# CHARACTERIZATION OF MATERIALS
Pr_pared by The Committee on
Characterization of Materials

MAB

# MATERIALS ADVISORY BOARD
## DIVISION OF ENGINEERING - NATIONAL RESEARCH COUNCIL

# CHARACTERIZATION OF MATERIALS

Prepared by

## THE COMMITTEE ON CHARACTERIZATION OF MATERIALS

## MATERIALS ADVISORY BOARD

Division of Engineering - National Research Council

as a service of the

National Academy of Sciences
and
National Academy of Engineering

to the

**Office of Defense Research and Engineering**

**Department of Defense**

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## NOTE

This report is made up of six separate reports or sections. Section I is the report of the Committee on Characterization of Materials; Section II, the report of the Committee's Panel on Composition; Section III, the report of the Panel on Structure; Section IV, Defects; Section V, Polycrystals; and Section VI, Polymers.

It should be noted that each of the above-mentioned reports is paginated separately with an individual table of contents for each report. Colored divider sheets separate the six sections.

# PREFACE

This report emphasizes the vital importance of materials characterization and defines it in self-sustaining fundamental terms, in order to establish a meaningful concept and one divorced from the empirical and often confusing and ambiguous variables which so frequently have found their way into various ideas about characterization. The nature of these ideas has depended on the sources; for example, the materials scientist thinking in atomic terms; the materials engineer invoking combinations of micro and macro descriptions and the procedural techniques by which they were obtained; the procurement and quality control engineer writing specifications which include micro, macro, procedural techniques, properties, "qualification" and simulated service tests, and anything else thought necessary to ensure repetitive procurement of a product which previously had been demonstrated as satisfactory for a given application. Conceivably, therefore, some may take issue with the definition of characterization in this report, preferring other definitions more directly dedicated to their own particular situations. However, it is for this very reason that it was necessary that "characterization" be defined in such a way that it contain the basic and adequate essentials for all groups; otherwise, it would be meaningless and futile.

At the same time it is recognized that, at the present state of the art, this report cannot solve the wide variety of production and procurement problems which exist; yet, it does provide a goal toward which scientists and engineers must conscientiously strive. The achievement of this goal is, in the final analysis, indispensable for a true science of materials – a science which would minimize the present costly empirical approaches. In some cases, this goal has been partially achieved already; in most cases,

it has not. Obviously, in the meantime, practicality will demand deviatior from this goal and supplementary empirical additions necessary for part lar applications (such as processing details) above and beyond the inform tion required by the basic definition. Such expediencies, however, should not be permitted to detract from aggressive programs designed to chara. terize materials fully and properly as discussed herein.

Finally, the Committee recognized that in a number of situations and materials communities an appreciation of the true significance of charac terization does indeed exist, but that the means for achieving it may well challenge the present state of the art. Some of the examples cited in this report illustrate this dilemma and the various panels' detailed reports, included as Sections II through VI, describe some actions and technical developments which must be undertaken to relieve it.

# SECTION I

# THE REPORT OF THE AD HOC COMMITTEE ON CHARACTERIZATION OF MATERIALS

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## ACKNOWLEDGMENTS

It is a great pleasure to express sincere gratitude and warmest thanks to the forty-seven members and liaison representatives who accepted the invitations to participate in this Materials Advisory Board study of the Characterization of Materials. The assignments were at best difficult and time-consuming and each of the men who participated did so willingly and unselfishly.

Many professional colleagues of the participants also served unofficially to expertly critique portions of the work. Their assistance and guidance are much appreciated.

Any recognition of the contributions to this study would not be complete without a grateful acknowledgment of the very valuable role of Mr. Donald G. Groves of the Materials Advisory Board professional staff, in the administrative and technical details of the work.

H. W. Leverenz

# CONTENTS

## SECTION I. THE REPORT OF THE COMMITTEE ON CHARACTERIZATION OF MATERIALS

## ABSTRACT

Characterization, the compositions and structures of materials, is the cornerstone of materials science. Meaningful interpretations of measurements of the properties of a material need identification of the significant compositional and structural features of that material.

Attempts to provide the superior materials that are critically needed in defense and industry are usually empirical and often wasteful of efforts and funds. That is so, chiefly because we do not yet have a fully developed science of materials that affords predictable and reliable results in devising and engineering new materials for specific tasks.

Because characterization has been used to mean many things to many people and is still loosely used, this Committee evolved the following working definition:*

> Characterization describes those features of the composition and structure (including defects) of a material that are significant for a particular preparation, study of properties, or use, and suffice for the reproduction of the material.

There is a widespread misconception about the function of descriptions of preparation and values of measured properties in the characterization of materials. True, every characterization method uses some property of atoms, ions or molecules, to determine the compositions, structures, and defects in materials. Nevertheless, it needs to be proved, always, that the property measurement reflects directly and unambiguously the relevant compositional or structural features of a material before it can be accepted as a valid characterization method. Most property measurements do not fall in this category and require, therefore, an independent means of characterizing

*See Preface of the Report

the structure or composition of the material. Clearly, much of solid-state research is concerned with the effort to understand properties, in terms of a particular composition and structure, but it cannot be emphasiz too strongly that a substantial fraction of this effort is of marginal value be cause it is carried on without a clear understanding of the true nature of, need for, characterization, and it fails to distinguish between property studies on characterized and uncharacterized materials. In short, the fundamental objectives of analytical chemistry and structural analysis hav not been heeded by much of the solid-state community and this has led to wasted effort and dollars.

Similarly, a description of method of preparation has often been taken to be necessary, or even sufficient, for the characterization of a material. Such a description is, however, only a substitute for the true characteriza tion of a material in terms that are independent of its past history. Clear it is not yet possible to escape the inclusion of method of preparation in th characterization of many practical engineering materials, because of the inadequacy of present characterization methods for the composition and structure of complex solids. Thus, for such materials and for some time to come, it will be useful to include the method of preparation - and perha selected properties - along with the partial description of composition and structure. At the same time it is plain that this sort of expedient "charac terization" is inadequate, and as we continue to use it we must strive for improved methods for composition and structure determination that will eventually make us independent of descriptions of past history.

It is not the purpose of this study to review characterization methods that are merely descriptions of the preparation method, or unexplained property measurements; these methods have not been good enough in the

past, and they will be still less adequate in the future. Our purpose, rather, is to emphasize the basic need for a major improvement in our abilities to characterize materials in terms of their compositions and structures.

One may ask: Why haven't scientists and engineers been more active and effective in characterizing materials ? They haven't, chiefly because (1) there is insufficient awareness of the meaning and importance of characterization, and (2) available means for characterization are inadequate. Within some scientific communities, such as that represented by physical metallurgists, an awareness of the need and its importance has been present to some degree. Thus, the second factor mentioned above has been dominant, especially in the light of the need to get things done.

An analysis of this present capability and the needs of materials science has been made and based on the findings and deliberations by this committee we recommend:

## A. GENERAL RECOMMENDATIONS

1. The term, characterization, should be used as defined herein.

2. A substantially larger fraction of the funds available for materials research should be allocated and used for characterization.

3. Government agencies concerned with materials work should take positive steps to ensure that characterization is given greater emphasis and the continuity of support that are required to advance materials science.

4. Greater awareness of the basic need for better characterization (of more and better materials) should be promoted by sponsors, faculty,

supervisors, and participants in work on materials research, development, and engineering.

5. Editors, referees, and policymakers of technical societies should insist on characterization of materials whose measured properties are sui mitted for publication.

6. A strong and sustained effort should be made to increase the effe: tiveness and status of those who work on characterizing materials.

7. Government agencies, such as the National Bureau of Standards, should be encouraged to exhibit stronger leadership in advancing characte: ization and its beneficial uses, especially in providing characterized reference materials.

8. Government agencies should encourage and support the growth of several strong centers of excellence in characterization of materials.

## B. A SUMMARY OF SOME OF THE COMMITTEE'S TECHNICAL RECOMMENDATIONS (FOR DETAILS REFER TO THE INDIVIDUAL PANEL REPORTS)

### 1. Composition

Greatly enhance capability for determination of major element stoichiometry. Improve analysis techniques for determination of O, N, C, S, B, and other anions. Improve valence state determinations. Develop methods for the location and analysis of inhomogeneities at the micron level. Develop survey techniques for the $\leq 1$ ppm range.

### 2. Structural

Fund greatly increased activity in optical methods (especially those utilizing coherent radiation) of structural characterization. Maximize the utility of x-ray diffraction by increasing the quality of the powde:

data file and extracting the maximum structural information from such data. Develop new high pressure and high temperature x-ray apparatus. The rapid utilization of the scanning electron microscope should be sponsored. Megavolt-range electron microscopes and pulsed-neutron spectroscopy likewise offer promise and deserve support.

### 3. Defects

Absolute point defect determination (concentration and structure) needs substantial support. Methods for surface defects need development.

### 4. Polycrystals

For characterizing polycrystalline systems, methods and theories of measuring internal stresses (micro and macro) are most important. Research on determining homogeneity and structure on the finest scale (< 1000Å) should be supported. Characterization of dislocation structures in heavily cold-worked and shock-hardened metals is needed. Quantitative metallography is needed for surface and transmission microscopy. Improve thinning techniques for transmission microscopy.

### 5. Polymers

In the polymer field, research should be supported in: rapid methods of molecular weight distribution; determination of supermolecular order in amorphous polymers, and in semicrystalline polymers; analysis of network structuration; methods to separate polyblends into their components; studies of nonpolymeric analogs (low molecular weight) of polymers; methods for characterization at the molecular level in presently intractable polymers.

Finally, there is an urgent need for immediate attention to all of these recommendations and action on as many as can be initiated in line with current requirements.

The Committee re-emphasizes that it has been increasingly concerned about the lack of attention and effort given to characterization and its essential role in building a stronger, more effective, materials capability in this country. Characterization action will likely continue to be procrastinated instead of given the immediate and sustained attention it deserves as the cornerstone of materials science. Accordingly, we urge that one or more nationally influential agencies appoint persons to ensure that the essence of this report continues to be publicized and acted on. Specifically, it is proposed that the National Research Council establish such a group to advocate an optimally proportioned effort on preparation, characterization, and measurement of properties to expedite the development of materials science.

# I. INTRODUCTION

## A. WHY THIS COMMITTEE WAS ESTABLISHED

In recent years there has been a substantial increase in government-funded research and development on materials. Since 1962, direct support of materials research and development by U.S. Government contract or grant has exceeded 200 million dollars a year. Of this sum, over 100 million dollars a year is classified as support of basic research on materials, according to a report of the Coordinating Committee on Materials Research and Development, of the Federal Council for Science and Technology, May 1964.

The big upswing in government support of materials research occurred without a proportionate and specific effort to provide materials that are "well characterized," or "precisely defined." With the substantial increase in number of scientists studying physical phenomena in materials, there has been expression of dissatisfaction with the inadequate degree of perfection of available materials, and with the paucity of quantitative information about their actual degree of perfection.

There has been, therefore, increasing concern that insufficient effort and money were being put into preparing and analyzing better materials. There has been concern, also, about the increasing number of scientifically frustrating studies of sensitive physical phenomena in presently available materials. Often it is not possible to identify the basic features of the material that determine the physical phenomena, and frequently it is not possible to reproduce the particular specimen of material on which the studies were made and reported in the literature. Such studies are clearly wasteful of effort and money in that they do not advance the understanding and quality of materials.

Here are some examples of the pre-Committee statements of concern.
about characterization:

1. "Progress in research in the science of solids is directly dependent
upon the ability of the researcher to reach conclusions about a particular
physical or chemical property of a solid, and this in turn is dependent upon
a precise knowledge of the characteristics of the specimen (single crystal
or polycrystalline) on which he is doing research. Confusion or limited
knowledge of the crystal's degree of perfection leads to inconclusive result
on its physical or chemical properties."

> [From-Coordinating Committee on Materials Research
> and Development Progress Report (to Federal Council
> for Science and Technology), 23 September 1963.]

2. "In the course of our study on ceramic processing, the members of
the MAB Ad Hoc Committee on Processing of Ceramic Materials have con
cluded, and will present as one of our major recommendations, that im-
proved methods of materials characterization are a basic need for reliabl
ceramic processing.

"Our Committee believes that the subject of materials characteriza
tion—i.e., phase and chemical composition, defect type and concentration,
structural order and disorder—is a serious limiting factor in specifying
or acquiring a very wide variety of materials for Department of Defense
use. Such characterization is essential not only in our field of ceramics,
but equally so in the single-crystal field, in metallurgy and metal-coating
systems, in any high-purity materials and some electronic components."

> [From-12 September 1963 Letter from the Chairman of the MAB
> Ad Hoc Committee on Processing of Ceramic Materials
> to the Executive Director, Materials Advisory Board.]

With the above situation in mind, this committee was brought into being

by a 14 April 1964 letter from the Assistant Director (Materials), Office of

the Director of Defense Research and Engineering, to the President of the

National Academy of Sciences.

## B. GENERAL SITUATION FACING THE COMMITTEE

At the time that this committee was established, in April 1964, the word characterization was being used increasingly, and with a wide variety of meaning.

At that time, for example, one division of the Department of Defense was supporting 33 active investigations in solid-state science, of which 24 were classified under the general heading:

### "Structural Characterization of Solids"

Here are some excerpts from the abstracts of objectives of five of these investigations which were actually listed as being part of "structural characterization."

1. "...study of the Fermi surface of aluminum, the Fermi surface and superconducting energy gap of mercury, and the construction of more elegant equipment for work below $1^{\circ}K$."

2. "...electron probe x-ray microanalysis will be applied to the determination of unknown binary and ternary phase diagrams, the measurement of diffusion constants in intrinsic and doped semiconductors, and studies of nonequilibrium processes in crystal growth."

3. "...use x-ray scattering to observe point defects...."

4. "...investigate the thermal vibrations in the vicinity of the surface of clean crystals of several metals."

5. "...preparation of organic semiconductors of the intermolecular-complex electron-transfer type, and for growth of materials for measurements of Fitzgerald audio-mechanical resonances in solids."

