (ii) Control of electron-hole properties of polycrystalline thin films;
 - (iii) Control and understanding of interfaces between metals, semiconductors and insulators; and
 - (iv) Investigation of properties of multicomponent semiconductor compounds.

2. Near-Surface Phenomena. Many phenomena are controlled by the characteristics of the surface and near-surface region: corrosion, catalysis, friction, wear, erosion, optical, and electronic properties. The following subjects merit support:

- (i) Continued development of techniques for examination of surface and near-surface chemistry (cf., Group I, NDE).
- (ii) Utilization of novel techniques for controlled production of both equilibrium and metastable phases: laser heating, ion implantation, molecular beam epitaxy, sputtering.

II. High Temperature Ceramic Materials

A. The Problem

Severe high temperature service requirements demand the use of ceramic materials. One example is the lining of coal gasification systems; applications of structural ceramics in low-cost gas turbines are plagued by the apparent inherent brittleness of ceramic materials.

B. Opportunity

Basic research in production of ceramics may provide structural materials with more predictable properties and, perhaps, more desirable properties. Candidate materials are oxides, carbides, nitrides, and mixed compounds. New methods of microanalysis will permit better characterization of the materials. Production of composite ceramics should provide better strength.

III. Development of Structure-Property Relationships in Polymers

A. The Problem

Polymers have many features of importance in energy conversion, utilization, and conservation. Control of the processing and fabrication of polymers can produce materials of greatly enhanced characteristics.

B. Opportunity

1. Polymers can replace metals in many applications. Their application can reduce weight of vehicles with consequent saving of fuel.
2. Variability in process control can give polymers with a wide range of corrosion resistance, elastic properties, dielectric properties.
3. Products can be tailored to end use with little waste of material and with small heat input because of low temperature of processing.
4. Areas where research might produce superior materials:
 - (i) Better understanding of deformation processes.
 - (ii) Control of internal structure to provide unusual properties.
 - (iii) Production of higher temperature materials for more severe service.

(iv) Recycling capabilities.

IV. Priority 2 — Cementitious Materials

A. The Problem

The setting of cements is a highly complex chemical reaction. For Portland Cement, the phases formed and the rates of reaction are partially known, but for many cements, the chemistry is virtually unknown. Since concrete is used extensively in construction of many energy conversion systems, since the production and casting of cement uses a great deal of energy, and since repair of concrete structures and roadways is energy and labor intensive, better methods of utilizing concrete is important in energy conservation.

B. Opporutnity

Modern methods of micro-analysis of small volumes permit measurement of the chemistry and physical arrangement of crystals formed during the setting of cements. They should also permit a better understanding of the additives used for special purposes--quick setting, salt and water resistance, corrosion resistance. The time is ripe to apply methods such as transmission and scanning transmission microscopy, Auger analysis, and energy analysis methods to the study of cements. The techniques are either available or are being developed both in universities and in national laboratories.

Such measurements of basic reactions in the setting of cements should permit better utilization of one of our most heavily used constructional materials.

MATERIALS SCIENCE WORKSHOP ON
MECHANICAL PROPERTIES

Held May 5 to 7, 1977 at Argonne National Laboratory

Organizers

U. F. Kocks, Argonne National Laboratory
J. R. Cost, ERDA, Division of Physical Research
A. G. Evans, Rockwell Science Center

Participants

A. S. Argon, MIT	C. Laird, Univ. of Pennsylvania
I. M. Bernstein, Carnegie-Mellon Univ.	C.-Y. Li, Cornell University
C. R. Brinkman, Oak Ridge Nat'l Lab.	N. H. Macmillan, Penn. State Univ.
R. M. Cannon, Jr., MIT	M. Meshii, Northwestern University
J. R. Cost, ERDA, Physical Research	J. W. Morris, Jr., Berkeley
T. B. Cox, ERDA, Fossil Energy	H. G. Nelson, Ames Res. Center, NASA
D. R. Diercks, Argonne Nat'l Lab.	C. E. Pugh, Oak Ridge Nat'l Lab.
A. G. Evans, Rockwell Science Center	J. R. Rice, Brown University
S. D. Harkness, Argonne Nat'l Lab.	T. E. Scott, Ames Laboratory
W. Herrmann, Sandia Albuquerque	S. M. Wolf, ERDA, Physical Research
U. F. Kocks, Argonne Nat'l Lab.	M. H. Yoo, Oak Ridge Nat'l Lab.

SCOPE

The Mechanical Properties Workshop was asked to deal with all problems of deformation and fracture of interest to ERDA, except with the following specific areas which were assigned to other workshops: deformation processing, welds and thick sections, erosion and wear, the corrosion aspects of stress corrosion cracking, irradiation creep, and non-destructive evaluation.

TOP PRIORITY MECHANICAL-PROPERTIES RESEARCH

An increased understanding of microscopic and macroscopic mechanical properties is critically needed in all energy technologies. Research areas with a high potential impact and a high probability of success over both the shorter and longer term are

- constitutive relations and damage accumulation laws
- criteria for the localization of deformation
- prediction of failure rates
- materials design and substitutability.

Research areas that need increased emphasis to develop the basic understanding important for the solution of critical problems are concerned with

- crack nucleation criteria
- relevant surface and interface properties
- the effects of chemical environments
- recovery, recrystallization and phase transformations occurring simultaneously with deformation

The highest priority should be placed on the comprehensiveness of mechanical-properties research, encouraging active overlap between

- microscopic and macroscopic approaches
- mechanical-properties research and other disciplines
- investigations on different classes of materials
- the scientific and the technological outlook.

1. INTRODUCTION

1.1 Perspective

Mechanical properties research is at a turning point. While in the 50's and 60's the microscopic and macroscopic approaches to deformation and fracture evolved as essentially independent disciplines, the 70's have brought increasingly effective interaction between the two. Simultaneously, the considerable increase in sophistication that has pervaded all of materials science has made it possible to proceed from merely qualitative considerations to increasingly quantitative treatments. Finally, the interaction between different mechanisms of both deformation and fracture is now being considered, and an integration over complex loading histories (such as alternating creep and fatigue) is being attempted. The glaring exception to this progressing sophistication and perspective of mechanical properties research is the interaction with the many kinds of aggressive environments, which besets most energy technologies.

Such a rapid development in both the breadth and depth of understanding provides exciting scientific challenges, and it portends a rapidly increasing usefulness of the results of such research. In some cases, the impact on technological advances or economy can be fairly direct; for example, the evolution of better founded constitutive relations for shape changes and of better founded failure criteria should make it possible to use structural materials with greater reliability for longer lifetimes, with savings in valuable materials, and with a considerably reduced need for data accumulation.

A better understanding of overall materials behavior has also helped with increasing success in materials development; for example, in the optimization of strength and toughness. The achievement of even a modest increase in design temperatures by an improved comprehension of high-temperature strength would have such outstanding impact on virtually all energy technologies that such research should be pursued, even when its chance of success is uncertain.

Finally, there are areas of mechanical properties research where the impact of any results on technological problems would be less direct, but which provide important fundamental input towards Engineering Materials Research. For example, the inelastic behavior of very small volume elements, in which continuum mechanics and macroscopic crystal plasticity are inapplicable, has a determining influence on the behavior near crack tips and in the vicinity of localized loadings such as by the impingement of particles on a surface. Such basic research must be performed if, for example, erosive wear is ever to be understood -- a phenomenon that is among the most frequently quoted problems in a variety of current energy technologies.

The need for basic mechanical-properties support within ERDA is particularly intense, inasmuch as the lifetimes of structural components will be substantially greater than those needed in other government systems. In addition, the service conditions are in many instances considerably more severe: thermal cycling and aggressive environments, for example, are recognized problems in fission, fusion, geothermal, solar, and fossil energy technologies. While applied

programs within ERDA will generate the engineering data required for specific performance of structural components, they will be highly selective in terms of the alloys and computational techniques used. The basic research program is needed to provide a further understanding of the phenomena and mechanisms controlling mechanical properties. As outlined above, there is now a well founded expectation that the results of such research will have both direct and indirect impact on ERDA technologies in the foreseeable future.

1.2 Outline

The main body of the report summarizes outstanding problem areas in Deformation (sec. 3) and Fracture (sec. 4). This division is somewhat arbitrary since the interaction between these modes of inelastic behavior is one of the most important and exciting areas of recent study. In consequence, the phenomenon of fatigue, which has outstanding impact on energy technologies, is dealt with under a number of different headings, such as Strain Localization, Microcrack Nucleation, etc.

The topical areas outlined below do not cover the entire spectrum of mechanical-properties research; they are rather to be looked upon as examples of problems for which a successful solution in the foreseeable future appeared probable, or in which there seems to be an especially glaring need for further insight. Their relevance, direct or indirect, is cited in various specific examples.

Preceding this discussion of phenomena, we address (sec. 2) Materials and Environments, which pervade the entire field and have gained in importance through the severe restrictions under which modern energy systems must operate. Another all-pervasive topic is Surfaces and Interfaces: both experimental and theoretical advances in this neighboring field offer exciting possibilities and sorely needed input into mechanical properties research (sec. 2.4).

In a final section (sec. 5), we address the question of Facilities and present a general Recommendation.

2. MATERIALS AND ENVIRONMENTS

2.1 Materials

To the benefit of mechanical-properties research, an increasing tendency can be observed to integrate the understanding gained from different kinds of materials: metals and alloys, ceramics, semiconductors and minerals, polymers and amorphous materials. It is a measure of the sophistication of the field that such old-time classifications have lost in significance and are being replaced by categories such as: two-phase materials, materials with a high Peierls stress or a low cleavage strength, and the like. It is thus not expected that specific "new materials" require a redirection of the mechanical properties research effort; rather, they should be incorporated into ongoing programs to broaden the base of understanding.

The distinction between "academic" and "real-life" materials is also becoming blurred. Materials for electrical and magnetic applications are often pure metals or simple compounds and are being subjected to increasingly severe mechanical (or thermal-cycling) loads. Materials selected for high-temperature strength are often essentially single-phase alloys. Single-crystal research is still appropriate when a separation of grain-boundary and grain-matrix effects is important.

For all these reasons, the following sections on phenomena will make little reference to special materials, but are meant to apply to large classes of them, and a broad spectrum of materials for investigation is generally recommended. It should be emphasized that important "new materials" need not be exotic: revolutionary improvements are yet being made in steels, which still constitute the major large-scale construction material.

A new materials problem with severe implications is that of large-scale gradients in microstructure; high-priority study under the Engineering Materials category is urged.