These five examples show that "characterization" was (and still is) being used to mean one or more of the following:

1. Preparation of a material.

2. Analysis (composition, structure, defects) of a material.

3. Measurement of properties of a material.

## II. WHAT IS CHARACTERIZATION ?

### A. PRELIMINARY DISCUSSION

The first task of this committee was to <u>define characterization</u>. In approaching that task, the Committee posed and considered the following questions:

1. What <u>do</u> different people mean when they use the word characteriza tion, as applied to materials ?

2. What <u>should</u> they mean by characterization ?

3. What are some examples of the benefits obtained by good character ization ?

4. What are some examples of the trouble caused by insufficient characterization ?

5. What are the greatest needs for characterization; e.g.,

(a) better techniques and instruments, or more and better use of existing techniques and instruments ?

(b) better characterization for improved preparation of materials, c for improved study of materials, or for improved use of materials ?

(c) more accurate and detailed characterization of materials in gen eral, or just certain features of certain materials ?

6. What are the significant features of a material that should be included in its characterization ?

7. Which materials and features merit the most emphasis for better characterization ?

The starting place for materials now, as in the past, is in nature, wher the elements and certain compounds occur only in impure and imperfect form. Purifiers (refiners) are prone to call their purified material <u>pure</u> (or <u>chemically pure,</u> or <u>ultrapure,</u> or <u>spectroscopically pure</u>), which mea

that they believe it appropriate to characterize the material as being considerably less contaminated than that provided by untidy nature, or perhaps less contaminated than the same material purified by other persons or processes. The purifier affixes a label stating that the material is some variety of pure, and sometimes includes an indication of the proportions of a very few major impurities. In terms of composition, that is the dubious starting point for materials work. The inadequacy of information about starting as well as final compositions is a basic flaw in the foundation of materials science: a flaw that becomes more intolerable as the magnitude of building on that foundation increases.

One striking example of the inadequacy of characterization is given by some electrical resistance ratios for top quality crystals of several purified elements (data from W. G. Pfann); the ratio of resistances at $273°K$ and $4.2°K$ being a measure of the purity and perfection of the material:

| | $R_{273}/R_{4.2}$ | |
|---|---|---|
| Element | 1961 | 1964 |
| Al | 7,000 | 26,000 |
| Cu | 1,700 | 8,000 |
| Mo | 3,300 | 12,000 |
| Ni | 900 | 2,200 |
| Re | 4,000 | 55,000 |
| W | 6,700 | 80,000 |

In both 1961 and 1964, aluminum was designated simply as Al, not even Al(1961) or Al(1964), and so these data remind us of the inadequacy and deceptiveness of simple chemical formulas. Simple formulas such as Al and $Al_2O_3$ represent idealized mental images. There are no real substances that have been rid of all contaminants, nor are there any perfect

crystals. Purification and crystallization carry part way from natural materials to ideal compounds and elements, but only part way.

The following sequence continues the transition from natural materials to semipurified ingredients which are used to prepare artificial materials having certain properties, and sometimes uses.

```
┌─────────┐     ┌─────────────┐     ┌──────────┐     ┌────────────┐     ┌────────┐
│  ores   │     │ ingredients │     │          │     │            │     │        │
│  and    │ ──▶ │    and      │ ──▶ │ MATERIAL │ ──▶ │ properties │ ──▶ │ use(s) │
│ refining│     │ preparation │     │          │     │            │     │        │
└─────────┘     └─────────────┘     └──────────┘     └────────────┘     └────────┘
                          correlate  ┌ ─ ─ ─ ─ ─ ┐  correlate
                                     │ with specific │
                                     │ composition,  │
                                     │ structure,    │
                                     │ and defects   │
                                     └ ─ ─ ─ ─ ─ ┘
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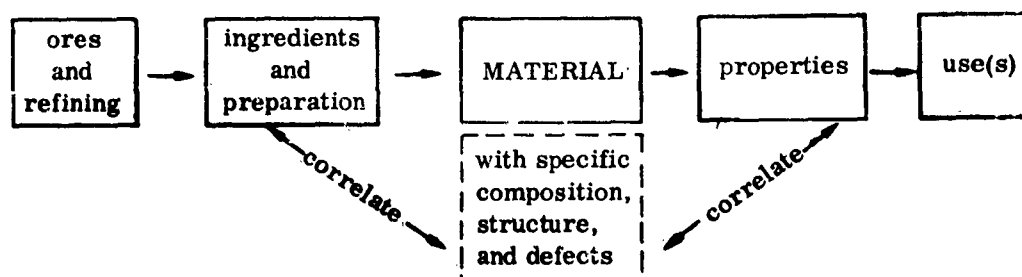
Here, we recognize that (1) the specific starting ingredients and preparati procedures determine the composition and structure (including defects) of prepared material, (2) the specific composition and structure (including defects) determine the properties of the material, and (3) the properties determine the usefulness of the material.

In the past, a person or small group of persons who made a new mater often carried through the entire preceding sequence of steps, sometimes omitting determination of material constitution and properties and letting the use tests provide crude feedback directly to stimulate or discourage a particular trend in choice of ingredients and preparative techniques. To-day, there are usually many different specialists who carry out the differ steps in separate locations and groups.

One consequence of this increasing specialization is that correlation of the results of separately located purifiers, preparers, analyzers, mea-surers, interpreters, appliers, fabricators, and eventual users has becom

inordinately fragmented and difficult. All too often the situation is that synthesizers make new materials, and hope someone will discover their merit; analysts use and devise techniques and instruments that provide increasing kinds and amounts of information about composition and structure, and hope that synthesizers, property investigators, and users of materials will find value in the analytical data; property investigators make measurements and attempt to interpret them (wishing there were more useful analytical data for interpretive correlation, and that better or other materials were available) and hope that others will recognize and use their published results; and users are impatient because practical progress is so unpredictable, and sometimes unrepeatable.

While it is true that many useful materials have been, and will be, developed by empirical making and testing, there are still many uses, critical to men and nations, that lack satisfactory materials despite decades of expensive making and testing. We need to build a science of materials in order to be able to produce more satisfactory materials with less expenditure of time and money, and with less hazard in use. The chief goal of materials research is to build that science of materials; to forge a chain of quantitative understanding that links preparative ingredients and methods with knowledge of the significant features of the resultant material; and links those significant features with the properties they occasion, and with the uses they permit. At present, the weakest - frequently, the missing - link in that chain is knowledge of the significant features of the material, which we identify as characterization of the material. It is characterization that is lacking, and is needed most of all to construct a science of materials.

## B. DEFINITION OF CHARACTERIZATION

The Committee evolved the following definition of characterization:

CHARACTERIZATION DESCRIBES THOSE FEATURES OF THE COMPOSITION AND STRUCTURE (INCLUDING DEFECTS) OF A MATERIAL THAT ARE SIGNIFICANT FOR A PARTICULAR PREPARATION, STUDY OF PROPERTIES, OR USE, AND SUFFICE FOR REPRODUCTION OF THE MATERIAL.

Characterization, in other words, is a useful quantitative description of the constitution of a material. Basically, characterization is a descrip tion of the kinds and locations of the constituent atoms and ions, to the extent that such a description is needed for correlation with properties, with performance in use, and for reproducing and improving the materia In practice, coarser features of structure, such as sizes, shapes, and distributions of grains and pores are often used as part of the character ization of certain materials, especially in ceramics and metallurgy. On an atomic scale, these gross descriptions represent dimensions and distributions of regular assemblages of atoms (grains, crystallites), and of absences of large numbers of atoms (pores, voids).

In the definition, attention is focused on the significant features of cor position and structure (including defects that are important deviations fr perfection) as the items that should be included in the characterization o material.

Pictorially, characterization includes significant information about th three key words, composition, structure, and defects, shown within the dotted rectangle of the following sequence:

```
┌──────────┐   ┌──────────────┐   ┌──────────────┐   ┌──────────────┐   ┌──────┐
│   Ores   │   │  Ingredients │   │              │   │              │   │      │
│   and    │──▶│     and      │──▶│   MATERIAL   │──▶│  Properties  │──▶│ Uses │
│ Refining │   │ Preparation  │   │              │   │              │   │      │
└──────────┘   └──────────────┘   └──────────────┘   └──────────────┘   └──────┘
```

Significant features of: ⎰ Composition / Structure / Defects ⎱ = <u>Characterization</u>
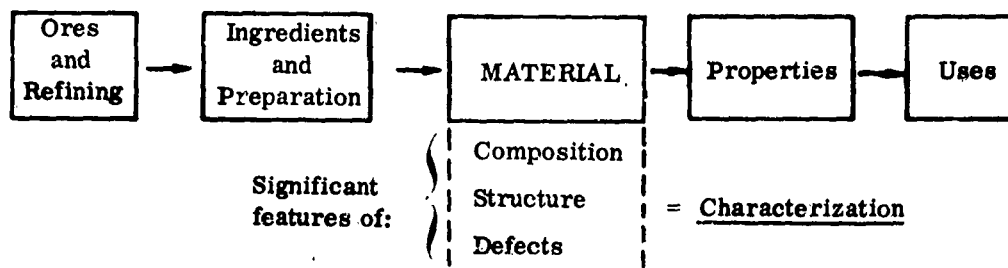
<u>Preparation is not necessarily included in the ultimate characterization,</u> <u>because preparation is not a quality of the final material.</u> Therefore, we should work toward eliminating the need to describe preparation, although its recording may be necessary in early and intermediate stages of work on a material. <u>Properties are not included in characterization, because</u> <u>properties are determined by composition and structure,</u> and so we should work to correlate composition and structure with properties until eventually the characterization suffices. (In this connection, the more that measurements of properties are used to analyze for specific features of composition and structure, the more correlation there will be between composition and structure and properties.)

There is a widespread misconception about the use of property measurements as a means of characterizing materials. True, every characterization method uses some property of the atoms; e.g., mass (mass spectrographic chemical analysis), characteristic nuclear decay (activation analysis), and x-ray scattering factor (x-ray analysis). Nevertheless, it needs to be proved, always, that the property measurement reflects <u>directly</u> <u>and unambiguously the relevant compositional or structural features of a</u> material before it can be accepted as a valid characterization method. <u>Most property measurements do not fall in this category and require,</u> <u>therefore, an independent means of characterizing the structure or</u>

composition of the material. Much of solid-state research is concerned with the effort to understand properties in terms of a particular composition and structure, but it cannot be emphasized too strongly that a substantial fraction of this effort is of marginal value because it is carried on without a clear understanding of the true nature of, and need for, characterization, and it fails to distinguish between property studies on characterized and uncharacterized materials. In short, the fundamental objectives of analytical chemistry and structural analysis have been misunderstood by much of the solid-state community, and this has led to wasted effort and dollars.

Similarly, a description of method of preparation has often been taken to be necessary, or even sufficient, for the characterization of a material. Such a description is, however, only a substitute for the true characterization of a material in terms that are independent of its past history. Clearly it is not yet possible to escape the inclusion of method of preparation in the characterization of many practical engineering materials, because of the inadequacy of present characterization methods for the composition and structure of complex solids. Thus, for such materials, and for some time to come, it will be useful to include the method of preparation - and perhaps selected properties - along with the partial description of composition and structure. At the same time it is plain that this sort of expedient "characterization" is inadequate, and as we continue to use it we must strive for improved methods for composition and structure determination that will eventually make us independent of descriptions of past history.

It is not the purpose of this study to review characterization methods that are merely descriptions of the preparation method, or unexplained property measurements; these methods have not been good enough in the

past, and they will be still less adequate in the future. Our purpose, rather, is to emphasize the basic need for a major improvement in our abilities to characterize materials in terms of their compositions and structures.

## III. EXAMPLES OF NEEDS AND USES OF CHARACTERIZATION

Some of the losses to science and technology, when there is inadequa
characterization, are indicated by these few (of many) DOD examples th
were furnished by liaison representatives to the Committee. (More ex-
amples are given in Appendix A of the Report of the Panel on Defects.)

### A. BERYLLIUM FOR AIRCRAFT & AEROSPACE STRUCTURES

The potential advantages of beryllium as an exceptionally low-densit
structural material have not yet been obtained. Present-day "purified"
beryllium is still too brittle because of "impurities." Part of the impur
problem is the concentration of carbon, nitrogen, and oxygen. Here are
quotations from MAB reports on the beryllium problem:

"It is recommended that research be undertaken to reduce the prese
obtained concentrations of C, N, and O in beryllium and to evaluate the
mechanical properties of this further refined material. This research,
however, must be coupled to the development of analytical techniques s
able for the accurate determination of the C, N, and O impurity levels."
(MAB-211-M, Oct. 1965)

"Major problem areas in the analysis of beryllium for impurities lie
the areas of oxygen determination (all ranges), carbon determination in
<100ppm range, and nitrogen in the <10ppm range."

"Of special importance is the determination of oxygen in low oxygen
beryllium. In this case the question of surface oxygen becomes especia
important." (MAB-203-M, July 1965)

### B. CATASTROPHIC FAILURE OF 175-MM GUN TUBE

Within the past year, the U.S. Army has experienced a catastrophic
failure of a mobile, large-bore, artillery gun tube. Extensive investigat
of the equipment and conditions leading to the incident revealed that sur
face damage inside the gun tube probably led to drastically reduced ope
ational life. It is postulated that some low atomic weight elements (carl

oxygen, and nitrogen) may have been absorbed interstitially from the atmosphere and the gases generated by shellfire, and that these contaminants coupled with mechanical stresses to produce early surface damage that led to premature failure.

Here is an example for the need of nondestructively characterizing interior surfaces and correlating changes in composition and structure with the occurrence of failure in a material used in an engineering application.

## C. FAILURE OF CRYSTAL DETECTORS IN RADAR EQUIPMENT

Diode crystal detectors were used in the first-stage pickup of WWII radars for frequencies above the range of available vacuum tubes. Initially, these crystal detectors worked very well, but as time progressed some failed. Then, it was found that one of five replacement crystals also failed. The crystals that failed behaved as if they were short-circuiting, but examination of the crystals did not disclose any visible defects. The problem was serious, causing undue delays in maintenance, adding to downtime, and creating a logistics-of-replacement problem which statistically could have hampered our combat effort. Postwar work indicated that failure was the result of whisker growth on the surfaces of the crystals that failed.

Under the conditions (including environmental) which existed, characterization and correlation were needed, but unavailable, to identify and control the compositional and structural features that caused whisker growth and subsequent failure.

## D. THIN-FILM MATERIALS FOR INFRARED DETECTORS AND IMAGING

Certain materials, such as lead sulfide, give substantial photoconductive response under infrared radiation, but only when they are in thin-film form. Use of such thin-film materials for infrared and optical pickup

devices is hindered by inadequate characterization for control and impre
ment of performance. Impurities (e.g., O in PbS), deviations from stoi-
chiometry and polycrystallinity are suspected to affect performance, but
progress and understanding require much better characterization.

Here are some examples of inadequate characterization in the techni;
literature:

E. In the book Dielectric Materials and Applications, J. Wiley & Sons
(1954), pp. 328-329, data are given on measured dielectric properties of
a number of organic materials. Many of these materials are listed as
containing additional constituents identified only very loosely, for exam;

    3.5% misc. (Bakelite)
    5%  filler (Goodrich)
    5%  plasticizer
    39% Marbon B (Am. Phenolic)

These are certainly not well-characterized materials, and do not me

publishing of precisely measured physical properties.

F. In Physical Review, 136, 5 October 1964, pp. A141-A144, measureme
are reported on the "thermoluminescence of x-ray and ultraviolet excite
CsBr crystals." It is stated that "single crystals from Semi-Elements,
Harshaw and Isomet were studied." No analytical data are given. The
different crystals gave different results, leading to the statement in the
conclusion: "The thermal luminescence resulting from ultraviolet irrad
tion is not well understood. If it be due to impurities, the fortuitous agr
ment with glow peaks in x-ray excited crystals where a definite correls
with F-band absorption exists would be hard to explain. Additional evid
for an association of glow peaks with color centers occurs in additively
colored CsBr crystals. Very low levels of ultraviolet radiation will pro
duce thermoluminescence in these crystals, but not in uncolored crysta.
Presumably the color centers are responsible for this difference. Cert
much more work needs to be done before a clear answer is available."

This example is given not because it is unusual, but because it is representative of the rising tide of papers reporting measurements of properties that are caused by unidentified defects. In general, those papers signify that materials science is not yet here. Measurements-of-properties science is here, but measured materials must be characterized to qualify a paper as reporting materials science.

G. In a recent spectroscopic study of a crystal of a transition metal compound (Journal of Chemical Physics, Vol. 35, p. 2236, 1962), results were reported for "yellow green $CrF_3$" which were quite surprising on theoretical grounds. Some months later (Journal of Chemical Physics, Vol. 37, p. 193, 1962) an erratum was published indicating that the sample previously reported was in fact "yellow green $NiF_2$" thus removing the difficulty in the interpretation of the results in the original paper.

In this case it was not that the means for characterization were unavailable but that, as all too frequently happens, the material simply was not characterized before its properties were reported.

The next example of need for characterization is a current one that typifies the kind of problem that occurs at the interface between (1) purifiers (suppliers) of ingredients, and (2) preparers of materials.

H. A luminescent material whose host crystal is prepared from a rare-earth oxide, here designated as $R_2O_3$, was found to be useful except for excessive low-level phosphorescence. Means to decrease the phosphorescence were sought. First, variations of the preparative parameters (mixing, crystallization temperature and time, cooling rate, etc.) were tried and found to have negligible effect on the phosphorescence.

Next, the quality of the starting ingredient $R_2O_3$ was investigated. The grade of $R_2O_3$ being used was labelled 99.99% purity, but this designation concerns only the purity relative to foreign rare earths; that is, there is only 0.01% total of other rare earths, although non-rare earths might exceed 0.01%. There are two other grades of $R_2O_3$, labelled 99.997% and 99.999%. These are made by recycling the 99.99% once more through the resin towers for 99.997% and twice more for 99.999%. These latter two numerical designations are fictitious, however, because the limit of the supplier's analytical technique is only 99.99%. The higher values are calculated from theoretical expectations of further purification, and the price of the 99.999% $R_2O_3$ is ten times higher than the 99.99% $R_2O_3$.

The first lot of 99.997% $R_2O_3$ from a major supplier was made into a phosphor in the laboratory and found to give a 10-to-1 decrease in phosphc rescence—just what was needed for device use. This result was found to be reproducible in larger pilot-plant preparations using batches from the same lot of 99.997% $R_2O_3$. It thus appeared that the problem was solved, and further lots of both 99.997% and 99.999% $R_2O_3$ were ordered. Of five lots from the first major supplier, and four lots from another supplier, none has even approached the performance obtained with the first 99.997% lot.

All the lots, when analyzed spectrographically showed little or no differences. In most cases, practically no rare earth contaminant could be found, not because traces were completely absent, but because the quantities of contaminants were below the limits of detection of the emission spectrograph.

Next, the mass spectrograph was used to analyze the good and the bad lots of $R_2O_3$. Out of the overwealth of information about many trace contaminants, no significant correlation could be found between (a) the presence, absence, or relative proportions of particular contaminants; and (b) the ability to make a low-phosphorescence phosphor.

At the time of drafting this report, the situation was as follows:

1. One, and only one, lot of $R_2O_3$ gave satisfactory results.

2. The material preparers do not know why that lot is superior and, therefore, cannot ask the purifier what to remove or add to reproduce that lot.

This is a typical example of the wasteful consumption of effort and money that can occur when the means for characterizing and controlling the starting ingredients are inadequate.

On the other hand, there are many examples of advantageous uses of characterization. Here are a few:

- **LUMINESCENT MATERIALS FOR RADAR AND TELEVISION KINESCOPES**

Highly purified zinc sulfide and cadmium sulfide are required to prepare cathodoluminescent phosphors for radar and television kinescopes. A successful purification technique was developed during over fifteen man-years of effort by an electronics company just before WWII. Since the process had to remove copper, for example, to below the part-per-billion range, existing analytical techniques were totally inadequate for compositional characterization. Nonetheless, the required degree of purification was proven to have been achieved by making a phosphor from the purified ZnS to which 1 ppb of Cu had been added. The visually detectable change in luminescence emission from a light blue with short persistence to a green with long persistence was used as (a) analytical evidence that the purified ZnS contained less than 1 ppb Cu (at that time there were no analytic means for detecting Cu below 1 ppm), and (b) correlation between composition and luminescence properties. Later, using x-ray diffraction, it was shown that hexagonal ZnS, crystallized at temperatures above $1000°C$, gave superior blue emission with silver activator, and gave superior long-persistent green emission with copper activator, superior, that is, to cubic ZnS, crystallized below $1000°C$. There was, then, a correlation between host-crystal structure and luminescence properties. This background of attainment and understanding was put to use in the crash program that provided the persistent cascade phosphor screen for PPI radar kinescopes in the early part of WWII. After the war, the same basic techniques and information were used to produce hundreds of tons of phosphors for both black-and-white and color television kinescopes.

This example from the past is cited to encourage more resourceful effort to produce purer and better characterized materials, even when available analytical facilities appear to be inadequate. Such a situation, which occurs frequently, presents a challenging opportunity to make more ingenious use of that which is available and that which can be contrived. Progress toward materials science requires that more of these challenges be accepted by competent researchers.

- ## SEMICONDUCTOR MATERIALS FOR TRANSISTORS, DIODES, AND INTEGRATED CIRCUITS

It is widely recognized that missile guidance equipment, computers, radios, and other electronic apparatus and systems have been revolutic. lzed by the advent of the transistor. Only a few specialists, however, recognize the vast amount of persistent and expensive effort that was re quired to produce germanium and silicon with the exceptionally high deg of purity, structural order, characterization, and correlation with send conduction properties that was needed to bring about that revolution on practical scale.

Here, as in the previous examples of ZnS, sensitive physical propert notably lifetime and mobility of electrons and holes - were used to help characterize purified semiconductor crystals in which traces of certai. foreign elements were deliberately incorporated. The measurements o lifetime and mobility of early specimens of Ge and Si did not provide numbers that were characteristic of Ge and Si, because unknown (un- characterized) defects determined those numbers. As the techniques fo reducing and identifying pernicious defects advanced, the measured val of lifetime and mobility changed; the latter approached the values chara istic of intrinsic Ge and Si, and lifetime reached the leve' determined t impurities concentration of the order of $10^{-10}$ with these improved mat. rials. Then, useful defects could be incorporated and distributed to prov electronic performance that was unattainable with the earlier specimen; of these elemental semiconductors.

A striking example of the limitations imposed by poor characterizati methods was encountered in the early development of Si as a transistor material. It was widely recognized that Si had inherent advantages over Ge for many purposes, but the best available material showed poor life- times and unexplained changes in the resistivity when the material was heated. After several years of extensive effort to identify the source of difficulty, infrared absorption finally revealed that concentrations of ox in the parts per million range were being incorporated into the Si as th result of a reaction with the fused quartz crucibles used to contain molt Si in crystal growth. The oxygen was responsible for the poor quality o the material. This finding pointed the way to the use of methods for cry growth which eliminated the oxygen problem and soon thereafter Si tran sistors became a reality.

- ## ZIRCONIUM FOR CLADDING OF FUEL ELEMENTS IN NUCLEAR REACTORS

One of the vital materials that was required to make practical fuel e ments for power producing nuclear reactors was a high melting metalli