Some types of "materials", such as composites, rocks, coal, concrete, etc., do not belong in any one class of the kind discussed above, but are rather mixtures of various classes. Since the multiplicity of such mixtures is unlimited, the appropriate research procedure is to identify and investigate general component problems rather than specific materials. Two important goals are:

- to derive appropriate superposition laws that allow one to calculate (whenever possible) the inelastic behavior of the composite once that of the constituent phases is known; and
- to understand (when simple superposition is inadequate) any additional mechanisms such as slippage and decohesion at the interfaces between the components, and nonlocal interactions.

Both require the use of sophisticated statistics, in part to delineate macroscopically "ductile" behavior from gross fracture.

2.2 Evolving Microstructures

The classical, and very successful, approach of physical metallurgy has been to describe in separate disciplines the microstructure and its control by thermomechanical treatment on the one hand, and the relation between an established microstructure and macroscopic properties on the other. A major shortcoming of this approach has been slow progress in the area where microstructure changes and mechanical deformation happen simultaneously. While the effect of an applied stress on transformations has been amply investigated, the effect of ongoing transformations during plastic flow and fracture has received little attention. Similarly, the phenomenon of dynamic recrystallization and associated twinning is only beginning to be understood mechanistically.

High-temperature energy technologies require a new emphasis on research in these critical areas.

2.3 Chemical Environments

Aggressive environments play an unprecedented role in new energy technologies, transcending in many ways the classical fields of corrosion and stress corrosion cracking. At high temperatures, many species can diffuse through the entire section, either into or out of the material, and thus change composition and microstructure. Neighboring fields in materials science should investigate, with highest priority, such changes in realistic materials and interact with the mechanical properties community if new types of microstructure should be found.

At low temperatures, only a few elements can diffuse long distances (hydrogen and sulfur being outstanding exceptions); more commonly, the effects of chemical environments are restricted to near-surface regions. Here, even the most basic characterization of "environment", and the different ways it can affect properties, seems to be lacking. Even cryogenic gases are "aggressive" in their effect on polymer crazing, and aqueous environments have a profound effect on strain localization in fatigue.

It was a general conclusion of this workshop that environmental effects on mechanical properties, especially at high temperatures, have not been treated with nearly the same sophistication as all other aspects of the problem; in fact, reproducibility of experimental observations has only rarely been attained. Some of the principal deficiencies leading to this impasse are the difficulties involved both in detecting and tracing the progress of small quantities of the active environmental species and in establishing the effect of these species on lattice or interface decohesion. The former problem can be partially addressed by appealing to the wide variety of techniques now available for surface and bulk analysis. However, innovative techniques are required for many of the critical problems and thus the strong participation of surface physicists is an essential constituent in a viable study. A critical issue is the effect on decohesion of various active species; a priori approaches for calculating these effects are not apparent. Nevertheless, some progress will inevitably be achieved if the problem is addressed by the pertinent physics/chemistry disciplines and such a participation is strongly urged.

2.4 Surfaces and Interfaces

The properties of interfaces have a critical impact on mechanical properties in many areas and appear to be ripe for a major advance in understanding. A basic research problem of great significance and general relevance to fracture phenomena, is an understanding of what allows (or causes) an interface to be capable of developing a crack. This is a fundamental aspect of ductile fracture nucleation (particle-matrix interfacial failure), of temper embrittlement in steels, of hydrogen assisted cracking, of fracture in ceramics, of creep-rupture cavity nucleation, etc. The area calls for basic work in the solid-state physics and thermodynamics of interfaces (including segregant adsorption of impurities and consequent alterations of cohesion), in lattice dynamics, dislocation theory, and other types of microstructural modeling and in relevant techniques of the experimental and quantitative chemical analysis of interfaces.

The efficiency of grain boundaries as sinks and sources for point defects in diffusive flow, and the associated problems of grain-boundary sliding (or grain-boundary dislocation motion) need further illumination. Especially in ceramics, these processes can be rate-limiting (as compared with diffusion).

The influence of surfaces and surface films is receiving renewed attention and is of especial concern for energy systems: near-surface behavior is important in erosion and wear, in fatigue crack nucleation and, in some cases, in the generation of plastic flow (or its concentration into persistent slip bands), which may have effects on bulk behavior.

This field could receive a significant new impetus from modern experimental techniques applied to actually important environments, as well as from sophisticated interatomic-potential calculations (provided these can be well matched to the macroscopic properties relevant in this case). Interactions between people oriented in the direction of mechanical properties and surface scientists as well as solid-state theorists would be mandatory.

2.5 Irradiation Effects

The energetic irradiation environment in fission and fusion reactors affects mechanical behavior directly through the introduction of additional defects, defect clusters, dislocation loops, voids, and gas-containing bubbles; and indirectly through radiation-induced segregation to surfaces or interfaces, changes in the precipitate structure, and possibly the formation of nonequilibrium phases. Recent advances in our understanding of the kinetics of these microstructural changes make a detailed study of mechanical effects an urgent need. Probably the most important one of these is a loss in ductility, for example by severe slip localization due to microstructural instability, or by the growth of macroscopic voids or bubbles. Reliable predictions of component life, so important to the nuclear technology, require a far better understanding of these phenomena than is currently available.

Creep during simultaneous irradiation is not quantitatively understood and needs large-scale testing under a variety of flux conditions; some materials of relatively simple known microstructures ought to be included along with commercial materials.

3. DEFORMATION

Increasing emphasis has been placed in recent and proposed deformation studies on establishing a credible connection between observations and mechanistic considerations on the microscopic scale on the one hand, and macroscopic properties and descriptions on the other. Various phenomena of outstanding interest are illuminated from both the microscopic and macroscopic points of view in the following paragraphs.

3.1 Strengthening Mechanisms

Significant advances have been made in the last decade in our understanding of yield and ductility as they are influenced by composition and microstructure. In some cases, it has been possible to apply the derived principles to the design of useful alloys. A promising field of recent interest is that of duplex precipitate structures. Much progress is still being made in various ferrous alloys; other materials of high interest are nickel alloys, titanium and zirconium alloys, and refractories.

Some important strengthening mechanisms are not yet well understood, such as solution hardening at high temperatures, clustering phenomena, and various irregularities at low temperatures, which may be connected with phase transformations. The influence of voids in the matrix, and of bubbles (primarily at grain junctions), needs considerable further study.

These developments have direct impact on various specific materials problems and energy technologies. Moreover, they have a general relevance to the important effort to conserve energy and materials. For example, any increase in high-temperature strength that permits higher design temperatures has a significant effect on efficiency of energy systems; and to achieve substitutability of rare elements, an understanding of the role of specific alloying components is necessary.

3.2 Evolution of Substructure and Defect Structure

The high-temperature properties of materials are strongly influenced by developments in the dislocation and subgrain structure through deformation and recovery processes. This is an area lagging behind low-temperature strengthening mechanisms in understanding, but in which current development is rapid. Interaction between investigators using different classes of materials has been very fruitful; for example, a parallelism between the behavior observed in geological materials and in metals has been found.

The principal mechanisms that must be understood are the processes by which dislocation tangles change into loose cell walls, then into sharp subboundaries, and sometimes eventually into large-angle boundaries. They depend on stress, temperature, strain rate, and loading path (e.g., monotonic or cyclic) and are to some extent reversible. The interaction between creep and fatigue is determined by these processes in the initial stages and near the all-important threshold stress for fatigue (if indeed it exists). The term "damage accumulation" should thus refer to substructure changes in the early phases of life, while in the later stages the lengths of cracks or the density of microcavities are more appropriate measures of the "damage" accumulated.

Alloying effects on these various "recovery" processes are little understood; they appear to outweigh the effects on slip per se at high temperatures at least in some cases. Deformation also changes the concentration of point defects, which have a direct effect on various physical properties; for example, the electrical properties of superconducting magnets may be severely affected by the generation of point defects due to fatigue. Point defects also may aggregate into voids or dislocation loops and thus have a direct effect on the microstructure. Finally, they may enhance diffusion and interact directly with other species, especially gases, and thus may have profound indirect effects. This is an area requiring a broader understanding more than an elucidation of particular problem cases.

3.3 Constitutive Relations

Macroscopic deformation must eventually be described by constitutive relations, which contain only macroscopically measurable parameters -- and as few of these as possible. This is another area in which an integration of the phenomenological and physical approaches to mechanical properties has recently led to significant advances and is expected to provide useful results in the foreseeable future. The formulation in terms of state parameters, rather than history variables, is physically well founded and connected to the notion of control of properties by microstructure; it should lead to a significant reduction in the number of tests that must be performed to quantify the mechanical behavior of a material and, if sound, will provide a basis for extrapolation to behavior beyond the scope of easy experiments.

To be practically useful, these constitutive relations must encompass radial and nonradial, monotonic and cyclic loading paths, they must address transient as well as steady-state behavior, and they must span the regimes of temperature and strain rate of interest for important classes of materials. Tentative use of current relations in engineering applications, with feedback to ongoing research, should be strongly encouraged. Simplification of the "laws" to be used can await their finalization after extensive testing.

Methods must be found to measure and monitor both micro- as well as macro-indices of mechanical property damage accumulating in solids as a consequence of the imposed environmental and service conditions. Microdamage such as microstructural changes must be related to macrodamage indices or those parameters that can be monitored and correlated for design of energy-conversion systems.

A special experimental need is for adequate capabilities to measure strains on the macroscale at elevated temperatures ($>200^{\circ}\text{C}$). Both uniaxial and multiaxial methods are desired.

Advances in this area are a critical need for lifetime prediction in components such as heat-exchanger tubing, turbine rotors (especially heavy sections), blading, piping, pressure vessels, and others. These components occur in several energy systems: fossil, geothermal, solar, conservation, and nuclear. An additional problem specific to the last area is nuclear fuel cladding. Although the current constitutive-equation effort is focused on metals and alloys, it is applicable and relevant to ceramics, polymers, and composites -- materials classes showing great promise for energy-related applications.

3.4 Dynamic Effects

For most normal design applications, an understanding of small-strain deformation and of the initiation of failure is sufficient. On the other hand, if the consequences of failure must be assessed in detail, either in accident situations (reactor accidents, safety as in containment of fragments from turbine rotor or flywheel failure, etc.) or in forming, processing, or breakage (high-energy-rate-forming, rock breakage, etc.) it is often necessary to have constitutive relations for large deformation (usually nonradial) and for post-failure behavior, that is, for materials containing cracks or other damage. In many applications, very high rates are involved.

This is a problem of high complexity: dislocation and twin nucleation, inertial barrier penetration, dislocation phonon interactions, etc., occur simultaneously. An especially serious and little understood problem is an observed reduction in ductility under some conditions at high strain rates.

Dynamic effects also occur at low macroscopic strain rates, when dislocations are underdamped and thus penetrate their barriers inertially. This occurs especially at very low temperatures, but has also been shown to have significant effects on solution-hardened materials over a wider temperature range. Such high-speed localized deformation may have serious consequences because of a possible rapid build-up of internal stresses in polycrystals.

3.5 Dislocations and Twins

Some properties of dislocations have a critical impact on important macroscopic phenomena. For example, the dislocation core structure and splitting as influenced by the stacking-fault energy often determine the planarity or waviness of slip and thus the intensity of developing stress concentrations; they determine the availability of slip systems and thus the ductility of polycrystals; and they have a significant influence on recovery and, indirectly, recrystallization. The core structure and dislocation splitting are now much more amenable to investigation than in the past, both by improved interatomic-potential calculations and by advanced electron-microscopic techniques such as weak-beam methods and lattice imaging.

Another most important area where individual dislocations determine macroscopic behavior is that of plastic deformation in small volume elements such as crack-tip neighborhoods and near-surface regions, where continuum treatments are in principle inapplicable. An understanding of mechanical erosion by the impingement of very small particles will have to rely on good ideas in this problem area.

The interaction of solutes with dislocations is important both for strength (including strain aging) and for short-circuit diffusion. It is amenable to new theoretical and experimental studies including, for solutes of high atomic number, analytical electron microscopy.

Elastic anisotropy, which is substantial even in most simple metals and very important in low-symmetry materials, enters the macroscopic strength by way of dislocation properties. Significant advances in the basic understanding and the advent of computers have made correct calculations feasible: more applications to specific problems should be encouraged.

The connection between dislocation theory and macroscopic flow has made great strides, particularly through the increased sophistication of statistical and computer simulation techniques. Well planned further studies are necessary to insure applicability of locally derived strengthening mechanisms to macroscopic properties.

Dislocation properties also determine whether flow is "laminar", i.e., by the quasi-viscous motion of straight dislocations, or "turbulent", jerky, and cell-forming; this has direct consequences on whether creep is accelerating or decelerating with time.

Deformation twinning is a mode of plasticity important in many of the hexagonal and low-symmetry materials that have recently become important, as well as in connection with allotropic transformations and with cracking. The nucleation of twins, as influenced by stress state and deformation, is poorly understood, especially in noncubic materials in which twinning is particularly important. The strengthening effects due to slip-twin interactions, and the role of deformation twinning in extending or limiting ductility also deserve further study.

3.6 Strain Localization

Plasticity research is usually undertaken under uniform deformation conditions. Yet one of the most important, and potentially dangerous phenomena is the spontaneous localization of strain over particular parts of the cross section or into intense bands of shear. Such localization can have a number of different causes: it may be a geometric instability, it may originate between previously formed voids, or it may be due to microscopic strain softening processes such as dislocation channeling and precipitate resolution. Finally, a particularly frequent mode of strain localization is the formation of "persistent slip bands" during cyclic deformation, at least above a threshold stress.

Strain localization can have serious consequences, either because of the formation of stress concentrations at its impingement on grain boundaries, etc.; or because of the consequent local degradation that may lead to the formation of cracks within the band of intense shear.

4. FRACTURE

Studies of fracture are concerned with the prediction of failure: in consequence, fracture data are extensively utilized in the design of structural components for virtually all energy systems, e.g., fossil, nuclear, conservation, solar. The emphasis of fracture studies in the last decade has been on the mechanics of the principal crack-propagation processes. While a continued comprehension of the mechanics of fracture is certainly of great import, an extension of the recent surge of interest in microscopic mechanisms is essential to future advances in our total understanding.

The following discussion of fracture is organized in a sequence suggested by the fracture process: crack formation, stable crack growth, followed by dynamic crack growth and possibly arrest. Thereafter, the nondestructive evaluation of defects and residual stresses (as required for failure prediction purposes) will also be considered.

4.1 Microcrack Nucleation, Growth, and Coalescence

The formation of a macrocrack involves the nucleation, growth and coalescence of microcracks. The modes of microcrack nucleation are many and varied. Several modes have already been described; four additional mechanisms of substantial practical significance are discussed below.

In brittle materials, microcracks are nucleated at stress concentrations produced by elastic or thermal mismatch at grains or second-phase particles. The crack formation is strongly influenced by the size distribution of "precursor" defects at interfaces, the steep stress gradients and the local microfracture toughness of the material. The solution to this problem, as in all other microcrack formation problems, demands intensive cooperation between researchers in solid mechanics, statistics, and materials science this cooperation has already begun.

Microcracks and voids can also form during creep. Such microcracks frequently derive from the stress concentration set up by boundary sliding. The formation process is thus dependent on the character of the stress singularity produced by sliding, the diffusive or plastic stress relaxation, and the operative nucleation criterion. The first two aspects of the problem can be addressed by a mechanics/materials study, but the last is an interface decohesion problem that requires several additional talents. Similarly, the nucleation of voids at second-phase particles needs further transdisciplinary study.

A third mode of crack formation occurs during cyclic deformation. Fatigue microcracks typically originate within persistent slip bands or localized bands of intense shear. In heterogeneous materials, this can be a consequence of stress concentrations generated near grain boundaries or interphase interfaces. In homogeneous materials, cracks may originate in persistent slip bands near free surfaces, but also at apparently random locations within bands of concentrated shear; the nucleation mechanisms are here especially poorly understood, nor has the role of the microstructure been clearly established. The resolution of the problem requires a strong initial emphasis on observations of microcrack formation, followed by a coordinated mechanics/statistics/materials study.

In polymeric materials, the precursors to macrocracks are crazes. The morphology of crazes and the dependence of their formation on material properties, e.g., molecular weight, are reasonably well comprehended. However, studies to examine the statistics of craze formation in terms of material heterogeneity and of the effects of orientation are needed.

The propagation and/or coalescence of microcracks are the next stages of macrocrack formation. The propagation of microcracks is beset by all of the problems associated with macrocrack propagation, with the additional complex problem of microcrack propagation across grain boundaries. The solution to this problem is impeded by the present intractability of three-dimensional stress analyses for "angled" cracks. Some important insights might be obtained using numerical solutions for carefully selected analogies or by semi-empirical/dimensional techniques. The coalescence of microcracks is determined by the stress (strain) intensification between approaching microcracks and the criterion for coalescence. Neither aspect is well comprehended for three-dimensional arrangements of microcracks. Some progress has been achieved in brittle materials -- where the coalescence criterion (based on the stress intensity factor at one of the microcracks exceeding a critical value) is relatively straightforward -- using a two-dimensional model. Statistics also play an important role in the evaluation of coalescence, through the spatial distribution of sites for initial microcrack formation. A closely coordinated mechanics/materials study should again prove fruitful for the evaluation of the coalescence process.

When extensive microfracture precedes ultimate failure, as it does in heterogeneous materials such as rocks, coal, and concrete, or anisotropic materials such as graphite and wood, microfracture can engender substantial nonlinearities in load response. This "deformation" often needs to be predictable, and constitutive equations are required for this purpose. The "deformation" that occurs under tensile loading can be addressed by the same microfracture analyses described above. Under compressive loading, additional mechanisms pertain, e.g., crack sliding under the imposed shear stresses resisted by surface asperities. Further studies of the mechanics of these processes are needed, in conjunction with statistical studies of microcrack distributions and microscopic studies of the actual crack opening and sliding mechanisms.

4.2 Crack Propagation

When initial crack growth precedes significant nonlinearity in the load/deflection response, the crack extension can be effectively characterized by the pertinent stress intensity factor, K . Techniques for evaluating K are also relatively well established, although some additional effort needs to be devoted to very high temperature techniques for structural ceramics, and to techniques for evaluating K parameters pertinent to weldments, joints, etc.

For crack extension preceded by nonlinearities in the load response (e.g., mild steels), the initial growth can be characterized by the crack opening displacement (COD) or the path independent integral, J . The test methods for obtaining these parameters are also reasonably well defined. However, the subsequent stable growth of the crack, which often allows a substantial increase

in load before attaining instability, is less well characterized and has led to highly conservative designs and inefficient materials usage. It is presumed that the stable crack extension is still uniquely determined by J , although more extensive justification (including an explicit incorporation of rate effects) is required; but the instability is specimen (system) dependent and is, as yet, inadequately characterized. Further experimental studies, coordinated with numerical (analytical) solutions for quasi-static crack growth, are needed to develop generalized instability criteria.

The resistance to crack growth can be strongly influenced by micro-structure. The pertinent relationships between crack growth and micro-structure are needed to design materials with optimum toughness and stable crack growth tendencies. In fully brittle materials, such as structural ceramics, crack growth occurs by the direct extension of the primary crack, and usually involves a bond rupture process. The crack growth resistance can thus be enhanced by effecting changes near the crack tip that reduce the crack-tip displacement (or K). Three primary toughening mechanisms of this type have thus far been identified: stress-activated stable microcracking (e.g., in Al_2O_3 alloys), stress-induced phase transformations (e.g., in ZrO_2 alloys), and fibrous grain "pull-out" (e.g., in Si_3N_4 alloys). However, coordinated stress analyses and empirical studies are needed to quantify and optimize the toughness; and additional toughening mechanisms (e.g., based on large internal strains) should be explored. For polymeric materials, crazing is a precursor to crack extension. Hence, akin to stable microcracking in brittle materials, arrays of nonpropagating crazes can be used to achieve high toughness. One approach for generating such controlled craze arrays is to utilize second-phase particles. Studies to investigate the respective roles of particle shape, dispersion, constitution and interface characteristics on craze development should be instituted in order to identify optimum approaches for polymer toughening. In metal systems, where substantial crack-tip deformation can precede crack extension, the details that pertain to specific systems are complex, and sometimes equivocal. There are two primary modes of extension: cleavage and hole growth, occurring separately or, more usually, in combination. The toughness for both modes is dictated primarily by the macroscopic stress/strain characteristic of the material, through its effect on either the stress amplitude in the plastic zone or on the restraint imposed by the ductile ligaments. However, toughening can be effected without varying the flow strength. These toughening effects are realized by suppressing cleavage crack or hole formation and/or by preventing premature slip localization or by introducing crack-path tortuosity. The most important structural features that dictate the toughening at constant strength appear to be precipitates and impurities. For example, multiple precipitate arrays in steels lead to substantial toughening by suppressing hole formation or slip localization; Widmannstätten precipitates in Ti alloys produce toughening by inducing tortuosity; whereas impurity segregation can encourage cleavage and thus degrade the toughness. These effects are only qualitatively understood. A substantial modeling effort to quantify toughening processes is crucial for systematic alloy design studies. Such an effort can only progress satisfactorily if, in addition to the materials scientist, there is an active participation from several disciplines, e.g., mechanics (to define the stress fields

due to macroscopic and localized deformation), surface physics (to analyze impurity distribution, especially at interfaces), statistics (to characterize size and spatial distributions of precipitates, etc.), and solid-state physics (to determine interface cohesion characteristics).