cladding. Pure zirconium has a suitable melting point and an exceedingly small cross-section for neutron absorption. It was known from earlier characterization work, however, that all of the zirconium metal commercially available was contaminated with about 2% hafnium. This material has a large cross-section for neutron absorption (105 barns) which would adversely affect the neutron economy of the reactor, and give rise to radioactive isotopes which would make the reactor difficult to work on during shutdown.

Armed with the knowledge of the need to eliminate hafnium, researchers evolved means to produce zirconium containing only 200 ppm of hafnium, thereby providing the best material for an outstanding cladding.

This example, as well as the two previous ones, points up the danger of attempting to "characterize" a specimen of material in terms of values of measured physical properties. If the composition, structure, and influential defects are not known (characterized), then the measured values resemble those that would be obtained by electrical measurements on a "black box" containing unknown kinds, numbers, and hookups of resistors, capacitors, transformers, transistors, etc. Different specimens of a given material, like different "black boxes," can look deceptively alike (and even have some like physical properties), but have significant internal differences.

## • PHOTOEMITTERS FOR OPTICAL DETECTION AND IMAGING

During research on new photoemitters, an attempt was made to co-evaporate lithium and antimony to determine what photoemission the co-deposited combination would have. The measured photoemission was exceptionally good, but then no sensible correlation could be found with the relative amounts of the separate elements put in the evaporators to make a series of deposits. Resourceful analysis of both composition and structure of the deposited films showed that lithium was not being deposited at all. Instead, the excellent photoemission was found to be due to sodium and potassium impurities that had been distilled out of the lithium. Further work showed that the best photoemitter containing sodium, potassium, and antimony was $Na_2KSb$, which is the precursor of the outstanding tri-alkali photocathode.

This example demonstrates the danger of attempting to characterize a material by extrapolation from the starting ingredients. Verification the completed material is needed for assurance.

The foregoing four examples suffice to portray the very substantial tical and scientific progress that can be made when characterization is achieved and used. It is worth noting that each of these successful uses of characterization occurred when the material was being purified, prepared, analyzed, and measured for a specific use. The specific performance requirements for a given use help to focus attention on significa features of composition, structure, and defects. They help also to estar lish a common purpose for the different persons, from various discipli who are involved in trying to meet the performance requirements.

## IV. COMMITTEE GOALS AND ACTIONS

A prime objective of the Committee was to present findings and recommendations that have operational significance. That is too audacious if it is interpreted as having operational significance for everyone immediately, but we hope to have provided a working definition, a viable philosophy, and guidelines for progressive action.

A keystone of the Committee's philosophy is to keep the concept of perfection in view, and to describe actual materials in terms of significant deviations from the ideal. In terms of action, much stronger effort is needed to minimize deleterious imperfections in materials, and to determine (analyze) their significant imperfections.

We know that complete perfection is unattainable, but we believe that it is in that direction that most fundamental progress will be made. As we advance toward perfection, it will become more meaningful to incorporate known imperfections and ascertain their effects. The effects produced by such controlled imperfections will provide the much-needed unambiguous correlations that are usually not attainable with present-day materials which contain a mélange of imperfections that influence properties indeterminately.

Many of our most useful materials have deliberately-introduced impurities and imperfections that are essential and function best in the absence of other defects. As we advance in our ability to prepare (and analyze) more perfect ingredients and host crystals, we increase the probability of providing superior new and useful materials with controllable kinds, proportions, and locations of beneficial defects.

In keeping with the philosophy of keeping the concept of perfection in view, we recommend that composition and structure be described in terms of:

(a) perfection; e.g., face-centered-cubic-Si, or body-centered-cubic-Fe, with specified dimensions, and

(b) significant deviations from perfection; e.g., kinds, proportions, and distributions of impurities, point defects, line defects, and so forth, that are of consequence in terms of the definition.

Another objective of the Committee was to present quanitative information about the current status of characterization. Accordingly, the field was subdivided for more detailed study by panels of specialists, including liaison representatives from the Committee, government agencies, and other MAB Committees. Separate panels were established for polycrysts and polymers, because they have unique problems, and so the following five panels were established and panel chairmen selected in mid-1965:

| Panel | Chairman |
|---|---|
| 1. Composition | M. S. Sadler |
| 2. Structure | R. Roy |
| 3. Defects | A. C. Beer |
| 4. Polycrystals | A. E. Gorum |
| 5. Polymers | R. F. Boyer |

In meetings of the Committee with the Panel Chairmen, several representative materials were chosen as "cross-tie vehicles" for the studies Panels 1 through 4. Among others, the common-denominator materials included Cu, Ti, Cr, Fe, Si, KCl, ZnS, $Al_2O_3$, $MnFe_2O_4$, and anthracene The Panels were urged, where possible, to give documented numerical data on our present abilities to prepare and characterize these material and others, and to make recommendations based on important discrepan cies between our present abilities and our needs, both practical and scientific. This formidable task was accomplished in about a year of

extra work by the many who participated in the Panel efforts. The reports and recommendations of the five panels are attached to the report of this committee.

The Panel reports give detailed quantitative information about our present capability to characterize materials. They provide reference data that are useful now, and provide benchmark data on preparative and analytical capabilities that must be improved in the future.

The Committee recommends that the "state of the art" presented in the Panel reports be studied and used as stepping stones to improvement. Substantial improvement will come when more people who should be concerned respond to the challenge of improving characterization of materials — keeping in mind that <u>characterization is more basic than properties</u>, because the composition, structure, and defects of a material determine its properties.

A further objective of the Committee was to call attention to the <u>need for bringing about a major change of attitude toward characterization of materials</u>.

Sponsors of materials research and development, faculty advisors, supervisors, researchers, and materials users have the prime responsibility for insisting on characterization and correlation. At the output end of this field, editors and referees of papers have the responsibility for insisting on characterization of the specimens of materials whose properties are described in the papers that they review and approve for publication.

With responsible leadership, the present rather careless general attitude toward characterization should change to an attitude of genuine concern about improving characterization and its beneficial uses in science

and engineering. When such a conscientious attitude becomes prevalent then the preparers, analyzers, property investigators, and users of materials will have the support and mutual concern that are required t. sustain effective cooperative effort on characterization. Without such support, concern, and effort, materials science will continue overlong ' exist more in name than in fact, because in its fundamentals of purific; preparation, and characterization it is now too often an art.

Special attention is called to the mounting danger of glutting our tec. cal literature with papers on inadequately characterized specimens of materials.

Consider, for example, the substantial volume of literature that the is on the behavior of electrons, and other particles, moving in a vacuu. where the mean free path of the electron is much longer than the distar between electrodes. Here is one well-characterized environment in whi study of electron behavior has provided unambiguous results of scienti and practical consequence.

Consider, next, the many thousands of different environments in whi electrons would find themselves, and behave differently, in ideal perfec crystals. Then consider the appallingly larger number of environments in which electrons, and other particles, find themselves in real imperf crystals, with their enormous varieties of kinds, proportions, and distr butions of (a) impurity defects, and (b) structural defects, both of which influence electrical, optical, and mechanical behavior.

This statement of the situation is offered as a reminder to scientist; editors that they should resist the publication of data and speculations ( inadequately characterized materials.

# V. CONCLUSION AND RECOMMENDATIONS

There is an obvious need for better materials and better characterization of materials. They are needed to advance the present art of materials toward the goal of becoming a true science of materials. They are needed, also, to provide superior practical materials for present and future uses that require much higher performance and reliability than present materials can provide. They are especially needed to increase the cost-effectiveness of materials research and development.

In terms of action, there is the question "Which particular materials should be chosen for the investment of effort and money that are required to attain a satisfactory degree of perfection (or controlled imperfection) and characterization ?" It is not now feasible to tackle all elements and compounds simultaneously, because there are over a million, and each has its idiosyncracies of chemical behavior and growth that require long-term individual attention.

As in the past, a small minority of industrial research laboratories may be expected to prepare and characterize certain materials that show exceptional promise for identified commercial uses. And, as in the past, this small segment of industry may be expected to provide the continuity of effort and financial support that are required to purify, prepare, and characterize the few such potentially useful materials.

But how is the U.S. Government to obtain the sustained, dedicated effort required to prepare and characterize the better materials that are needed for defense, and for the various large-scale projects that are funded by government agencies ? In principle, as in industry, important end-uses could be identified, materials requirements specified, and inter-disciplinary technical teams organized, funded, and supervised to provide

a definite goal, incentives for success, good working communications between team members, and capable leadership. In practice, this worka operating procedure is often vitiated by the disruptive influences of shoi term (e.g., one-year) funding of projects, and at times in some governm agencies by short-term (e.g., three-year) turnover of personnel respons for budgets, funding, and monitoring of projects. Also, there is often a fragmentation of the over-all project, geographically and organizatior..l that lessens good working communications and teamwork. A satisfactor, answer to the initial question requires changes in the traditional behavic patterns of the people responsible for and involved in government-spons research and development on materials.

And how are researchers in universities, where they are traditional! uncommitted to practical objectives, and to the objectives of others, to get the very large number of different, near-perfect, well-characiriec materials that they wish to have for study as individuals rather than as teams ? In principle, materials researchers in universities would solve the really basic problems of purification, preparation, and characterizat of each material before proceeding to measurements of properties and t interpretation. In practice, purification, preparation, and analysis for characterization are deemed to be socially inferior activities on campus This negative attitude may be occasioned, in part, by the short-term turnover of graduate students who get advanced degrees for publishing n measurements and interpretations. On the other hand, few are involved creating more-perfect, well-characterized materials which others can measure and report to have properties reliably correlatable with the significant features identified in characterization. This goal is obviously desired, and is certainly needed to achieve materials science in general

The first problems to be solved, however, are again people problems —
problems that exist because of attitudes and traditions. There are signs
that a few dedicated materials researchers in a few schools are taking
constructive action to solve these people problems, and it is to be hoped
that succeeding generations of graduate students will emerge with a posi-
tive view of characterization, and some experience in achieving and using it.

A. GENERAL RECOMMENDATIONS (FROM THE AD HOC COMMITTEE)

1. The term, "Characterization" should be used as here defined —
Characterization describes those features of the composition and structure
(including defects) of a material that are significant for a particular prepara-
tion, study of properties, or use, and suffice for reproduction of the
material.

2. A substantially larger fraction of the funds available for materials
research should be allocated and used for characterization, as here de-
fined. Also, increased funding should be provided for the specific recom-
mendations given in Section B.

3. Government agencies concerned with materials work should take
positive steps to ensure that characterization is given greater emphasis
and continuity of support, particularly in research that is expected to ad-
vance materials science.

4. Greater awareness of the basic need for better characterization (of
more and better materials) should be promoted by sponsors, faculty,
supervisors, and participants in work on materials research, development,
and engineering. Education is needed to improve the climate for
characterization.

5. Editors, referees, and policymakers of technical societies should
insist on characterization of materials whose measured properties are

submitted for publication — and resist attempts to characterize with ambig ... s terms such as 'pure,' 'ultrapure,' '99.9999%,' and 'defect-free.' Survey articles on characterization and correlation should be published periodically to highlight the progress that has been made beyo: the present state of affairs (see the Panel Reports).

6. A strong and sustained effort should be made to increase the effec-tiveness and status of those who work on characterizing materials; e.g., by more intimate involvement and co-authorship with those who prep... and measure materials, and by ensuring that funding and facilities for characterization are included as primary items in budgeting for a ma-terials project. (Separate budgeting and accounting are often necessary to ensure that the necessary support is not only provided but used for characterization.)

7. Government agencies such as the National Bureau of Standards shc be encouraged to exhibit stronger leadership in advancing characterizati and its beneficial uses, including standardizing designations for characte ized materials, and increasing the production and distribution of well-characterized reference materials.

8. Government agencies should encourage and support the growth of several centers of excellence in characterization of materials, preferab' in centers where there is strength and coordinated effort in preparation of materials as well as in measurements of properties. The centers would be expected to make major advances in (1) the techniques, capa-bilities, and applications of characterization, (2) the growth of more effective materials science, based on quantitative characterizations cor-related with preparations and properties, and (3) the education of sci-entists skilled in characterizing materials, and in using the basic inforn tion obtained by characterization.

9. The Materials Advisory Board is urged to establish, at a later date, a new Ad Hoc Committee or Committees on Characterization of Materials designed to carry out four major missions: (1) Determine any change in the position of characterization from the time of this report, (2) Survey and recommendations on the then state of characterization relative to major needs, (3) Special survey and recommendations on characterization of the surfaces of materials, and (4) The characterization of powders.

10. Finally, and in addition to the foregoing, the Committee strongly urges that one or more national agencies appoint persons to ensure that the messages contained in this report continue to be publicized and appropriately implemented. Moreover, it is proposed that the National Research Council - National Academy of Sciences - National Academy of Engineering establish a special Board or Committee designed to advocate and advance those appropriate scientific efforts on materials preparation, characterization, and measurement of properties in order to expedite the needed development of materials science.

## B. SPECIFIC TECHNICAL RECOMMENDATIONS* (FROM THE PANELS)

Compositional Characterization

1. Development of new and improved techniques for the determination of stoichiometry (with respect to detectability, costs, and convenience) beyond the $\pm 0.1\%$ level.

2. Improved techniques for determination of O, N, C, B, S, halogens.

3. Better techniques for the determination of the distribution (and

*More detailed recommendations and the justification for these recommendations may be found in the individual Panel Reports.

kind and concentration) of impurities with spatial resolution at the micro level and below; the assessment of sample homogeneity by nondestructiv techniques.

4. Improved techniques for determination of location and distribution impurities — both on a micro and macro scale.