4.3 Slow Crack Growth

There are three primary modes of slow crack growth: environmentally assisted, cyclic, and viscous; they can occur separately, in parallel or in sequence. Substantial progress in the comprehension of these processes has been realized in recent years, but many important deficiencies remain.

The effects of environments are related primarily to their role in lattice or interface decohesion through hole and/or cleavage crack formation ahead of the primary crack: a poorly understood phenomenon. The effect of the microstructure as it influences the crack path and the mode of crack extension (e.g., hole formation or cleavage fracture) in the presence of the environment is clearly important and requires detailed study. Stress distributions in the plastic zone require further quantification through pertinent numerical analyses.

Cyclic crack growth (fatigue) has many of the microscopic features (such as slip localization) associated with cyclic microcrack initiation. These damage accumulation processes are of particular importance at the fatigue threshold, and their comprehension should be actively pursued. In addition, the details of the stress or displacement variation in the plastic zone are of crucial importance. For example, crack closure can dictate the effective stress intensity factor or crack opening experienced by the crack during each cycle; the closure process must, therefore, be accountable in terms of the elastic/plastic properties of the material; the understanding of how the nonrecoverable increment in the crack-opening displacement is converted into a crack extension in terms of microscopic mechanisms (including the role of static fracture processes) is incomplete. A continuation of recent materials/mechanics studies should see advances in these areas.

Viscous crack growth (creep rupture) involves the nucleation of microcracks in a zone ahead of the primary crack (or the nucleation of grain-boundary cavities), their propagation and finally their coalescence (especially with the primary crack or void). In most instances, the propagation is diffusion-controlled, a process that has been widely studied in the last decade; certain ambiguities remain, however, and further studies are to be encouraged. The coalescence phenomenon is more uncertain, largely because a generalized crack coalescence criterion has not been established.

Another important aspect of slow crack propagation is its characterization in terms of crack growth rates. Again, difficulties are encountered in the presence of extensive plasticity. Schemes based on the crack-path integral ΔJ (fatigue) or its time-dependent equivalent C^* (creep) have been proposed. However, they are not expected to be general, and their limitations should be determined experimentally. Also, of course, more general characterization approaches must be sought.

4.4 Dynamic Crack Propagation and Arrest

In a number of material systems, it is important to be able to predict the extent of rapid crack propagation, beyond criticality. For example, in nuclear pressure vessels, crack arrest must occur before the crack extends through the thickness and causes leakage. A pertinent crack arrest criterion is thus an essential requirement. When the cracks are small relative to the dimensions of the component, crack arrest is essentially defined by a material-dependent stress intensity factor, K_a (equal to K_c for ceramics, but usually $< K_c$ for metals and polymers). However, when the crack length becomes comparable to, or larger than, the smallest component dimension, the apparent stress intensity factor at arrest is $< K_a$ (except when the medium surrounding the component has a relatively large acoustic impedance, whereupon arrest can occur at $K \approx K_a$). The additional extension of the crack derives from the kinetic energy developed by the material around the separating crack and from stress waves reflected at the component boundaries. The material motion and the stress waves can augment the apparent stress intensification at the crack tip, and extension will proceed until the effective stress intensity factor diminishes to $\sim K_a$.

A crack arrest condition that accounts for the increments in crack length caused by kinetic effects has been computed for simple geometries. However, a generalized crack arrest criterion needs to be developed. This would involve experimental studies of crack arrest, coordinated with numerical (e.g., finite difference) stress analyses of rapid crack propagation.

4.5 Non-Destructive Evaluation

Current NDE techniques could be significantly improved by better methods to characterize the size, shape, and type of defects or cracks in structural components. A most fruitful approach would be a study that correlates modern experimental methods of quantitative defect characterization with crack mechanics. Initially, such a study would generate relations between the failure probability (for specific lifetimes, environments, expected stress histories, etc.) and the inferred defect characteristics. Of even greater importance would be the subsequent determination of the proportion of parts that are actually satisfactory, even though they are rejected by a particular inspection procedure based on a specified allowable failure probability. Feedback to the employed methods of defect characterization and crack mechanics will identify their deficiencies, and will thus emphasize those aspects of the failure prediction process that most adversely contribute to the rejection rate.

The formation and growth of cracks can be strongly influenced by residual stresses, which augment the applied stress. A nondestructive determination of the magnitude of these stresses, e.g., in welds, near surfaces, is important for effective failure prediction. Techniques for estimating internal stress are available, e.g., x-ray diffraction, ultrasonic surface waves, ultrasonic velocity differentials; but these techniques are not sufficiently developed to be universally applicable. In particular, stress gradients in regions of irregular geometry cannot be explicitly evaluated. Further developments in test techniques are thus to be encouraged. Crack growth in residual stress fields is also poorly characterized. However, numerical techniques for establishing stress intensity factors in residual stress fields are available, and these should be used to obtain solutions for problems of particular interest.

5. FACILITIES AND GENERAL RECOMMENDATIONS

5.1 Facilities

This panel saw no need for new major facilities serving the mechanical-properties community, except that a comprehensive and modern surface and interface investigation set-up (about 300 k\$) should be bought by or made primarily available to a group interested in the effects of interfaces on mechanical properties.

Great opportunities for advance of materials research are provided by large-scale computing facilities, for example, for finite-element continuum mechanical analysis and for lattice dynamics. Many important problems in fracture and plastic deformation await the application of large-scale computing techniques, but many investigators (especially university investigators) are critically limited by available computing facilities at their institutions. Hence, it is important to the fostering of work in mechanical properties that ERDA take steps to gain access for individual investigators to large ERDA computers, and provide the necessary assistance in setting up the hardware for telephone line communication via terminals, provide appropriate travel funds, etc.

5.2 Recommendation

The overwhelming need in order for basic research in mechanical properties to be able to impact real technological problems is for manpower funding at a level that permits comprehensive research. Most of the critical problems at this time involve a multiplicity of boundary conditions, such as monotonic and cyclic loading as well as temperature changes; a multiplicity of simultaneously acting mechanisms of deformation and fracture; and a multiplicity of environments of unprecedented severity. While research on individual components of these problems is of high scientific interest and is needed to provide building blocks for any more complete treatment, any impact on applications can be realistically expected only if the different building blocks can be interfaced with each other and synergistic effects studied. The present state of

the art in the mechanistic understanding of mechanical properties appears to warrant a major expenditure for such comprehensive study and augur for a reasonable chance of success.

A recommendation of this workshop is that the entire spectrum of "proximity" between basic research and currently recognized technological problems be supported on a continuing basis and that both researchers and engineers be encouraged to make tentative use of research results in technological applications.

In view of the fact that mechanical properties (and corrosion-related phenomena) are the most frequently listed outstanding problems that limit energy systems performance or even feasibility, it would appear that mechanical properties research should be funded with higher priority than in the past.

FINAL REPORT OF THE
MATERIALS SCIENCES WORKSHOP ON
THERMODYNAMICS AND ELECTROCHEMISTRY

Held May 18 to 20, 1977 at Argonne National Laboratory

Organizers

F. A. Cafasso, Argonne National Laboratory
J. R. Cost, ERDA, Division of Physical Research
L. S. Darken, Pennsylvania State University
N. H. Nachtrieb, University of Chicago

• Participants

J. Ackerman, ERDA, Argonne Nat'l Lab.	L. Kaufman, Man Labs, Inc.
R. Alkire, Univ. of Illinois	O. Kleppa, Univ. of Chicago
C. Angell, Purdue Univ.	N. Lichtin, Boston Univ.
T. Beck, Electrochem. Tech. Corp.	G. Mamantov, Univ. of Tennessee
M. Blander, Argonne Nat'l Lab.	J. Margrave, Rice Univ.
M. Bowman, Los Alamos Scientific Lab.	V. Maroni, Argonne Nat'l Lab.
J. Braunstein, Oak Ridge Nat'l Lab.	R. Marr, Sandia Laboratories
F. Cafasso, Argonne Nat'l Lab.	B. Morosin, Sandia Laboratories
E. Cairns, General Motors Corp.	N. Nachtrieb, Univ. of Chicago
A. Cooper, Case Western Reserve Univ.	J. Newman, Univ. of California
J. Cost, ERDA, Physical Research	R. Osteryoung, Colorado State Univ.
S. Dapkunas, ERDA, Fossil Energy	G. Rosenblatt, Pennsylvania State Univ.
L. Darken, Pennsylvania State Univ.	M. Saboungi, Argonne National Lab.
R. Epple, ERDA, Physical Research	R. Selman, Illinois Inst. of Tech.
H. Franzen, Iowa State Univ.	S. Srinivasan, Brookhaven Nat'l Lab.
A. Ghosh, Exxon Research & Eng. Co.	O. Vetter, Vetter Associates
D. Gruen, Argonne Nat'l Lab.	L. Wittenberg, Mound Lab.
H. Hanley, Nat'l Bureau of Standards	W. Worrell, Univ. of Pennsylvania
R. Humphreys, ERDA, RDD	S. Yosim, Atomics International

Final Report of the Materials Sciences Workshop on
Thermodynamics and Electrochemistry

Table of Contents

- I. SCOPE AND PRIORITIES OF FIRST RANK
 - A. Introduction
 - B. Conclusions
 - C. Recommendations and Priorities
- II. REPORT OF THE STUDY GROUP ON HIGH-TEMPERATURE THERMO-DYNAMIC AND TRANSPORT PROPERTIES OF SOLIDS
 - A. Introduction
 - B. Nonstoichiometric Solids
 - C. Multicomponent Systems
 - D. Electrochemical Phenomena
 - E. General Comments
 - F. Members of Study Group
- III. REPORT OF THE STUDY GROUP ON HIGH-TEMPERATURE THERMO-DYNAMIC AND TRANSPORT PROPERTIES OF LIQUIDS
 - A. Introduction
 - B. Interrelations of Technologies with High-Temperature Liquid Materials
 - C. Ranking of Materials of Interest
 - D. Conclusions
 - 1. General Technology Research Needs
 - 2. Technology Specific Research Needs
 - 3. Special Research Areas
 - E. Members of Study Group
- IV. REPORT OF THE STUDY GROUP ON PHASE DIAGRAMS AND PHASE TRANSFORMATIONS
 - A. Summary
 - B. Introduction
 - C. Recommendations
 - D. Members of Study Group

Table of Contents (Cont'd)

- V. REPORT OF THE STUDY GROUP ON ELECTRODE MATERIALS AND PROCESSES AND ELECTROLYTES
 - A. Electrochemical Aspects of ERDA Programs
 - B. Identification of High-Priority Topics
 - 1. Electrocatalysis
 - 2. Solid Electrolytes
 - 3. Electrode Morphology
 - 4. Modeling
 - 5. Corrosion
 - 6. Data Base
 - 7. Liquid Electrolytes
 - C. Members of Study Group

APPENDIX

List of Tables

Table III-1	Energy Technology Areas Utilizing High-Temperature Liquids
Table III-2	High Temperature Liquids and Associated Research Areas and Applications
Table III-3	Theoretical and Experimental Approaches in High-Temperature Liquid Research
Table IV-1	A Few Specific Examples of Systems Requiring New or Improved Thermochemical and Phase Diagram Data for Applications in Energy Technology
Table V-1	Electrochemical Components of ERDA Programs
Table V-2	High-Priority Electrochemical Topics

I. SCOPE AND PRIORITIES OF THE FIRST RANK

Thermodynamics and electrochemistry are two fields which can contribute significantly to the advancement of ERDA's energy mission. In recognition of this, a Workshop whose goals were to identify areas in which basic thermodynamic and electrochemical research relevant to this mission are needed and to establish priorities among the identified research areas was held at Argonne National Laboratory on May 18-20, 1977. For the sake of completeness and because their omission would introduce some artificiality into the Workshop deliberations, transport phenomena were included as a discussion topic of the Workshop. The workshop identified many areas of research that should have a significant impact on the energy area and concluded that the three areas of highest priority are: (1) thermodynamic research involving data generation, evaluation, and compilation on model and practical liquid and solid multicomponent systems and emphasizing the interplay of theory, experiment, and computer modeling for the prediction of stable and metastable equilibria in systems of special interest to ERDA; (2) electrocatalysis research, especially studies of the physics and chemistry of this electrochemical surface phenomenon; (3) basic research on the kinetics and mechanism of corrosion, erosion, and scaling phenomena under extreme environmental conditions.

A. Introduction

The Workshop was organized so as to allow for discussion, information exchange, and interaction between basic scientists working in thermodynamics, transport phenomena, and electrochemistry and scientists and engineers closely allied with the ERDA energy technologies. This was accomplished through invited talks and study group meetings which involved a total of 38 participants who were drawn from universities, industry, the national laboratories, and ERDA.

The talks, delivered on the mornings of the first two days of this two and one-half day Workshop, were concerned with overviews of the status and needs of the energy technologies on the first day and with scientific overviews that emphasized relevant research in the areas of thermodynamics, transport phenomena, and electrochemistry on the second day. The speakers, their subjects, and their affiliations are given in the Appendix.

The Study Group meetings took place each day after the morning talks and also during the morning of the third day. Each of the four Study Groups organized addressed itself to one of the following topics: (1) High-Temperature Thermodynamic and Transport Properties of Solids, (2) High-Temperature Thermodynamic and Transport Properties of Liquids, (3) Phase Diagrams and Phase Transformations, and (4) Electrode Materials and Processes and Electrolytes. Each group wrote a report on its conclusions and recommendations. These reports constitute Sections II-V of this final Workshop report. Some general conclusions and recommendations which were culled from these documents by the organizers are given in Section I.B below. The priorities assigned to the recommendations in Section I.C represent the

organizers' interpretation of the sense of the reports and discussion of the Workshop as a whole. For specific recommendations, the reader is referred to the individual Study Group reports in Sections II to V.

B. Conclusions

Thermodynamics and Transport Properties Study Groups: Among the conclusions reached by the first three of these groups are the following:

(1) A broad readily addressable data base is indispensable to the energy technology and materials programs. To the existing fund of information, which needs critical evaluation and compilation, must be added new thermodynamic measurements on solids and liquids.

(2) To fully utilize this information base and to determine whether additional data are needed, greater emphasis needs to be given to the development of models for the prediction, correlation, and extrapolation of thermodynamic data. This would entail the wider use of computers and the encouragement of fundamental-theory research. Such models would minimize the amount of experimental data needed for the development of various energy technologies.

(3) Corrosion is a phenomenon that pervades almost all the energy technologies; it should therefore be made the focus of concentrated experimental thermodynamic and transport studies, with a theory program undergirding these studies.

(4) Experimental and theoretical research is needed on ionic and electronic conductivity in solids (especially ceramics); this work needs to be done under well-defined conditions, with emphasis on materials potentially useful as electrolytes, electrodes, and chemical potential probes.

(5) An expanded program of basic research on ionic liquids—especially molten salts—and concentrated aqueous solutions should be undertaken, with special attention being given to the development of theories of pure liquids and solutions. The potential of liquid systems that exhibit both ionic and metallic conduction ("ionic alloys") should also be explored. These studies would make substantial contributions to several technologies, including those related to the development of energy systems.

(6) The general understanding of the nature of aqueous solutions of minerals under conditions of temperatures and pressures relevant to geothermal sources has been limited by insufficient experimental data and inadequate foundations in theory. A significant step towards overcoming this limitation can be taken by the development of a theory of polar liquid mixtures, including their equations of state, and by the generation of data on the solubility of minerals in geothermal fluids.

(7) Theoretical and experimental studies of phase transformations and stability in metastable systems (including glasses and amorphous solids) should be pursued because of their special pertinence to understanding the behavior of geothermal fluids, solids under intense radiation fluxes, and solar energy conversion.

Electrochemistry Study Group: This group concluded that a major thrust is needed in fundamental research on electrocatalysis, with an expansion of effort on both solid and liquid electrolytes, the morphological changes occurring in electrodes, and the derivation of theoretical electrochemical models. This effort, bolstered by work to generate needed thermodynamic and transport data, would best meet the needs of R&D programs on advanced batteries, fuel cells, and industrial electrolytic processes. This conclusion is founded upon the realization that the greatest needs in these developmental programs are (1) to effect larger exchange current densities at hydrogen, oxygen, and halogen electrodes; (2) to select optimal solid electrolytes for a large number of ions, with useful properties over a wide temperature range and over a broad range of oxidizing conditions; (3) to identify liquid electrolyte-electrode systems having low oxygen overpotentials in fuel cells; (4) to gain an understanding of the interdependence of electrocatalysis on electronic, geometric, and morphological factors, as well as knowledge of definitive reactions at semiconductor-electrolyte interfaces; and (5) to establish control mechanisms for the prevention of sintering and poisoning of fuel cells.

C. Recommendations and Priorities

On the basis of these conclusions, the Workshop recommends as first priority:

(1) A first rank program on the generation, evaluation, and compilation of thermodynamic data for liquid and solid multicomponent systems essential to the energy technologies and the materials science programs. The acquisition of these data, however, should not stand in isolation, but should be coupled closely with modeling and theory in recognition of the desirability to extend and generalize concepts.

(2) A major program on the surface chemistry and physics that emphasizes research on electrocatalysis that will lead to a better understanding of (a) how to lower barriers to the transfer of charge across electrode surfaces; (b) how to avoid catalyst poisoning and deactivation; and (c) what the relationships are between catalyst function and electronic, geometric, and topological factors. The use of advanced surface and *in-situ* techniques for these studies is urged.

(3) Full support of basic thermodynamic, transport, and electrochemical studies on corrosion, erosion, and scaling under various environments (ionic media, gradients of temperature and chemical potential, etc.), with emphasis on understanding rate-limiting factors and mechanisms.

As a second priority, the following are recommended:

(1) A strong fundamental program on the transport of charged matter through solids and liquids. In this connection, a search for (a) new materials with high-temperature stability and high ionic mobility and (b) nonaqueous electrolytes with enhanced conductivity is urged.

(2) Experimental studies on minerals in melts and in aqueous solution, covering the range of temperatures and pressures found in geothermal sources and keyed to the development of the capability to predict the thermodynamic and transport properties of geothermal liquids from theory or models.

(3) Theoretical and experimental investigations to understand the interrelationships between thermodynamics and kinetics of phase transformations in metastable materials identified as being important in advancing technologies.

(4) Theoretical and experimental studies of ionic liquids, especially molten salts, in view of their present and potential wide technological application (*e.g.*, electrochemical cells, pyrometallurgical processing of ores and nuclear fission fuels, coal gasification and liquefaction, etc.).

II. REPORT OF THE STUDY GROUP ON HIGH-TEMPERATURE THERMODYNAMIC AND TRANSPORT PROPERTIES OF SOLIDS

A. Introduction

The study of the thermodynamic properties of systems at high temperatures continues to be of fundamental importance to the developing energy technologies. Thermodynamic information is required for the prediction of stability with respect to corrosive attack, materials interactions, and vaporization losses in high-temperature environments. Furthermore, the interplay between chemical thermodynamic research and the preparation of new materials has been important in providing materials having useful properties.

There are important areas of research closely related to basic thermodynamic properties measurement which should not be overlooked. For example, numerous corrosion phenomena that occur at interfaces between solids and gases or plasmas have both a thermodynamic and a kinetic component, and these phenomena are not well understood. Solid surfaces in environments such as those found in coal-gasification, coal liquifaction, MHD, thermo-nuclear-reactor and other energy-related systems require characterization with regard to structure, stability, composition and impurity segregation. Modern surface methods such as Secondary Ion Mass Spectrometry (SIMS), Auger, and Photoelectron Spectroscopy (PES) enable surface characterization which, when coupled with thermodynamic analysis, will provide valuable insights into corrosion reactions.