5. New methods (especially those that are nondestructive) for the determination of the valence state and the ratio of valence states of variab valence ions in a solid.

6. Improved survey techniques for $\leq 1$ ppm determination.

## Structural Characterization

7. Research in optical methods of structural characterization can prove especially rewarding because of the radical advantages introduce by the new coherent light sources. Both surface and scattering studies should be supported.

8. Among the x-ray methods, the following areas call for increased research:

(a) Increase number and quality of ASTM powder data file.

(b) Optimize and maximize structural information derivable from powder data.

(c) Decreased limitations of single crystal accuracy.

(d) Develop precise high and low temperature and high pressure apparatus.

9. In electron microscopy and diffraction, support should be extende to:

(a) Scanning electron microscopy exploitation.

(b) Improvement of instrumentation and techniques especially for thinning of samples for transmission.

(c) Purchase of very high voltage ($>1$ mev) electron microscopes

10. Pulsed neutron time-of-flight spectrometry is a recent breakthrough and its application to diffraction and high pressure studies promises high rewards to increased support.

11. Some relatively large coherent efforts in developing new methods and new approaches to determining the structure of noncrystalline solids are urgently needed.

Defects Characterization

The following general areas include various specific subjects for increased research support, details of which are given in the Panel on Defects Report herein:

12. Improved techniques (both on a micro and macro scale and including in situ methods) for determination of kind, concentration, and distribution of defects.

13. Better information on the equilibrium and kinetic behavior of defects, including their formation and annihilation.

14. Better understanding of the interrelationships between measured physical phenomena and defects, as well as among various defects.

15. Improved techniques for characterizing surfaces.

Characterization of Polycrystalline Materials

16. The development of methods to determine the magnitude, nature, and distribution of internal stresses (microscopic and macroscopic) requires major support.

17. Characterization of dislocation structures in heavily cold-worked and shock-hardened metals.

18. More extensive research on quantitative metallography (stereology) for both surface and transmission microscopy.

19. Improvement of thinning techniques to broaden use of transmission microscopy.

20. Improved techniques for determination of structures, including defect nature, in the 10 - 100Å region; determination of impurities in small regions < 1000Å.

## Polymer Characterization

21. More exact and facile analysis of the chemical identities, location and spatial configurations of the units which make up polymer chain structures.

22. Rapid, inexpensive methods of molecular weight distribution analy

23. More research on supermolecular order characterization on "amo phous polymers."

24. Needed further detailed characterization of the supermolecular st of aggregation in semicrystalline polymers, especially in structures achieved by the crystallization of polymers from their molten states.

25. Needed methods of analysis and theories of structuration of actual polymeric networks.

26. Special experimental approaches needed to be devised for charact ization at the molecular level in intractable polymers.

27. New, rapid methods needed to separate polyblends into their const uent molecular species and to analyze these species.

28. Increased research on the characterization and study of low molec lar weight compounds which can serve as nonpolymeric analogs of polyn

# SECTION II

# THE REPORT OF THE PANEL ON COMPOSITION

NATIONAL ACADEMY OF SCIENCES -
NATIONAL ACADEMY OF ENGINEERING
DIVISION OF ENGINEERING - NATIONAL RESEARCH COUNCIL
MATERIALS ADVISORY BOARD
AD HOC COMMITTEE ON CHARACTERIZATION OF MATERIALS

PANEL ON COMPOSITION

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# FOREWORD

A survey has been made of analytical techniques for characterization of materials with respect to composition with the objectives of uncovering limitations in our present capability and of defining areas where improvements are needed. As a result of this study, it is recommended that encouragement and support be given to development of new and improved techniques for:

1. Determination of stoichiometry of major and minor phases.
2. Determination of oxygen, nitrogen, carbon, boron, sulfur, the halides, and other anions.
3. Determination of sample homogeneity.
4. Determination of location and distribution of impurities.
5. Determination of valence.

Also recommended is support of research to develop better survey techniques for analysis of impurities at levels of 1 ppm and below.

Improved recognition of the importance of characterization is needed to insure better characterization of materials in the future. The following recommendations are made with this objective in mind:

1. The climate for characterization and the stature of researchers involved in characterization needs to be improved through education of the scientific community, journal editors, and contracting officers. Publications describing well-characterized materials should be encouraged and funded research should provide for adequate characterization.

2. High purity, well-characterized starting materials should be made more readily available and standards for reagent grade materials should be updated and made more meaningful.

3. Exchange of well-characterized materials between competent researchers should be encouraged.

While improvements are needed, it is important to avoid promotion of characterization as a panacea, and to avoid funding of needless pedestr research, especially collection and dissemination of data when such inf mation is not really pertinent or when it can be provided by other and effective means.

Finally, it is recommended that a separate MAB panel be establish in the near future to specifically study characterization of surfaces.

# CONTENTS

## SECTION II. THE REPORT OF THE PANEL ON COMPOSITION

## Table of Contents (continued)

# CHARACTERIZATION OF MATERIALS
# WITH RESPECT TO COMPOSITION

## I. INTRODUCTION

Underlying all materials research is the principle that composition and structure determine properties of materials. Detailed information of composition and structure is therefore of fundamental importance to future development of our knowledge and understanding of material behavior and to improvement in our ability to control and tailor properties for specific applications. This kind of information is encompassed in the word characterization for which the MAB Ad Hoc Committee on Characterization of Materials proposes the following definition:

> "Characterization describes those features
> of the composition and structure (including
> defects) of a material that are significant
> for a particular preparation, study of prop-
> erties, or use, and suffice for reproduction
> of the material."

This Panel was asked by the above-mentioned Committee to focus its attention on characterization of materials with respect to composition and with the following objectives:

1. To assess current capability for characterizing chemical composition.
2. To study the extent to which existing techniques are used.
3. To point out areas where current capability is limited by techniques or by availability of equipment and trained personnel.
4. To recommend ways of improving the state of the art.

## II. CURRENT CAPABILITY FOR DETERMINATION
## OF CHEMICAL COMPOSITION

### A. INTRODUCTION

The scientific literature contains numerous references to materials of
5-9's and 6-9's purity. Such statements are often misleading and of question-
able validity since the estimates are in many cases derived from resistivity
measurements supplemented by direct emission spectrographic analyses
(with a sensitivity of only 1-10 ppm for most elements). To establish that
a sample of material contains less than 1 ppm total impurities would
clearly require conducting analyses for all elements present using tech-
niques with sensitivities and accuracies in the range of 1-20 ppb.

The magnitude of effort required is illustrated by the work of Professor
Ph. Albert of the CRNS Laboratory on zone-.·efined aluminum.[1] Samples
are analyzed for over 60 elements plus the rare earths by high sensitivity
neutron activation using detailed radiochemical procedures. Such elements
as carbon, oxygen, and nitrogen are determined by photonuclear or charged-
particle activitation. This procedure requires the efforts of a 4-man team
for 12 hours plus an additional person for nine days and another for two
weeks to analyze the rare earths.

At the conclusion, the amounts of individual contaminants are totaled
(for many there are only experimental upper limits of 1-10 ng.) and it is
thus possible to establish that a particular sample of aluminum contained
less than 2 parts per million total impurities (i.e., not quite 6-9's pure).

### B. MAJOR FEATURES OF COMPOSITION

Characterization of materials with respect to composition ideally involves
identification of all chemical constituents present and the determination of
their concentration, electronic state, state of combination, location, and
distribution throughout a sample. It is convenient to describe composition

by the following terms:

#### Characterization of Major Phase

- Identification
- Stoichiometry
- Homogeneity
- Valence
- Location of Atoms

#### Characterization of Minor Phases and Impurity

- Identification - including valence state and state of combination
- Concentration
- Location
- Homogeneity

#### Characterization of the Surface

## C. ANALYTICAL TECHNIQUES

### Microscopic Examination

Optical and electron microscopy are especially useful for determination of uniformity, inclusions, crystallinity, and particle size. The electron microscope can often be used also for electron diffraction which is of value in determining crystallinity.

### Refractive Index & Petrography

Refractive indices of transparent and opaque solids can be measured by conventional mineralogical techniques. Questions of morphology can be answered simply to assist in establishing identity.

### Density

This parameter should be measured routinely for it is one of the properties of materials that is easy to determine with relatively high accuracy. It yields important information on porosity and, in certain cases, on concentrations of vacancies and interstitials.

### Wet Chemistry

The "workhorse" of the analytical chemist for years, wet chemistry, is still the most broadly applicable and widely used technique for establishing composition. The chemistry of ionic equilibria[2] has become increasingly important to analyses of major and minor components through application of coordination chemistry[3] and homogeneous precipitation reactions.[4]

### Coulometry

Coulometry,[5,6,7] or quantitative electrolysis, is applicable to both major constituent and trace analysis. In the former application, it is one of the most precise and accurate analytical techniques with reliability at the 0.002% level; here, it is especially useful for primary standardization and for the determination of stoichiometry. Trace determinations at the sub-microgram level are possible and this is an area where more applications can be expected. Coulometry is essentially titration with electrons; hence, it should be useful in any analytical situation where conventional titrimetric methods are applicable. Methods may be classified according to whether they employ constant electrolysis current or precise control of electrolysis potential. The former is the more convenient technique but the latter provides some advantage of selectivity of electrode reaction.

### Mössbauer Spectroscopy

This new analytical method has been used to great advantage in the determination of chemical structure.[8] It complements the other hyperfine interaction spectroscopies (such as nuclear magnetic research) in several ways. The technique observes the changes in two energy levels within the nucleus as a function of chemical environment, as contrasted to changes in the ground state only in NMR. This Mössbauer technique is primarily used in the solid state as contrasted to NMR. The broadening of NMR spectra due

to solid-state interactions is absent in Mössbauer spectroscopy because recoilless emission in Mössbauer spectroscopy demands no solid-state (phonon) interaction.

The technique has proven itself to be a powerful tool for measuring properties such as magnetic and electric field interactions in the solid state. It has proven very useful in the fields of metallurgy, solid-state physics, coordination chemistry, biochemistry, and the theory of the hyperfine interaction.

At present, the number of elements with which this effect can be observed with high practicability is limited to iron, tin, iodine, gold, and a few rare earths. As the problems of radio chemistry relating to this are resolved, the number of usable elements can be expected to increase by a factor of 3 to 5.

Most Mössbauer measurements have been made on materials in which the Mössbauer resonating element is a macro-constituent in the matrix. Some work has been done in which the matrix investigated constitutes the source of Mössbauer spectroscopy and where the resonating element is present as an ultra-trace impurity in the matrix.

### Electron Probe Microanalysis

In many types of specimens, the distribution of components on a microscopic scale is as important as the average composition. This is particularly true for many alloys, minerals, ceramics, and semiconductor devices. The development of the electron probe, capable of investigating the distribution on a micron scale of all elements of atomic number above five at concentrations down to 0.1% or less, permits studies of microstructure to an unprecedented degree. The fact that this technique permits quantitative determinations with errors of less than 5% relative, in most cases, makes it

even more attractive. The application[9,10,11] of microprobe analysis to the most diverse types of specimens has been well developed, as has its extension to characterization of minor and trace amounts. The impact of this technique upon metallurgy, geology, and other branches of science is considerable; however, at present, progress is limited largely by availability of instruments (about 200 in the USA) and of trained operators.

### Emission Spectroscopy

Qualitative analysis by emission spectroscopy[12] permits simultaneous detection of some 70 metallic and metalloid elements by rapid procedures. Only a few milligrams of sample are required, and the elements can be determined at concentrations from trace levels up to the level of major constituents. An estimate of the concentration of an element can be made, often within one order of magnitude or somewhat better, from the intensities of the lines. The sensitivity of detection of each element depends on the nature and amount of the sample, the excitation procedure, and the properties of the spectrograph and the detector. Table I, from a paper by Addink,[13] lists limits of detection on a weight and concentration basis, for a particular procedure of analysis involving d.-c. arc excitation of a 10-mg sample. However, it should be pointed out that these figures do not represent the ultimate that can be accomplished in spectroscopic detection, since special procedures have been developed to extend the sensitivity for certain elements by one or two orders of magnitude. Other procedures permit the detection of nonmetallic elements, including carbon, nitrogen, oxygen, and the halogens, often at concentrations as low as 10 ppm.

The lower limit of quantitative analysis by emission spectroscopy is generally somewhat higher than the detection limit. This is inherently true, since a just-detectable signal cannot, in general, be measured quantitatively

TABLE I

SENSITIVITY OF DETECTION IN THE D.-C. ARC
(DATA OF ADDINK)

| Element | Wavelength, A | Lower limit of detection[a] | |
| | | % | Micrograms |
| --- | --- | --- | --- |
| Ag | 3280.68 | 0.0001 | 0.01 |
| Al | 3961.52 | 0.0002 | 0.02 |
| As | 2288.12 | 0.002 | 0.2 |
| Au | 2675.95 | 0.0005 | 0.05 |
| B | 2497.73 | 0.0004 | 0.04 |
| Ba | 4554.04 | 0.0001 | 0.01 |
| Be | 2348.61 | 0.0001 | 0.01 |
| Bi | 3067.71 | 0.0003 | 0.03 |
| Ca | 3933.66 | | |
| | or 4226.72 | 0.0001 | 0.01 |
| Cd | 2288.01 | 0.001 | 0.1 |
| Co | 3453.50 | 0.0004 | 0.04 |
| Cr | 4254.34 | 0.0002 | 0.02 |
| Cu | 3247.54 | 0.00008 | 0.008 |
| Fe | 3719.93 | 0.0001 | 0.01 |
| Ga | 2943.63 | 0.0005 | 0.05 |
| Ge | 2651.17 | | |
| | or 3039.06 | 0.001 | 0.1 |
| Hf | 2940.77 | 0.02 | 2 |
| Hg | 2536.51 | 0.003 | 0.3 |
| In | 3256.09 | 0.001 | 0.1 |
| Ir | 3220.78 | 0.04 | 4 |
| K | 3446.72 | 0.3 | 30 |
| La | 3337.48 | 0.004 | 0.4 |
| Li | 3232.61 | 0.004 | 0.4 |
| Mg | 2852.12 | 0.00004 | 0.004 |
| Mn | 2576.10 | 0.00015 | 0.015 |
| Mo | 3132.59 | 0.003 | 0.3 |
| Na | 5895.92 | 0.0001 | 0.01 |
| Nb | 3194.97 | 0.01 | 1 |
| Ni | 3414.76 | 0.0002 | 0.02 |
| P | 2535.65 | 0.002 | 0.2 |
| Pb | 4057.82 | 0.0003 | 0.03 |
| Pt | 3064.71 | 0.0008 | 0.08 |
| Sb | 2598.06 | 0.002 | 0.2 |
| Si | 2516.12 | 0.0002 | 0.02 |
| Sn | 2839.98 | | |
| | or 3175.01 | 0.001 | 0.1 |
| Sr | 3464.45 | 0.02 | 2 |
| Ti | 3372.80 | 0.001 | 0.1 |
| Tl | 2767.87 | 0.007 | 0.7 |
| V | 3185.39 | 0.002 | 0.2 |
| Zn | 3345.02 | 0.003 | 0.3 |

[a] Approximate values based on a 10-mg. sample vaporized completely in the arc.

with satisfactory precision. Lack of suitable standards may also restrict the limit of quantitative analysis. If the sample form is suitable, standards can often be prepared from the sample by the method of additions. Precon-centration methods are also useful for spectrographic analysis, facilitating the preparation of standards because the matrix has been simplified. On the other hand, preconcentration methods or preparation of standards by the method of additions increase the chances for contamination of the sample. "Common matrix" methods, involving dilution of the samples with a material such as gallium oxide, are not applicable to the analysis of the purest materials, since the dilution process raises the limits of detection.

### Mass Spectrometry (Spark Source)

This method is capable of detecting all elements in a sample, and the sensitivities of detection with present equipment and techniques[14] approach 10 ng/g. The limits of detection for oxygen and nitrogen are higher because of residual gases in the vacuum system, and elements adjacent in mass to the matrix elements will also have somewhat poorer detection limits. With the instrumentation and techniques now available, the precision of analysis is poorer than with some other methods, so that the method is most useful for survey analyses, where semiquantitative results are adequate. However, more precise analyses can be expected in the future. Literature reports[15,16] indicate that analytical curves can be safely extended below the lowest available standards, and there is hope that for this reason the availability of standards certified at the ppm level will permit quantitative analyses to be done at concentrations near the limit of detection. Improve-