B. Nonstoichiometric Solids

As a rule, solids at high temperatures are nonstoichiometric. Much of the existing thermodynamic and transport data base has been established assuming idealized line compositions. As a result, the data are inadequate for describing and understanding high-temperature phenomena such as materials compatibility and corrosion. For example, it is well known that the oxygen-to-uranium (O/U) ratio in UO_2 and the resulting strong variation of oxygen chemical potential determines the compatibility or corrosiveness of UO_2 fuel with respect to various cladding materials. Experimental measurements of partial and/or thermodynamic and transport properties as a function of stoichiometry are required. Special attention should be addressed to the accurate characterization of the composition. Emphasis should be on systems which will provide data for the development of models useful for the prediction and extrapolation of thermodynamic and transport properties. Transition-metal sulfides are a class of materials which could serve as model systems. Furthermore, detailed thermodynamic and transport knowledge of these systems is needed to understand sulfide scaling problems in coal-gasification environments and compatibility problems in advanced alkali-metal battery systems.

C. Multicomponent Systems

In the developing energy technologies, many of the materials required for containers and cladding are usually multicomponent in the sense that they include more than one independently varying species. This is also

true of corrosion products resulting from gas-solid or liquid-solid interactions. Further, these multicomponent phases are frequently formed, or are present in regions where temperature gradients are high, particularly in energy processes involving heat transfer or heat flow. In addition to needing thermodynamic and transport data over composition ranges, the effects of thermal gradients should also be investigated. For example, carbon diffusion through metal-carbide coatings can be either reduced (ZrC) or increased (NbC) by a thermal gradient. Multicomponent systems relevant to the evolving energy technologies include transition-metal sulfide systems which are particularly important in coal gasification (Fe-Cr-S, Fe-Al-S) and in high-temperature battery applications (Li-Fe-S, Na-Al-S).

D. Electrochemical Phenomena

We recommend investigations of ionic and electronic conductivity mechanisms in ceramic materials under well-defined thermodynamic conditions. Particular emphasis should be given to materials that are potentially useful as solid electrolytes or electrodes. New solid electrolytes have applications in high-temperature fuel cells, batteries and electrochemical probes. One example is the need for an electrochemical probe to monitor carbon activities in liquid sodium coolant reactors.

New ceramic electrode materials which have essentially equal ionic and electronic transport numbers should be very useful in batteries and fuel cells. Such electrodes are attractive for cells involving gas mixtures because the charge-transfer reaction occurs over the entire gas-electrode area rather than being geometrically restricted.

E. General Comments

The data base for accurate thermodynamic and transport properties of high-temperature materials is usually a limiting factor in the selection and use of materials in applied programs. Therefore it is recommended that the critical evaluation and compilation of such data be rejuvenated. Furthermore, we must maintain the capability for the measurement of necessary thermodynamic data by either calorimetric and/or equilibrium techniques.

Finally, we note the necessity of increasing the awareness of basic researchers to problems arising in applied fields. Although it would be a mistake to convert basic researchers into applied technologists, mechanisms for increasing communication between these two groups should be fostered.

F. Members of Study Group

- W. Worrell (Univ. of Penn.) Chairman
- M. Bowman (LASL)
- A. Cooper (Case Western Reserve Univ.)
- J. Cost (ERDA)
- S. Dapkunas (ERDA)
- H. Franzen (Iowa State Univ.)
- D. Gruen (ANL)
- R. Humphreys (ERDA) (Part-time)
- V. Maroni (ANL) (Part-time)
- R. Marr (Sandia Labs)

III. REPORT OF THE STUDY GROUP ON THERMODYNAMIC AND TRANSPORT PROPERTIES OF HIGH-TEMPERATURE LIQUIDS

A. Introduction

Liquids at high temperatures, defined for present purposes as those exceeding 100°C, play a central role in the production or consumption of energy in numerous technologies. Table III-1 lists areas employing energy-related technologies in approximate order of decreasing relative priority.

Table III-1. Energy Technology Areas Utilizing
High-Temperature Liquids

Fossil Fuels
Energy Conservation Efforts
Nuclear Fission
Batteries and Fuel Cells
Environmental Concerns
Nuclear Fusion
Solar Energy and Industrial Waste Heat
Energy Storage (other than batteries)

Broadly, the high-temperature liquids involved in these technological areas are included in the following categories: (1) concentrated aqueous salt solutions; (2) molten salts; (3) liquid metals and semiconductors; (4) silicates and related slags; and (5) non-polar liquids, including, but not limited to, the molten chalcogens and various organic substances.

Certain basic problems run through all of their uses; these include the need for container materials and corrosion prevention. There is also a broadly felt need for fundamental data on the thermodynamic, transport, electronic and structural properties of these liquids.

B. Interrelations of Technologies with High-Temperature Liquid Materials

Most of the developing energy technologies involve interactions with high-temperature liquids. For example, in the fossil fuel utilization of coal by gasification, liquefaction, and combustion processes, the fused salts, Na_2CO_3 , ZnCl_2 , AlCl_3 , and sulfates are used as reaction media. The handling of the molten slag ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$), molten sulfates and vanadates, and off-gas particulates must be considered in the corrosion of structural materials. In addition, the behavior of organic products in these fused salts must be recognized.

Opportunities exist for the conservation of energy in the metallurgical industry by a better understanding of the fused salts involved. In the reduction of alumina, cryolite baths and newly developed chloride cells are important, as are the slags in the manufacture of iron and steel.

In nuclear fission and fusion, the liquid alkali metals and fused fluoride salts are used as coolants and breeder systems. The solubility of the non-metals (C, O, N, hydrogen isotopes) in these fluids is important. Liquid metals (*e.g.*, Zn) and fused salts (*e.g.*, molten chlorides) are important in fuel processing, and a knowledge of the interactions of reactor coolants with structural materials, as well as with fuel and fuel cladding, is required in reactor safety analysis.

In batteries and fuel cells, the electrode materials, *e.g.*, liquid alkali, alkaline earth metals, and sulfur, are considered together with the molten electrolytes, *e.g.*, carbonates, hydroxides and chlorides. The behavior of sulfides and polysulfides in these electrolytes is important.

In the solar and waste heat energy fields, fused salts and organic fluids may be used directly as the solar absorbers and heat-transfer fluids. Direct conversion of solar to electrical energy utilizes semiconductor crystals which may be grown from molten melts or may directly utilize liquid semiconductors.

In geothermal energy utilization, the high temperature-high pressure liquid brines are the primary fluids. Secondary working fluids may be used in the power cycles and utilization of molten magmas is being considered.

During cleanup of the environment from certain industrial waste products, aqueous carbonates, molten carbonate-sulfate, and slurry processes are being utilized.

For thermal energy storage, eutectic salt systems are utilized. Reversible gas-liquid equilibria, particularly those involving the atmospheric gases, will probably be capable of much greater thermal energy storage and need to be considered.

C. Ranking of Materials of Interest

The materials of interest are ranked according to priorities based upon the importance of the technologies to which the materials are applied and to the overall frequency of use of these materials to these technologies. The rankings of the materials are then as follows:

(1) Molten Salts. These are being considered for application in the six most important technology categories. Molten salt systems of particular interest are the alkali metal carbonates, acidic chlorides and chloride-containing melts.

(2) Liquid Metals. These are being considered in four of the six most important technology categories. Metals of particular interest are the alkali metals and the alkaline earth metals.

(3) Aqueous Solutions. Above 100°C, these are predominantly of interest to stack-gas purification processes (environmental) and to geothermal processes.

(4) Silicates. These are predominantly of interest in fossil fuel and conservation technologies, especially the $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ class of silicates.

In these classes of materials, there are specific areas of research which appear to be needed. These are listed in Table III-2.

Table III-2. High-Temperature Liquids and Associated Research Areas and Applications

	<u>Area of Research</u>	<u>Application</u>
<u>Fused Salts</u>	Alkali Carbonates	
	- Sulfur chemistry	Gasification; fuel cells
	- Acid-base chemistry	Corrosion reaction
	- Water interactions	Fuel cells
	- Volatilization	Gasification; fuel cells
	- Contact vapor explosions	Safety
	Acidic Chlorides (ZnCl_2 , AlCl_3)	
	- Carbonium ion stabilization	Catalysis
	- Thermodynamic and transport properties	Batteries
	Mixed Halide Melts	
	- Solubilities, <i>e.g.</i> , Al_2O_3 , sulfides, metals, He, Xe, etc.	Al production; batteries; ore processing; molten salt reactor
	- Complexing, <i>e.g.</i> , $\text{Al}^{3+} + \text{O}^{2-}$ in cryolite and chloride melts	Al production by Hall and ALCOA processes
	- Transport	Batteries
	- Solution chemistry	
<u>Metals</u>	Lithium	
	- Solubility $\text{C} + \text{O} + \text{H}(\text{D}, \text{T}), \text{N} +$ structural materials	Fusion blanket processing; corrosion
	- Magnetohydrodynamics	Pumping
	- Extraction equilibria	Processing and purification
	- Alloys	Alternative blanket; liquid electrodes
	Sodium	
	- Solubilities $\text{C} + \text{O} + \text{H} + \text{N} +$ structural materials	Fission coolant; corrosion; mass transport
	- Contact vapor explosions	Nuclear safety
	Other Metals (<i>e.g.</i> , Zn)	
	- Activities + solubilities	Nuclear reprocessing

Table III-2 (Cont'd.)

	<u>Area of Research</u>	<u>Application</u>
<u>Aqueous</u>	Activities + pH at high T,P,X Solubilities at high T,P,X Metastabilities Hydrodynamics at high flow rates Thermodynamic properties of hydrates	Corrosion; scale formation; bubble formation; flash-induced shock Matter and energy transport Capacity for energy storage
<u>Silicates</u>	CaO·Al ₂ O ₃ ·SiO ₂ Melts - Solution thermodynamics - experimental and theoretical	Coal conversion (slag); MHD; metal production
<u>Other</u>	Liquid semiconductors Organic liquids	Solar Liquefaction

From these areas of research and from our discussions, we can define very general theoretical and experimental approaches for solving specific needs. These are listed in Table III-3.

Table III-3. Theoretical and Experimental Approaches in High-Temperature Liquid Research

Thermodynamic Properties

- Calorimetry (ΔG_f , ΔH_f , ΔS_f , C_p , ΔH_m)
- Emf's
- Vapor pressures and vapor species
- Statistical mechanics of solutions and single-component fluids
- Solubilities
- Aqueous measurements at high P and T
- PVT equations of state

Dynamic Behavior

- Transport properties

Structure Probes

- Diffraction (ordering, coordination)
- Spectroscopy (valence, structure)

Electronic

- Pseudopotential theory for metals and alloys

Table III-3 (Cont'd.)