ments in instrumentation and techniques should make possible more precise spark-source mass spectrometric analyses in the future.

### X-ray Fluorescence Spectrometry

This technique[17] is useful for the determination of major and minor constituents with a typical sensitivity of 20 to 200 ppm, depending on the atomic number of the element and the nature of the specimen. In favorable cases, or when preconcentration methods are used, the sensitivity may be extended to as low as 0.1 ppm.[18] Commercial instruments are available or under development for analysis with x-ray wavelengths shorter than 10Å; this permits the determination of any element heavier than sodium (atomic number 11).

The precision of x-ray spectrometric analysis is frequently competitive with quantitative "wet" chemical analysis and often superior to other instrumental techniques. For x-ray analytical techniques to be accurate, standards of composition close to that of the specimens, or suitable correction procedures for any existing inter-element effects, must be available. X-ray analysis is widely used in industry because of its accuracy. Of additional advantage, it is usually rapid and often nondestructive. The specimens analyzed can cover a broad range of types including alloys, powders, solutions, slag, slurries, and ores.

Current research[18] of importance to the characterization of valence, coordination, electronegativity, conductivity, and crystal structure is being conducted on the effects of these parameters on the shape, intensity, and position (displacement) of long wavelength x-ray spectral lines and absorption edges.

## Flame Emission and Atomic Absorption Spectrometry

These two spectroscopic methods[19,20] employ rather similar equipment, and some commercial apparatus offers interconvertibility. The methods are complementary in that elements with poor detection limits by the one technique can often be determined with high sensitivity by the other. They also share many problems, particularly with respect to interferences.

The sensitivity of detection of some elements by flame emission or absorption spectrometry can, in many instances, be very low. The limit of detection of sodium by flame photometry is often determined by the residual content of the water or other solvent used for the sample; e.g., 1 ng/g of sodium can be detected without difficulty. Other elements have detection limits ranging from 1 to 1000 ng/g by one or the other of these two techniques while the limit of detection is relatively poor for the metalloids and nonmetallic elements.

Both methods require that the sample be dissolved, which necessarily causes some dilution and a consequent loss of sensitivity. In addition, matrix effects can cause serious errors unless standards can be prepared which are similar in composition to the samples. The use of organic solvents, rather than water, often improves the limits of detection, occasionally by an order of magnitude or more. Flame emission and absorption measurements are thus often especially suited to the determination c impurities following solvent extraction.

Atomic fluorescence signals can also be observed in the flame, and some preliminary work[21] indicates that this method may provide very low limits of detection. Both cadmium and zinc have been detected at concentrations well below 1 ng/g.

## Spectrophotometry

Absorbency measurement is one of the most widely used techniques, as evidenced from a survey of analytical publications.[22] It is used continually in many laboratories for trace analysis because it is fast, sensitive, and relatively precise (1-5% relative standard deviation). While in most cases, the reactions are not specific, many methods involving masking are readily available to provide selectivity, thus eliminating the need for separations. Preconcentration techniques can be applied but impose a restriction on the detection limit based on the reproducibility and magnitude of the blank. Theoretical considerations[23] set the limit of detection attainable in ternary coordination systems at 5-10 ng. Spectrophotometry has the additional attribute that its precision can be increased to a 0.1% relative standard deviation by differential techniques.[24,25]

### Polarography

This is a versatile technique[26,27,28,29] applicable to the determination of trace, minor, and even major constituents in solution. In principle, any element capable of electro-oxidation or -reduction can be determined and the polarographic behaviors of some 80 elements have been described. Polarographic half-wave potentials are ordinarily sufficiently different to make possible the simultaneous determination of several elements present in the same solution, thus minimizing the need for pre-separations in many instances. Sensitivities in the range 0.1 to 0.001 ppm can be obtained depending upon whether conventional or modified techniques such as cathode-ray or hanging-drop polarography are employed. Precision near the limit of detection is about 20%, increasing to about 1% in favorable concentration ranges. Differential techniques under development make possible the determination of micro-amounts of major constituents with a precision of 0.02 to 0.05%.

## Activation Analysis

This technique is particularly useful for ultra-trace analysis in that it
eliminates appreciably the problem of reagent or sample contamination
during analysis. The large number of variables (such as type and energy of
irradiating particle, time of irradiation and measurement, type of detector
used, etc.) that can be judiciously altered for particular analyses make the
technique relatively free from serious systematic errors or biases. A
typical value for the random errors is ±5% at the 100 ng level. To date, the
technique cannot be considered a multi-element analysis. Efforts in the
past few years have been in the direction of chemically separating the
radioelements into selected groups after irradiation (similar to the work
of Albert, described herein). Such group element separations result in less
time expended (e.g., hours instead of days) without increasing either the
systematic or random errors. Additional effort is being expended on the
automation of these group element separations to further decrease the time
of analysis.

At present, great use is made of gamma ray spectrometry in providing
"non-destructive" analysis of simple systems by this technique. The method
can often provide rapid analysis but becomes unreliable as the system be-
comes complex. Unfortunately, gamma ray spectrometry alone is not usually
suited for most trace (i.e., $<\mu g$) analyses of "materials." Continuing im-
provements in detectors and methods of irradiation may alter this situation
in the future.

Activation analysis with neutron generators (fast neutrons) and electron
linear accelerators (high energy photons) provides independent and absolute
methods for the determination of oxygen at the 10-100 $\mu$ g (neutron generator)
and submicrogram (Linac) levels. The Linac also holds promise of analysis
for submicrogram amounts of nitrogen and carbon although much development

of methods must be done before measurements can become routine with the Linac.

### Vacuum Fusion

This method is particularly important in the area of trace determinations of gaseous components of interstitial compounds or solid solutions, and supplies critical information about the effects of trace amounts of gaseous elements on the properties of materials. The vacuum fusion method has evolved from early studies[30] to a considerable growth in the understanding of the process,[31] and the design of highly efficient apparatus.[32] Whereas traditional equipment handles only a few samples a day, recent new equipment analyzes up to 60 samples per day. This makes it much easier to treat the analytical results statistically and to evaluate the many parameters of the method. Basically, except in the hands of the most competent analyst, the reliability of the results depends on control or calibration with known standards.

### Nuclear Magnetic Resonance (NMR)

NMR is a well-established method for identifying and studying structure of molecules in the liquid state. Since solids are in general characterized by broad resonance lines with little fine structure, application of NMR to characterization of solids with respect to composition is limited and highly specialized. Sensitivity varies with the kind of nucleus present but generally does not exceed $10^{19}$ nuclei/$cm^3$ or 0.1 atomic percent. With double resonance schemes[33,34] and modifications thereof,[35] sensitivity for impurities[36] can be improved to the order of $10^{16}$ nuclei/$cm^3$.

In metals with cubic lattice symmetry, determination of impurities at concentrations of 0.1 atomic percent have been made using quadrupole interactions and changes in the Knight shift. Another approach involves study of the coupling between the nuclear spin system and the lattice through

measurement of the spin-lattice relaxation time. In nonmagnetic solids, paramagnetic impurities affect the relaxation time dramatically and these effects can be detected with impurities in the 10-100 ppm range. However, these latter methods are not specific for a single impurity but are influenced by valence, size, or other property which may be common to a number of impurities.

### Electron Spin Resonance (ESR)

This technique is useful for studying conduction electrons in metals and semiconductors and bonding of transition metal ions and other paramagnetic species. It is generally more suitable for determining environment than for identification of elements and measurement of concentration. Sensitivity varies with the paramagnetic species, and for transition elements under optimum conditions is in the range of $10^{10}$ spins/cm$^3$. Therefore, it can be used to detect trace impurities in special cases; e.g., free radicals in an organic matrix or transition metals in a diamagnetic solid.

### Residual Resistance Ratio (RRR)

This method measures the sum of the "electrically active" elements and is sensitive to parts per billion. It does not identify impurities and different impurities affect residual resistance to varying degrees with some contaminants having little or no appreciable effect. RRR finds wide application in characterization of metals but from an analytical viewpoint it is of value primarily to check consistency of other analytical data.

### D. SUMMARY

The sensitivity, precision, and area of application of techniques described above are summarized in Table II.

TABLE II

PRECISION AND SENSITIVITY OF ANALYTICAL TECHNIQUES

| Technique | Applications | Sensitivity | Precision | Reference |
|---|---|---|---|---|
| Wet Chemistry – Titrimetry | Major & minor phase – concentration; also impurities | $10^{-2}$M in solution<br>$10^{-5}$M in solution<br>$10^{-6}$–$10^{-7}$M in solution | 0.01%<br>0.1%<br>0.2 – 1.0% | 37,38 |
| Wet Chemistry – Gravimetry | Major & minor phase – concentration | 1000 ppm/1 g. sample | 0.01% | 38 |
| Wet Chemistry | Major phase – valence | | 0.01% | |
| Coulometry | Major phase – concentration | | 0.001 – 0.005% | 7,28 |
| Mössbauer Spectroscopy | Major phase – valence also impurities – valence | Down to 0.1% – 0.0001% depending upon density of matrix | Semi-quantitative now | 8,39,40 |
| Electron Probe Microanalysis | Homogeneity of major phase minor phases | Down to 0.1% over a 1-5 micron scan diameter | 0.5% | |
| Emission Spectroscopy | Impurities (survey) | 0.1 – 100 ppm | 5 – 10% | 12,13 |
| Spark Source Mass Spectrometry | Impurities (survey) | 0.01 – 0.1 ppm | Semi-quantitative now | 14,15,16 |
| Atomic Absorption | Impurities | 0.005 – 0.1 ppm in solution<br>0.1 – 10 ppm in solution | 5 – 10%<br>1 – 5% | 20,41 |
| Flame Emission | Impurities | 0.002 – 0.1 ppm in solution<br>0.1 – 10 ppm in solution | 5 – 10%<br>1 – 5% | 19<br>42,43 |
| Spectrophotometry | Impurities | 0.005 – 0.1 ppm in solution | 5 – 10% | 23,44,45 |
| Polarography | Impurities | All in solution:<br>0.1 – 1 ppm<br>10 – 100 ppm<br>.005 ppm<br>0.001 ppm (with anodic stripping pre-concentration) | 2–10%<br>0.1 – 0.02%<br>20%<br>5 – 10% | 28<br>29<br>28,46,47<br>48,49 |
| Neutron Activation | Impurities | 0.001 – 0.01 ppm | 2 – 10% | 50,51,52,53 |
| Vacuum Fusion – Mass Spectrometry | Impurities – $O_2$, $N_2$, $H_2$ | 0.07 ppm<br>100 ppm | 20%<br>5% | 54,55 |
| X-ray Fluorescence Spectrometry | Major & minor constituents | 20 – 200 ppm generally: 0.1 at best | 0.1% | 17,18 |

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## III. APPLICATION OF CURRENT TECHNIQUES
## TO CHARACTERIZATION OF MATERIALS

### A. CHARACTERIZATION OF MAJOR PHASE

#### Identification

For elements and for many simple compounds the matter of identification is trivial. However, in the case of complex compounds, phase identification is a prerequisite to detailed characterization. Indeed, problems frequently arise through improper identification of phases present and the failure to investigate homogeneity. The methods used for phase identification are principally x-ray diffraction and measurements of index of refraction and other optical properties. X-ray identification using, for instance, Debye-Scherrer powder techniques is capable of detecting approximately 2-5% of a foreign phase under favorable circumstances. X-ray diffraction and observation of optical characteristics by standard petrographic techniques are used to identify the phase present, while petrographic techniques alone are often capable of greater subtlety in detecting traces of foreign phases. However, ordinary microscopic observations including examination between crossed polarizers are often neglected. Such examination combined with etching and similar metallographic techniques is often capable of shedding light on phase homogeneity in both metallic and nonmetallic crystalline solid

#### Stoichiometry

Classical techniques are still the mainstays in determining the concentration and stoichiometry of the major phase. In this connection wet chemical analysis, including gravimetric, volumetric, and electrochemical techniques, is mainly used. However, some instrumental techniques, and in particular, x-ray fluorescence, are beginning to show considerable promise, especially because of their rapidity of execution. Moreover, there is a definite possibility of automating wet chemical techniques for analysis of

solid materials in the way that routine clinical analysis is being automated. The precision ordinarily expected for stoichiometric determinations is probably in the range $\pm 0.01$ - $0.1\%$ at best in the case of compounds like $KCl$ and $MnFe_2O_4$.

The exact determination of stoichiometry when precise results are required almost always depends upon indirect measurements and upon a "logical chain of reasoning" which is often not entirely tenable. Conductivity and mobility measurements together with assumptions as to the origin of donors or acceptors sometimes allow estimates of stoichiometry to be made in semiconductors. Similarly, precise lattice parameter and pycnometric density determinations provide some means of estimating vacancy concentration and in some cases stoichiometry.

### Homogeneity (Including Impurity Distribution)

In addition to determining the presence of "impurities" or ions in solid solution, one of the major areas of difficulty is the study of the distribution of such "impurities." The importance of knowing how the impurities are distributed, whether completely statistically at the atomic level or in a single 'inclusion', is vital to every interpretation of properties measured on the phase. In this field the last five years have brought a step-function advance by the introduction of the electron microprobe. Yet its spatial resolution is limited to about a micron and its sensitivity and precision (about $0.1\%$) are poor. However, use of the cathodoluminescence in the probe provides a tool in some cases for detecting inhomogeneities at the ppm level with micron resolution. The scanning electron microscope used judiciously can provide in favorable cases some data on impurity distribution at the $0.1\mu$ level. For single crystal materials, x-ray topography (rocking curve, Lang, anomalous transmission photographs) is a powerful

qualitative mapping method for observing homogeneity. Quantitative com-
parisons between successive samples in special cases can be done.

### Valence

Once the stoichiometry has been determined, it is conventional to assign
valences of multivalent elements in a compound in order to preserve elec-
trical neutrality. This presents difficulties when more than one multivalent ·
element is present in the same compound or where several valency assignmen
are possible for a given element in the compound; e.g., iron in Prussian
blue. If it is possible to get the compound into solution without altering
the valence, the classical wet chemical and electrochemical methods,
which are quite precise (0.01%), permit the determination of valence. For
iron and some other elements, Mössbauer spectroscopy is applicable with
a precision of about 0.1%. Improvements in the precision of Mössbauer
measurements are likely. High resolution x-ray spectra also give informa-
tion on valence which is applicable to most elements. In actual practice
the valence is often deduced from the color of the compound. Absorption
spectroscopy is useful in particular circumstances, but it will probably be
limited to the determination of valence of trace elements. Similarly, electron
spin resonance is applicable to elements present in trace concentrations.

### Location

The location of the atoms of the principal phase is determined by x-ray
and neutron diffraction but the sensitivity is only of the order of 0.1% at
best. Other quantitative techniques for site location have not been developed,
although ESR, NMR, and Mössbauer spectroscopy are useful in obtaining
qualitative information in some circumstances.

## B. CHARACTERIZATION OF MINOR PHASES AND IMPURITIES

Most elemental constituents of either organic or inorganic impurities can
be detected down to about 10 ng/g if desired, though the limit of quantitative

determination is generally higher. The sensitivity of quantitative analysis by most instrumental methods is frequently limited by a lack of suitable standards. Detection and determination of organic impurities in an organic matrix is an especially difficult problem.