Modeling

- Thermodynamic calculation of equilibria and near equilibria in complex systems
- Computer simulation

Interfacial Phenomena Studies

- Corrosion
- Nucleation and metastable states

The most important approaches are thermodynamic. Almost all of these approaches are presently part of ERDA's research programs, but the total effort is inadequate. An increase in the total support, as well as shifts of emphasis to more relevant materials, is needed. In addition, changes in emphasis of individual items are recommended. For example, measurements and evaluations of calorimetric and other thermodynamic data, which are part of the fundamental underpinning of all technologies, need expansion. Theories of liquids and of high-temperature solutions should be studied more extensively as they minimize the amount of data needed to understand and predict behavior of liquid systems. Diffraction (neutron and X-ray) studies coupled with computer simulations of liquids are important fundamental avenues to the understanding of liquids which cannot be tied closely to technologies but which should nevertheless receive increased support. A small effort on pseudopotential theory of liquids might be initiated to evolve a better understanding of the electronic properties of alloys. A generalized capability for the calculation of equilibria in complex systems is needed not only within ERDA-sponsored programs, but also as a resource for energy-related industries.

D. Conclusions

From the above problem areas and materials-character considerations can be distilled a selection of priority research needs based either on the special importance of the research to an individual technology involving a single class of liquids, or on the recurrence of problem areas in different technologies, as follows:

1. General Technology Research Needs (not in order of importance)

Several broadly important needs are identified as:

(a) The establishment of a central capability for the modeling of complex chemical equilibria. It would be natural for this facility to constitute one arm of the projected (NSF-ERDA) national center for computation in chemistry.

(b) Complementary to item (a), the large-scale expansion and consolidation of existing data evaluation and storage centers.

(c) Companion to the above, generation of additional thermodynamic data of good quality on well-chosen systems.

(d) An expanded program of basic research on ionic-liquid and concentrated-solution structure, thermodynamics and nonequilibrium properties with special attention to development of theories of pure liquids and solutions and to computer simulation studies for testing concepts and theories.

(e) Special attention to two areas of chemical phenomenology; (1) the nucleation of stable from metastable states (see Table III-2), and (2) the corrosion of container materials and its control by manipulation of the chemical character of the environment (*e.g.*, pH, pCl, pF, pO).

2. Technology Specific Research Needs

The outstanding example of a specific technological research need is the data gap and comprehension gap in high-temperature and high-pressure properties of brine solutions which are retarding the exploitation of geothermal energy sources. Needs are (1) a data generation center, and (2) encouragement of fundamental research to develop an adequate theory of such fluids under sub- and supercritical conditions as objectives.

3. Special Research Areas

Research programs should have enough flexibility to incorporate research on exotic or newly discovered materials for which specific technological applications have not yet emerged. Among such materials, we recognize the liquid "ionic alloys," which have been used and are of some potential in metals processing.

E. Members of Study Group

M. Blander (ANL) - Co-chairman
 L. Wittenberg (Mound Lab.) - Co-chairman
 C. Angell (Purdue Univ.)
 S. Dapkunas (ERDA)
 R. Humphreys (ERDA) (part time)
 J. Margrave (Rice Univ.)
 V. Maroni (ANL) (part time)
 N. Nachtrieb (Univ. of Chicago)
 O. Vetter (Vetter Assoc.)
 S. Yosim (Atomics International)

IV. REPORT OF THE STUDY GROUP ON PHASE DIAGRAMS AND PHASE TRANSFORMATIONS

A. Summary

In view of the wide range of materials problems pacing the development of new energy sources, it is recommended that vigorous support be provided for fundamental research into coordinated theoretical, experimental and computational methods for coupling thermodynamic and phase diagram data. This work should be directed toward generation of physical and operational models, as well as suitable data bases, that would provide explicit information on stable and metastable equilibria in metallic, oxide, sulphide, halide, and other multicomponent systems over wide ranges of temperature and pressure. Critical evaluation of existing data is essential.

B. Introduction

The requirements of society for an expanding variety of energy sources have magnified the need for evaluating materials performance under a wide range of conditions. Furthermore, the evaluation of potential systems for energy generation often hinges on a critical assessment of the properties and behavior of the materials needed. Moreover, in many cases, attainment of a performance target for a new energy system depends critically on the synthesis of novel materials.

A study of the thermodynamic properties and phase diagrams of a wide range of materials and experimental conditions can provide a rational basis for these investigations. Specifically, one requires an operational means for predicting materials characteristics prior to experiment and interpreting experimental data.

On a fundamental level it is important to obtain basic molecular data to complement thermodynamic and phase equilibrium information. Such data include crystallographic, vibrational and electronic information, defect characterization, comparison of surface and bulk characteristics, and such bulk properties as density, thermal expansion, and electrical and thermal conductivity.

Such data should be acquired for systems of practical interest and for model systems that will allow interpretation of unusual behavior. It is essential to correlate different properties of a single system, as well as the same property for many systems.

The range of thermodynamic data needed includes the properties of pure components, solutions, and compound phases such as specific heats; entropies; heats of formation, fusion and vaporization; and excess enthalpy and entropies. Information on these properties should allow calculation of chemical potentials, vapor pressures, integral Gibbs free energies, as well as vapor-liquid characteristics.

Care should be taken to ensure the internal thermodynamic consistency of existing data. Moreover, critical assessment is recommended to establish and maintain a reliable data base and to identify further experimental needs.

Table IV-1 provides some examples of systems which require new or improved thermodynamic and phase diagram data for practical application in energy technology.

C. Recommendations

1. Continuing critical evaluation of data on phase diagrams and equilibria and related thermodynamic properties is essential, as is the establishment of a readily accessible data base, including sources of the data and estimates of reliability. ERDA is urged to use its resources to assure that such an effort is carried out.

2. It is important to stimulate investigations of those systems which will help one to predict the phase behavior of other systems, particularly that of the complex systems of present or potential interest in energy technology. Basic experimental measurements and theoretical studies should be carried out on such model systems, as well as on systems of immediate interest (see Table IV-1).

3. There is particular value in extending the range of experimental investigations of phase equilibria to higher temperatures, such as may be encountered in nuclear reactors and other high-temperature energy conversion schemes. Higher pressure (ten to a few hundred atmospheres) studies on fluid equilibria are also of value.

4. Research in the following areas would be valuable in extending our understanding of phase transformations relevant to energy technology:

- (a) Basic work to extend understanding of phase behavior in 3-, 4-, and 5-component system.
- (b) Theoretical and experimental studies of phase transformations and stability in metastable systems, including glasses and amorphous solids. These are found in geothermal fluids, are formed in alloys exposed to intense radiation fluxes, and are also related to solar electric conversion.
- (c) Basic work on the interrelationships between thermodynamics and kinetics of phase transformations. This is relevant to gaining an understanding of local equilibrium and departures therefrom in corrosion and other processes.
- (d) Computer simulation of phase behavior and phase transformations in condensed mixtures.
- (e) Theory of polar liquid mixtures, equations of state, and complete thermodynamic descriptions are needed.

Table IV-1. A Few Specific Examples of Systems Requiring New or Improved Thermochemical and Phase Diagram Data for Applications in Energy Technology*

<u>Type of System</u>	<u>Application Areas</u>	<u>Remarks</u>
I. <u>Metallic</u>		
Li-Al, Li-Si, Li-Sn Li-Ca, Li-Mg, Li-Al-Si	Battery Technology (High Temperature)	Potential for Improved Electrodes
U-Pu-Th	Nuclear Fission	Solid Phases and Liquidus
Th(U)-Fe-Cr-Ni	Nuclear Fission	Phase Diagrams and Stability
V-Ti-Na	Nuclear Fission	
Li-Be, Li-Pb, Li-Si Li-B, Li-C-Cr, Li-C-V	Magnetic Fusion (CTR)	Blanket Material
Fe-Cr-Ni(Ti,Si,C)	Nuclear Fission	Void Swelling on Long Exposures
H-D-T	Magnetic Fusion (CTR)	Separation and Re- covery
II. <u>Oxide Systems</u>		
ZrO ₂ -CaO, ZrO ₂ -Y ₂ O ₃	Fuel Cells	Electrolytes (stabil- ity in reducing and oxidizing environ- ments)
Ce-O ₂ -Gd ₂ O ₃ , UO ₂ -ZrO ₂	Fuel Cells	"
LiAlO ₂	Fuel Cells	Phase Stability (3 polymorphs)(P-T)
LaCrO ₃ -MgO-Al ₂ O ₃	Fuel Cells	Connectors (stability in oxidation/reduc- tion)
Nb ₂ O ₅ -TiO ₂ -ZrO ₂	Fuel Cells	
PuO ₂ -UO ₂ -ThO ₂	Nuclear Fission	Solid Phases and Liquidus

Table IV-1 (Cont'd)

<u>Type of System</u>	<u>Application Areas</u>	<u>Remarks</u>
III. <u>Sulphide and Oxide Systems</u>		
(NiS,Cr ₂ S ₃)-(Na ₂ O,K ₂ O)	Fossil Energy	Reducing Conditions
(Al ₂ O ₃ ,Cr ₂ O ₃)-(NiS)	"	"
(Na,Li)-(Fe,Ti,Nb)-(S,O) (Fe-S), (Ti-S), (Nb-S)	Battery Technology (High Temperature)	
Li-Fe-S-(LiCl,KCl)	Battery Technology (High Temperature)	
IV. <u>Mixed Systems</u>		
Li-Al-H, Li-Pb-H	Magnetic Fusion	
Li-(LiF,LiCl)-(Li ₂ O,Cr ₂ O ₃)	"	
V-Ti-(CsI,RbI)	Nuclear Fission	Spent Fuel Interactions
Si-SiO-SiO ₂	Solar Energy	Growth of Large Silicon Crystals
Na ₃ AlF ₆ -Al ₂ O ₃ -NaF-CaF ₂	Aluminum Electrolysis	Energy Conservation
V. <u>Aqueous and Polar Systems</u>		
H ₂ O-NaCl-MgOH-CaCO ₃	Geothermal Energy	Temperature to 350°C
H ₂ O-SiO ₂ -(Ba,Ca,Fe)SO ₄	"	Pressure to 5000 psi
H ₂ O-FeCO ₃	"	
H ₂ O-Tars, Oil, Phenols	Coal Gassification	Recovery
H ₂ O-H ₂ S,COS,HCN, etc.	"	Scrubbing
CO ₂ -H ₂ O-Petroleum	Tertiary Oil Recovery	
CO ₂ -H ₂ S-CH ₄ , etc.	Liquified Natural Gas (LNG)	Cryogenic Temperatures
H ₂ O-ZnCl ₂	Geothermal Energy; Coal Gasification	Cover Broad Composition Range

*Most of these examples were taken from lectures presented in the first session of this Workshop.