### Survey Methods

Emission spectroscopy is the most generally applicable of the survey methods. It is used widely for characterization of solids, powders, liquids, and gases, and has the capability of detecting up to 70 elements by d.-c. arc excitation. Determination of nonmetallic elements is also possible with emission spectroscopy, but this requires special techniques which are rarely used.

Spark-source mass spectrometry can detect all elements, with sensitivities often as good as 10 ng/g. Residual gases in the vacuum system restrict detection limits for oxygen and nitrogen.

X-ray spectroscopy can also be employed for survey analysis of impurities and has the advantage of being nondestructive. Lower limits of detection are rarely better than 10 to 100 ppm, and the elements of the first period cannot be detected at low concentrations.

Electrical measurements are useful for determining the total content of electrically active impurities in conductors and semiconductors. The shape of the freezing curve can give considerable information on total impurities in a material with suitable melting point. However, this technique is of little importance for most metals, which melt at high temperatures, or for materials which decompose on melting.

### Quantitative Methods

All of the techniques listed in the "Analytical Techniques" section and summarized in Table II can be applied to the quantitative determination of impurities. The most serious limitations of these methods are the relatively

poor detection limits for some, the need for standards for most instrumental methods, and the hazard of contamination in solution and other methods which require preliminary handling of the sample.

Activation analysis is especially suitable for trace characterization, since it permits most sample handling to be done after the activation step, and thus contamination problems are minimized. However, the method requires quite costly equipment and considerable effort.

Spectroscopic methods (emission, mass, x-ray) provide for determination of many elements in small absolute amounts but are limited in the amount of sample that can be analyzed; they are also useful methods when used after separation or preconcentration, as a group, of several impurities. These techniques are also limited by the availability of suitable standards. Most of the other methods listed in the section on "Analytical Techniques" are restricted to the determination of one or a few elements at a time. Thus, considerable effort will be required for the complete characterization of a material by these techniques.

Organic impurities in organic matrices can sometimes be separated by gas chromatography and determined by mass spectrometry or other suitable methods. Detection limits are usually no better than perhaps 10 ppm.

The various techniques which can give information on valence and location all suffer from relatively poor sensitivity (perhaps 1000 ppm) and are thus more suitable for the characterization of the major phase than of the impurities. Magnetic resonance techniques (NMR and ESR) have low limits of detection, but both are limited in applicability.

For determinations at the microgram level, the method of vacuum fusion must be modified in such a way as to utilize the mass spectrometer to identify the gaseous components. Homogeneity of the sample is often a limiting factor in the analysis for a trace constituent.

## Determination of Vacancy and Interstitial Concentrations

A comparison of the macroscopic density of a crystal with the density calculated from the x-ray determined lattice constant, molecular or atomic weight, and Avogadro's number reveals, in principle, the presence of lattice vacancies or interstitials. The presence of interstitials makes the macroscopic density greater than that calculated from the x-ray lattice constant; the macroscopic density is less than the calculated density if vacancies are present. If vacancies and interstitials are present in equal concentrations, as in the case of Frenkel defects, the macroscopic and calculated densities agree. The probable error of the determination of the macroscopic density is about 10 parts per million, although in favorable cases it may be as small as a few parts per million. The probable error of the size of the unit cell calculated from the x-ray lattice constant is ordinarily about 25 parts per million and can be as low as 10 ppm, most of which is due to the wavelength uncertainty. The uncertainty of the relative abundances of isotopes adds further error. These uncertainties seriously limit the usefulness of the technique since the vacancy or interstitial concentrations in crystals near room temperature are frequently of the order of 5 parts per million or less and too small to produce an observable density difference.[1,2]

An elegantly simple but difficult technique consists in the comparison of the macroscopic change in length, L, with temperature of a specimen and the change in the x-ray determined lattice constant, a. If vacancies are present, their fractional concentration for cubic crystals is $\Delta N/N = 3(\Delta L/L - \Delta a/a)$.[3] The precision in the determination of $\Delta N/N$ is approximately 10 parts per million. Since $\Delta N/N = \exp(s/k)\exp(h/kT)$ and $s/k$ can be estimated theoretically, the method yields h, the enthalpy of formation of vacancies. It has been successfully applied to a few crystals, such as aluminum where the vacancy concentration was found to be $9.4 \times 10^{-4}$ at

the melting point ($660^\circ$C), and silver where the vacancy concentration was determined to be $1.7 \times 10^{-4}$ at $960^\circ$C, the melting point.[4,5]

The ionic conductivity of polar crystals can be used to determine vacancy and interstitial concentrations.[6] If only one type of defect is present or mobile, the conductivity, $\sigma = Ne\mu$, yields the product of the defect concentration, N, and the mobility, $\mu$. It is frequently possible, however, to fix N at a known value by preparing a mixed crystal containing an ion of different valence than that of the host crystal. Sodium chloride is an example where cation and anion vacancies occur in equal concentrations but where the mobility of the anion vacancies is sufficiently smaller than that of the cation vacancies so that the transport number of the sodium ion is approximately unity. Calcium chloride can be added to sodium chloride with the divalent calcium ion substituting for sodium ions in the sodium chloride lattice. The excess charge of the calcium ions is compensated by the incorporation of sodium ion vacancies into the lattice. If the concentration of calcium is of the order of 100 parts per million, the concentration of sodium ion vacancies is equal to that of the calcium ions, and temperature independent. The measurement of the conductivity of such crystals determines the mobility of the sodium ion vacancy and may be used with the measured conductivity of the pure crystal to determine the concentration of sodium ion vacancies in pure sodium chloride. It has been possible to use this technique with silver chloride and bromide, which possess Frenkel defects or equal concentrations of silver ion vacancies and interstitials, to determine the Frenkel defect concentration and the mobilities of both vacancies and interstitials.

Ionic conductivity measurements permit the detection and measurement of very small concentrations of vacancies and interstitials which may be in range of parts per billion in favorable cases.

The diffusion coefficient of an ion in a polar crystal is proportional to the contribution of the ion to the ionic conductivity. The technique of adding an ion of valence which differs from that of a host ion can be used in conjunction with the measurement of the diffusion coefficient instead of the ionic conductivity to determine vacancy or interstitial concentrations. Diffusion measurements are both more difficult and less precise than conductivity measurements, however. Diffusion measurements, which are commonly made with radioactive tracers, have the advantage that the movement of a single ionic species can be followed whereas the conductivity is ordinarily a sum of separate conductivities due to each of the ions present in the compound. Potassium chloride is an example where both ions contribute significantly to the ionic conductivity, and diffusion measurements have proven valuable. As is probably quite common in the case of Schottky defects, association of cation and anion vacancies to form neutral defects, vacancy pairs, occurs in potassium chloride. The contribution of these pairs, cation and anion vacancies occupying adjacent lattice sites, to the diffusion coefficient of the chloride ion can be observed with radioactive tracer techniques and the concentration of pairs determined.[7] Vacancy pairs do not contribute to the ionic conductivity since they are electrically neutral. Neutral defects are also formed by association of a cation vacancy with an impurity ion such as calcium in sodium chloride and are not directly detectable by conventional conductivity measurements. As in the case of vacancy pairs, the dipole moment of the neutral defect may make a measurable contribution to the a.c. conductivity or dielectric loss. Concentrations of neutral defects which possess dipole moments may be measured in this manner.[6]

A few examples exist such as the anion vacancy in the alkali halides where the vacancy or interstitial is responsible for an optical absorption band whose magnitude is a measure of the concentration.[8]

When deviations from stoichiometric proportions are associated with vacancies or interstitials, chemical analysis suffices to determine the defect concentrations. An example of such a system is titanium carbide where the sodium chloride structure is stable over the carbon range from $TiC_{0.6}$ to $TiC_{1.0}$. The lower carbon concentration represents 50% vacancies in the f.c.c carbon sublattice.[9]

In the case of tantalum carbide, vacancies in the carbon sublattice result in deviations from stoichiometry and the x-ray lattice constant is sufficiently sensitive to the vacancy content to be a useful measure of the vacancy concentration.[10]

## C. CHARACTERIZATION OF SURFACES

Undoubtedly, among the least understood and most poorly characterized features of a solid is the surface. Defect solid-state theory, useful for interpreting and predicting the electronic behavior of semiconductors and insulators, has been utilized with good results to analyze and interpret chemisorptive processes occurring on such solids.[11] Despite the sophist cation of solid-state physics, it has become increasingly clear that the bull electronic properties of metals, semiconductors, and insulators are not of themselves adequate to explain interfacial electronic phenomena. More attention is being given to the special electronic states and environment of atoms located at phase boundaries. Many electronic processes which are forbidden in the bulk solid become possible at surfaces.[12]

Electronic "mapping" of solid surfaces on an atomic scale is now in progress, utilizing such tools as field emission microscopy, surface infrared and nuclear magnetic resonance spectroscopy, low-energy electron diffraction, electron-probe techniques, and surface-conductance measurem

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## IV. UTILIZATION OF EXISTING TECHNIQUES

### A. LITERATURE EXAMPLES

Published information on characterization of seven different materials has been gathered from the literature to serve as a guide in studying the extent to which existing analytical techniques are used. These seven materials are:

- Copper
- Titanium
- Silicon
- Potassium Chloride
- Zinc Sulfide
- Manganese Ferrite - $MnFe_2O_4$
- Anthracene

Collectively they represent an extremely broad spectrum of analytical problems and illustrate both strong and weak points in application of the present state of the art. The results summarized in Table III do not necessarily represent the best that can be done but are fairly typical of published information on highly purified materials.

### B. CASE STUDY—MANGANESE FERRITE - $MnFe_2O_4$

Since results cannot be conveniently summarized in Table III, literature data on $MnFe_2O_4$ are discussed below.

#### Stoichiometry

The purest sample of manganese ferrite was prepared by Wickham, Whipple and Larson.[15] They reacted $MnFe_3(AcO)_8(OH)_3$ and $Mn(AcO)_2 \cdot 4H_2O$ in the absence of air to form $Mn_3Fe_6(CH_3CO_2)_{17}O_3(OH) \cdot 12C_5H_5N$. This product was ignited to the ferrite at $1300^\circ C$ and quenched in nitrogen. This final ignition must be carried out at a high temperature and the produ

TABLE III

PUBLISHED DATA ON PURIFIED MATERIALS

| Materials | Method of Preparation | Impurities (ppm) | | | | | | | | | Method of Analysis |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Copper[1] | Zone refined | Sb | Cr | Co | Fe | Mn | Ni | Si | Ag | Sn | Spectrographic Analysis |
| | | No | 1 | 60 | 10 | * | 10 | * | * | * | |

*Not Detected

| Materials | Method of Preparation | Impurities (ppm) | Method of Analysis |
|---|---|---|---|
| Copper[2] | Zone refined | Fe 0.5  As <0.0001  Ag 0.01-0.02  Sb <0.0001 | Activation Analysis |
| | | Mn <0.0001  Zn <0.05  Na <0.001  Cr 0.002-0.003 | |
| | | Ag 0.04  Se <0.001  P 0.03-0.01 | |
| Copper | | Sb[3] 0.05   Au + Tl[3] 0.05   Be[4] 0.01   B[5] 0.05 | Spectrophotometry |
| | | Al[6] 0.1   P[7] 0.1 | |
| Titanium[8] | Decomposition of TiI_4 on a heated surface | Al 65  Fe 65  Mn 40  Cu 10  Pb 25  Sn 20  N 20 | Spectrographic Analysis |
| Silicon[9] | Thermal decomposition of silane | Fe <0.017  Cu 0.011  Bi <0.0016  As 0.001  P <0.001 | Neutron Activation Analysis |
| | | Tl <0.00091  Zn <0.00041  Ni <0.00027  In <0.00032 | |
| | | Ga <6.2 x 10^{-6}  Sb <3.7 x 10^{-6}  Mn <6.2 x 10^{-7} | |
| Silicon | | B[10] 0.01  Sb[3] 0.05  Au + Tl[3] 0.05  Ni[11] 0.005 | Spectrophotometry |
| Potassium Chloride[12] | Single crystal growth from melt | Br <1  C <20  Fe <1  I <1  N 2  Na <0.8 | Spectroscopy, flame photometry, wet chemical, neutron activation analysis |
| | | OH 0.01  P <1  Pb 0.06  Rb 1  S <1 | |
| Zinc Sulfide[13] | Single crystal growth from vapor phase | Al 1.2  Ca not detected  Cu 3  Fe 1.5  Mg 2  Mn 0.2 | Spectrographic Analysis |
| | | Ni <1  Pb not detected  Sb <10 | |
| Zinc Sulfide[3] | | Cu 0.1  Au + Tl 0.1  Sb 0.1 | Spectrophotometry |
| Anthracene[14] | Gas chromatography, zone refining, gradient sublimation, scavenging | Tetracene <1  Anthraquinone <1  Fluorene <1  Phenanthrene <1 | Fluorescence, optical absorption, emission spectroscopy, gas chromatography |
| | | Carbazole 1-10  Cr <0.1  Fe <0.5  Mg <0.2  Pb <0.1  Si <0.5 | |
| | | Mn <0.05  Cu <0.1  Ag <0.1  Al <0.1 | |

quenched through the temperature region where two phases exist, or cooled under an equilibrium oxygen pressure which would have to be continuously varied with decreasing temperature.[16] Chemical analysis of the final product is summarized in Table IV.

### Valence

When the final composition of the single-phase ferrite, sintered at high temperatures, and annealed to obtain the desired properties is considered, a serious problem in analysis becomes apparent; viz., the determination of the oxidation states of manganese and iron. There are at least two possible oxidation states for each metal: $Fe^{+2}$ and $Fe^{+3}$ and $Mn^{+2}$ and $Mn^{+3}$. It has not been possible to determine the specific quantities of all four present in a particular ferrite material. A method,[17] however, has been developed for the determination of the total divalent metal and the total trivalent metal present in the material at any point in the manufacturing process. The ratio of divalent metal to total metal $M^{+2}/(M^{+2} + M^{+3})$ may be computed and for a perfect single-phase spinel $M^{+2}M_2^{+3}O_4$ should equal 0.333. If oxidation states higher than +3 are present, they can be reported and discussed in terms of equivalent quantities of +2 and +3 states.

It is not possible to dissolve a solid ferrite in any reagent solution in which the oxidation states present in the solid are preserved with certainty in the same amount in the solution, and then to proceed to analyze the solution for each one. It is possible, however, to react the solid ferrite with a suitable reagent solution. In this solution there will be produced or consum as the sample dissolves, an accurately measurable quantity of some chemi cal substance equivalent to the value for the solid. For example, the triva- lent iron and trivalent manganese present in manganese ferrite will react, as the solid dissolves in a hydrochloric acid solution of potassium iodide, t

## TABLE IV

### DATA OF WICKHAM, WHIPPLE & LARSON

| Compound Sought | Weight % Fe | | Weight % Mn | | Mole Ratio Fe/M$^{2+}$ | Ignition Temp. ($^{\circ}$C) | Active O eq./mole | Cubic Lattice Constant $a_0$(A$^{\circ}$) | Saturation Magnetic Moment* $\mu_B$/molecule |
|---|---|---|---|---|---|---|---|---|---|
| | Found | Theory | Found | Theory | | | | | |
| MnFe$_2$O$_4$ | 48.33±0.02 | 48.43 | 23.68±0.03 | 23.82 | 2.008±0.005 | 1300** | 0.034 | 8.512±0.001 | 4.5±0.01 |

*Measured at 4.2$^{\circ}$K in a field of 10,000 oersteds.

**Quenched in nitrogen, contains 0.12 percent by weight excess active oxygen.

liberate an equivalent quantity of elemental iodine which can be determined by titration with standard sodium thiosulfate solution. A high degree of accuracy is difficult to obtain because the final solution containing all the iron in the ferrous condition is unstable in the air, and the entire procedure must be carried out in the absence of air.

A procedure for determining the value of $Mn^{+2} - Fe^{+2}$ is outlined as follows: Total iron and manganese are easily determined by classical methods. Of the possible four cations present in the solid, $Fe^{+2}$, $Fe^{+3}$, $Mn$ and $Mn^{+3}$, it is possible to calculate the sum quantity present of any two of them. The reagent used is an approximately 0.1N vanadyl sulfate ($VOSO_4$) solution in dilute $H_2SO_4$. The trivalent manganese present in the solid ferrite oxidizes the tetravalent vanadium to the pentavalent state. Any ferrous ion present reduces the pentavalent vanadium to the tetravalent state or the ferrous ion will reduce any trivalent $Mn^{+3}$ present to the divalent state. Divalent manganese and trivalent iron will dissolve unchanged and are stable. Vanadium (IV) sulfate and vanadium (V) sulfate solutions are stable in air. The net reaction between the solid ferrite and a measured quantity of the standard vanadyl is the disappearance of a quantity of $VOSO_4$ equivalent to the difference, $Mn^{+3} - Fe^{+2}$, unless the quantity of $Fe^{+2}$ exceeds that of $Mn^{+3}$. The excess $VOSO_4$ is easily determined by titration with standard $KMnO_4$ solution. The relative mean deviation for a number of determinations was found to be 0.3 percent and the relative mean error less than 1.0 percent.