5. It is important to obtain basic molecular data (structural, spectroscopic, thermophysical, surface) to complement thermodynamic information for both model and practical systems.

D. Members of Study Group

L. Kaufman (Man Labs) Chairman
L. Darken (Penn. State Univ.)
H. Hanley (NBS)
O. Kleppa (Univ. of Chicago)
G. Rosenblatt (Penn. State Univ.)
M. L. Saboungi (ANL)

V. REPORT OF THE STUDY GROUP ON ELECTRODE MATERIALS AND PROCESSES AND ELECTROLYTES

A. Electrochemical Aspects of ERDA Programs

Electrochemical studies impinge on most of ERDA's energy programs. In many cases, electrochemical information is essential to the success of a program. In other cases, such information can lead to greater process efficiency. The relationship between ERDA energy programs and the electrochemical components involved in these programs is listed in Table V-1.

Table V-1. Electrochemical Components of ERDA Programs

<u>ERDA Program</u>	<u>Electrochemical Aspect</u>
Coal	
Slurry transport	Erosion, corrosion
Gasification,	Sulfidation
Liquefaction	Stress corrosion cracking
Nuclear	
Fission	Stress corrosion cracking of zirconium and stainless steel, Na containment
Fusion	H-isotope separation, Plasmas
Geothermal	Corrosion, scaling, downhole sensors
Ocean Thermal Energy Conversion	Stress corrosion cracking in NH ₃ , seawater
Solar Electric	Photovoltaic Photo-electrochemical redox couples, electrolytes, corrosion
Fuel Cells	Electrodes, electrolytes, separators, interconnects,
Batteries	"
Industrial Electrolytic Processes	"

B. Identification of High-Priority Topics

The electrochemistry study group identified topics that should be given high priority. These topics are listed in Table V-2. The nature of the problems associated with these topics is discussed below. Because effort should be made to solve or, at the very least, ameliorate these problems, the study group urges that work in these areas be supported by ERDA. A discussion of these topics is given below.

Table V-2. High-Priority Electrochemical Topics

Electrocatalysis
Solid Electrolytes
and Membranes
Electrode Morphology
Modeling
Corrosion
Data Base
Liquid Electrolytes

The topics in the above table were selected from some 25 that were listed and discussed. The order of priority is as listed, but the last five are nearly of equal priority.

1. Electrocatalysis

One of the main reasons for efficiency losses in electrochemical energy conversion and storage and in industrial electrochemical processes is the slowness of the reactions of one or both electrodes in electrochemical cells. The majority of these technologies involve hydrogen, oxygen, or halogen electrode reactions. Finding reversible oxygen electrodes (*i.e.*, with an exchange current density $>10^{-3}$ amp cm^{-2}) has been the most difficult problem. A major effort should be made to develop reversible oxygen electrodes, particularly ones using mixed oxides with a spinel or perovskite structure. It is also essential to carry out theoretical studies that will lead to correlations between heterogeneous catalysis and electrocatalysis and to the determination of the dependence of electrocatalytic activation on electronic, geometric and magnetic factors. The mechanism of time variation of electrocatalytic activity due to poisoning or sintering effects, as found in fuel cells, needs to be investigated in detail. An in-depth understanding of the reactions of semiconductor-electrolyte interfaces will improve the prospects of developing efficient electrochemical devices to convert solar energy into electricity.

A field in its infancy is electrocatalysis of electro-organic reactions. In general, these reactions involve many more intermediate steps than electro-inorganic reactions, and their mechanisms are thus more complex. Work in this area will accelerate the development of organic fuel cells for application in transportation and in electro-organic synthesis.

In situ surface analysis techniques are needed for an understanding of the mechanism of electrocatalysis.

2. Solid Electrolytes

Solid electrolytes (including polymeric electrolytes) for batteries and fuel cells offer unique opportunities in the development of new cells because of their high specificity for the ionic species transported. Work on solid ionic conductors for Na^+ , Li^+ , O^{2-} , H^+ , S^{2-} , OH^- and other ions is particularly important. Preference is indicated for solid electrolytes having useful properties over a wide temperature range and a wide range of oxidizing (Cl_2 , S, O_2 , etc.) and reducing (Na, Li, H_2) conditions.

3. Electrode Morphology

Electrode morphology encompasses a wide array of topics of central importance to electrochemistry. Some examples are (1) electrodeposition and dissolution (of importance in rechargeable batteries with Zn, Fe, Li, Al, alloy, and other electrodes); (2) charge-discharge behavior of valence-change electrodes (*e.g.*, FeS_x , PbO_2); (3) intercalation electrodes; and (4) the behavior of porous electrodes for use in fuel cells, batteries, electrolysis cells, and industrial electrolytic cells. A fundamental understanding of the mechanisms by which these electrodes operate should be an important objective of this work.

4. Modeling

Fundamental studies usually involve testing hypotheses of materials behavior. If such hypotheses can be expressed as mathematical models, the development and testing of rational explanations for experimental observations are made easier. The development of models of electrochemical systems is therefore an integral component of a materials research program. The use of models is particularly helpful in electrochemical systems owing to the complexity inherent in describing the transport of energy and species to electrochemically reactive surfaces. Also, the testing of a particular hypothesis as, for example, is done to develop insight into localized corrosion processes, is often so complex that a model is needed to relate the various interactions between thermodynamic and kinetic properties of the overall system. Certainly the development of high-rate porous electrode structures is closely related to the use of models by which such structures may be characterized and their behavior understood.

5. Corrosion

Corrosion is a problem common to all developing energy technologies. Scaling and intergranular attack occur in high-temperature processes, including coal gasification and liquifaction, fission and fusion reactors, and geothermal power development. Erosion-corrosion is encountered in coal-slurry pipelines, as well as in coal processing and burning. Localized corrosion, in the form of crevice corrosion,

pitting, and stress corrosion cracking, plague all technological processes. Basic research on the above types of corrosion is necessary to provide the understanding requisite to the selection and development of appropriate materials.

6. Data Base

A common need pervading research in all of the energy technologies is access to a reliable data base on thermodynamic, kinetic, and transport properties. The major purpose of such a data base would be to provide information needed for the development of new or improved processes. A coherent broad-based program supported by the entire spectrum of materials science programs is needed. Initially, it should provide for collection, collation and critical evaluation of existing data such as those in the JANAF Tables, Phase Diagrams for Ceramists, Hansen's compilation of phase diagrams, and other sources. This evaluation should be the basis of identification of serious discrepancies and data gaps in specific areas of the materials science programs. In addition, funding should be provided for the acquisition of data in critical areas. Special needs are the physico-chemical properties of concentrated electrolytes, including molten salts, refractory borides, carbides, nitrides, oxides and sulfides. Support is needed not only for the acquisition and compilation of requisite data but also for the development of predictive methods of estimating unknown properties.

7. Liquid Electrolytes

There is an urgent need to find acid electrolytes which can replace phosphoric acid in fuel cells. One acid which looks attractive is trifluoromethane sulfonic acid (TFMSA). The oxygen overpotentials in this acid are less than in phosphoric acid. Anion adsorption has an influence on the electrocatalysis of the oxygen evolution reaction. Because TFMSA wets Teflon, it cannot be used as the electrolyte in fuel cells with Teflon-bonded porous electrodes. An investigation of substituted TFMSA may help in finding improved acid electrolytes which do not wet Teflon.

One of the major problems with nonaqueous lithium batteries is the low conductivities of these electrolytes. Finding nonaqueous electrolytes with about the same conductivity as aqueous systems will be most beneficial in the development of such batteries for electric vehicle application.

Studies of the properties of molten salt electrolytes (*e.g.*, carbonates, halides) and associated problems (*e.g.*, carbonate volatility, electronic conductivity, compatibility with diaphragm materials) are basic research areas which will greatly help fuel cell and battery development.

An understanding of the mechanism of photoelectrochemical processes in solution will be beneficial in developing devices for the conversion of solar energy to electric energy.

C. Members of Study Group

R. Alkire (Univ. of Ill.) - Co-chairman
 E. Cairns (General Motors Corp.) - Co-chairman
 T. Beck (Electrochem. Tech. Corp.) - Co-chairman
 J. Ackerman (ERDA)
 J. Braunstein (ORNL)
 R. Epple (ERDA)
 K. Ghosh (Exxon Res. and Engr. Co.)
 N. Lichtin (Boston Univ.)
 G. Mamantov (Univ. of Tenn.)
 B. Morosin (Sandia Lab.)
 J. Newman (Univ. of Calif.)
 R. Osteryoung (Colorado State Univ.)
 R. Selman (Ill. Institute of Tech.)
 S. Srinivasan (BNL)

APPENDIX

Invited Speakers and Session Chairmen of
Workshop on Thermodynamics and Electrochemistry

I. Session on Materials Problems and Research Needs
Chairman, N. H. Nachtrieb (University of Chicago)

<u>Speaker</u>	<u>Subject</u>	<u>Affiliation</u>
J. Ackerman	Materials Problems and Research Needs in Fuel Cell Technology	Fuel Cell Programs, ERDA, Argonne, IL
E. Cairns	Materials Problems & Research Needs in Advanced Battery Technology	General Motors Research Labs, Warren, MI
S. Dapkunas	Basic Materials Research Requirements in Fossil Energy Applications	Fossil Energy, ERDA, Washington, DC
R. Humphreys	Nuclear Fission—Status and Direction	Reactor Development and Demonstration, ERDA, Washington, DC
V. Maroni	Materials Problems and Basic Data Needs in Magnetic Fusion Energy Technology	Argonne National Laboratory, Argonne, IL
O. Vetter	Some Basic Chemical Problems in Geothermal Operations	Vetter Associates, Laguna Beach, CA

II. Session on Energy-Related Materials Research
Chairman: L. S. Darken (Pennsylvania State University)

C. A. Angell	Energy-Relevant Aspects of Molten Salt and Concentrated Electrolyte Solution Research	Purdue University, Lafayette, IN
J. Margrave	Thermodynamic Deficiencies, Discrepancies, and Loopholes Related to Electrochemical Phenomena	Rice University, Houston, TX
R. Osteryoung	Recent Trends in Research in Electrochemistry	Colorado State Univ., Fort Collins, CO