### Site Location

Experimentally there have been three ways of acquiring information on the distribution of the ions over the available sites in ferrites; namely, with the aid of x-ray diffraction, neutron diffraction and from the magnitude of

the saturation magnetization near absolute zero. The Mössbauer effect has yet to be applied to site location determination in ferrites. The scattering cross section of atoms for x rays is determined by the number of electrons in the atom. For this reason there is only a slight difference in the scattering power of the atoms of transition elements, and the distribution of these ions cannot usually be determined this way. The scattering power for thermal neutrons is partly determined by the magnetic moment of the nucleus of the atoms, due to interaction with neutron spin. This often varies considerably for atoms having roughly the same number of electrons. Therefore, neutron diffraction is able to provide information on the occupation of the two spinel sites by ions of the transition elements. By this technique Hastings and Corliss[18] have reported an ion distribution corresponding to the formula $Mn_{0.8}Fe_{0.2}(Mn_{0.2}Fe_{1.8})O_4$. The saturation magnetization of $MnFe_2O_4$ also shows an anomaly. Neutron diffraction experiments on several specimens by Hastings and Corliss have shown that at $4.2°K$ the average magnetic moment of ions on the octahedral sites is twice as large as that of the ions on tetrahedral sites, and that the resultant moment corresponds to $4.3 \mu_B$. Wickham et al[15] measured the saturation magnetization at $4.2°K$ and obtained a value of $4.5 \mu_B$ for their sample of manganese ferrite. For stoichiometric $MnFe_2O_4$ this value is hard to explain. An explanation for the resultant moment of $4.6 \mu_B$ has been given by Harrison et al[19] based on the simultaneous occurrence of $Mn^{+3}$ and $Fe^{+2}$ ions.

## C. FACTORS DETERMINING USE

These and other literature examples demonstrate the pronounced tendency of most investigators to use only a few, often only one, of the existing analytical techniques in characterization of materials. The chief workhorse,

other than wet chemistry, is emission spectroscopy which is popular be-
cause it is broadly applicable and is a survey technique which requires rel:
tively small expense in terms of time, money, and sample size. There are
only a modest number of research organizations with large analytical grovj
staffed with skilled professional people and, therefore, the capability for
comprehensive characterization of materials. The availability of technique
the availabihty of trained personnel, and the cost and time required for
meaningful analytical measurements are all major factors in determining
current utilization of existing analytical methods. The Panel's best
estimates on use are summarized in T'ble V.

TABLE V

USE OF EXISTING ANALYTICAL TECHNIQUES

| TECHNIQUE | USE | | REQUIRED FOR GREATER USE | | | |
|---|---|---|---|---|---|---|
| | Low | High | Better Training & Education | More Trained Personnel | Greater Convenience | Other |
| Wet Chemistry – Titrimetry | X | | | | | Automation |
| Wet Chemistry – Gravimetry | | X | | | | Automation |
| Coulometry | X | | X | X | | |
| Mössbauer Spectroscopy | X | | X | X | | Application to more elements |
| Electron Probe Microanalysis | X | | | X | X | Lower cost |
| Emission Spectroscopy | | X | X | | | Better standards |
| Spark Source Mass Spectrometry | X | | | | X | Lower cost / Better standards |
| Atomic Absorption | X | | X | X | | |
| Flame Emission | X | | X | | | |
| Spectrophotometry | | X | | | | |
| Polarography | X | | X | X | | |
| Neutron Activation | X | | | X | X | Development of multi-element approach |
| Vacuum Fusion – Mass Spectrometry | X | | | X | X | |
| X-ray Fluorescence | X | | | | X | |

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## V. CONCLUSIONS AND RECOMMENDATIONS

### A. ANALYTICAL TECHNIQUES

The Panel recommends that encouragement be given to development of new and improved analytical techniques in areas where existing methods are clearly limiting. For example, present techniques do not allow determination of stoichiometry to much better than ± 0.1% and are unsatisfactory for adequate characterization of most materials. Consequently, we recommend that present techniques for the determination of stoichiometry be improved and that new techniques be developed.

Techniques for determination of metallic and cationic impurities are nearly routine in the range down to about 10 parts per million while techniques for determination of nonmetallic and anionic impurities are probably an order of magnitude less sensitive. Present progress in the understanding of the properties of epitaxially deposited semiconductors where the transport reagent is a halide is severely limited by our inability to determine the halides with any accuracy in the 10 to 0.1 ppm range. Only recently was it realized that so-called super-pure silicon (multi-pass zone-refined material) was quite contaminated with oxygen. Good techniques for the analysis of oxygen would have saved an enormous amount of time in this area had they been available. Even in the case of cationic impurities, when analyzes below the 10 ppm range are desired, the techniques become awkward and time consuming. Consequently, attention should be devoted to development of new techniques or improvement of existing techniques for analyses of oxygen, nitrogen, carbon, boron, sulfur, and the halides. In addition, less expensive survey techniques for metallic impurities below the 10 ppm range are an important need.

Better methods for determining location of impurities, their distribution

and homogeneity, should be developed. Indeed our ability to determine homogeneity of the major phase itself is inadequate, and our techniques in this area should be improved.

The Panel feels that characterization of the surface is sufficiently complex and different from characterization of bulk composition to merit a separate study. While only a cursory survey was made of this subject, it is our impression that present techniques are inadequate for obtaining significant quantitative data on the composition of the surface.

B. GENERAL

The Panel believes that in order to assure that the materials of the future are adequately characterized, the following actions are indicated:

a) The stature of researchers involved in characterization must be improved. Analytical chemistry, in particular, must again be made respectable. Both trace and high-precision analysis require broad experience with materials, highly developed techniques, and extensive knowledge of chemical principles such as is acquired only by continuous investigation of chemical composition. Such investigations are often at the frontiers of scientific measurement and merit the highest respect.

b) Definitive characterization needs additional research support. Too often, the material needs are ahead of the state of analytical knowledge and characterization is done by methods only applicable in a limited wa to a given problem. The characterization problem is often the major stumbling block in an investigation but little attention is devoted to it. Research programs on properties of molecules should include adequate budgets to support the compositional requirements.

c) A general education of researchers, journal editors and referees, and contracting officers to assure that materials are adequately characteri

that papers describing adequately characterized materials are encouraged, and that funded research devotes adequate attention to characterization is in order.

d) A wider dissemination and a wider availability of the tools of characterization are needed. Indeed, a change in viewpoint with respect to the use of many physical tools would be helpful. For instance, semiconductor measurements provide some of the most beautiful and elegant means of characterizing materials, provided the researcher appreciates their limitations.

e) The availability of high purity and well-characterized starting materials must be improved. Up-to-date standards for reagent grade or certified purity materials would be a great help in this direction.

f) The encouragement of the exchange of well-characterized materials between competent researchers would be beneficial.

# SECTION III

## THE REPORT OF THE PANEL ON STRUCTURE

NATIONAL ACADEMY OF SCIENCES -
NATIONAL ACADEMY OF ENGINEERING
DIVISION OF ENGINEERING - NATIONAL RESEARCH COUNCIL
MATERIALS ADVISORY BOARD
AD HOC COMMITTEE ON CHARACTERIZATION OF MATERIALS

PANEL ON STRUCTURE

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## FOREWORD

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## CONTENTS

## SECTION III. THE REPORT OF THE PANEL ON STRUCTURE

# STRUCTURAL CHARACTERIZATION OF MATERIALS

## I. INTRODUCTION

In principle, a solid is characterized absolutely if one can list all the atoms or ions present, their spatial distribution, and the bonds holding them together. The goal of structural characterization is, in fact, no more than to describe precisely the arrangements of the atoms in a solid. In so doing, it spans the range from the grossest spatial features (such as the external morphology and cracks visible to the naked eye) down to the finest detail of atomic arrangement (such as the omission of single ions from their expected location in a periodic array).

We shall be concerned in this section with an analysis of the various parameters which help us to describe fully the location of the atoms within a solid. We shall also present an analysis of the various experimental methods by which each of these parameters is measured; the capability in terms of resolution, precision, limitations, etc., of each method. Furthermore, we will report on our informed viewpoints concerning the extent to which capability to analyze structure is actually utilized in the major laboratories concerned with materials science and engineering. Finally, on the basis of the above and the procurement needs of the Department of Defense, we shall recommend action not only in supporting research, but also in the field of 'educational' and editorial policies.

One does not need to apologize in such a report that, although written by specialists, it is indeed addressed to the nonspecialist in structural characterization; to the materials scientists and engineers; and to the physicists and chemists concerned both with the conduct and administration of research leading to the development of better and more useful materials.

## II. APPROACH TO THE PROBLEM

The simplest conceptualization of the problem of structural characriz￼
tion is as follows: visualize a real material of dimensions, perhaps
1 cm x 1 cm x 2 mm, on which it is proposed that some very sophisticated
physical measurements be made. However, before these are made, there
is the problem of ascertaining, describing, and reporting precisely on
what these measurements will be made since every solid is characterized
absolutely by the nature of the elements present, and their arrangement.
Clearly, the "what" requires a description also of the chemical composit:
This Panel is concerned exclusively with this arrangement.

Table I presents one probable scheme of the kind of information one
needs to obtain about real specimens, as well as the methods which today
are available to obtain each particular type of information. Moreover, the
sequence of listing of the information is intended to convey likely, rationa
series of steps in obtaining increasingly detailed structural information.
In other words, the first few steps are quite essential for every piece of s
state work; the next group is necessary for most scientific studies; and
the last two or three are required when sophisticated physical measure-
ments are to be made on the material.

Thus, the first aim would certainly be to determine whether our mate'
is single phase or not - this can be accomplished both by chemical and
structural means of characterization. Here, the polarizing microscope
and powder x ray (and electron diffraction) can in a matter of minutes
provide answers in the case of many real solids. From the same instru-
ments, we would know whether or not the phase(s) were crystalline or nc
crystalline - the rapid increase in the number of devices based on glass:
makes this an important problem. Next, we have listed a simple examin:

which is of interest, to determine the existence of possible changes of structure within the variation of ambience. Many errors and difficulties can be avoided by obtaining this easily determined information early. The next group of measurements is concerned with the description of symmetry (or its absence) from the macroscopic scale of the angles between the faces of a crystal and flaws in them, to the microscopic symmetry of the first coordination sphere of anions surrounding a cation of interest. The final group concerns the determination of the exact position of the atoms, the orientations of the magnetic moments of the electron spins, and the nature of the bonding between the atoms.

However, while we can view the scope of structural characterization in a conceptualized scheme, as outlined above and shown in Table I, we will not present our analysis in the same format. The reasons are quite pragmatic. Structural characterization is performed by instruments and operators trained in a particular instrumental approach, and a survey in depth of their present capability and research needs will be most effective if conducted in these same categories. There is, however, one category which will be seen to be defined by the class of material rather than by the instrumental method, and that is the entire field of noncrystalline or short-range-order-only solids. These will form a unit and their study by all methods will be treated together.

## TABLE I

### STRUCTURAL CHARACTERIZATION AND METHODS FOR ACCOMPLISHING IT

| | |
|---|---|
| Number of, and phases present | Optical microscopy, x-ray diffraction. Small sizes or amounts: electron microscopy and diffraction. |
| Distinguish SROO* from LRO* | Microscopy, x-ray diffraction. |
| Change of structure (transitions) | Differential thermal analysis, microscopy or x ray vs. T or P. |
| Macroscopic morphology, crystal system information | Goniometry, optical microscopy. |
| Unit cell and space group | X ray, rarely neutron, and electron diffraction. |
| Site symmetry in LRO or SROO | Visible absorption; I-r absorption, x-ray diffraction, ESR, x-ray emission and absorption. |
| Position of Atoms | General: x-ray diffraction. Special cases (H; atoms close in at. no.): neutron diffraction. Small ($\ll 2000\,\text{Å}$ dimensions: electron diffraction). |
| Spin configuration | Space Group: neutron diffraction. Point Group: magneto-electric. Direction of magnetization: D.C. magnetic. |
| Bonding (electron dynamics) | Electron density: x-ray diffraction. Spin density: neutron diffraction. Indirect methods. |

* SROO = short-range-order-only, noncrystalline

INCREASING COMPLEXITY
DECREASING FREQUENCY OF USE

## III. PRESENT CAPABILITY IN
## ANALYSIS OF STRUCTURE

### A. INTRODUCTION

It is regrettable that many materials laboratories often function with little or no characterization equipment or personnel whatsoever. At the other extreme, only in a _very few_ research complexes do we find a complete array of equipment for structural characterization operated by research specialists in each field. Structural characterization, which would suffice for many purposes, can be conducted with equipment that is very moderate both in capital cost and operator time and availability. Since the filling-in of a major gap in a research program must always face the administrator with the question of capital and manpower cost, an attempt has been made to provide some data on this subject. Even the most sophisticated characterization is often only a fraction of the cost of the measurement of various properties. Hence, the continued neglect of structural characterization as an integral part of all materials research becomes increasingly difficult to excuse.

Below, in turn, each of the classes of methods by which the 'structure' of a material can be determined is treated in detail.

### B. STRUCTURAL CHARACTERIZATION BY OPTICAL TECHNIQUES

#### Introduction

An optical step is almost inevitable in many materials characterizations; clearly, the first and most obvious thing to do with a new material is to look at it! However, with the wide gamut of sophisticated techniques available for materials studies, what was in earlier times a long, hard look, has now frequently degenerated to a mere cursory glance; and much useful, sometimes vital, information that could be easily obtained from a more perceptive optical study is completely missed.

In the following, we attempt a very brief systematization of the types information that can be obtained from a thorough optical study. Methods that depend primarily on the wavelength of the light are not considered since they are dealt with elsewhere. Thus, we have omitted all emission and absorption spectroscopic methods.

We find it convenient to describe the remaining studies under three main topic headings:

• Morphological and surface studies: In this category, we consider ess tially those methods of characterization which rely on examination of th detailed surface topology of a natural, cleaved, or etched surface. Such studies can be carried out on all solids with well-defined surfaces.

• Bulk properties: In this category are considered methods which can be applied to transparent solids such as refractive index measurement, refraction anisotrophy, rotary dispersion, etc.

• Scattering phenomena: We consider both scattering from distributed and from individual centers, and the very useful information which can obtained on imperfections in transparent crystals.

## Morphological and Surface Studies

Information relevant to the following materials parameters may be obtained from surface studies:

• Crystal symmetry: The external morphology of well-formed crystal can frequently provide to the trained observer quick information on the crystal symmetry; this is often a useful precursor to a full x-ray, elec or neutron diffraction study of the structure. Both naked eye and gonio-metric information are useful, although the latter is now only rarely em ployed.

• Crystal perfection: Etched surfaces can provide quantitative inform:

on internal surfaces and on line defects. Emerging dislocations show
etch pits at the surfaces, and etch pit counting is a standard method for
determining dislocation content. The symmetries of etch pits can give use-
ful additional information on the crystal symmetry.

• Domain studies: Ferroelectric domains etch at different rates accord-
ing to the orientation of the polarization vector with respect to the surface.
Etching is a standard method for observing 180° domains in perovskite
ferroelectrics. Ferromagnetic domains can be viewed by decorating the
flux emergent at the wall region by a colloidal magnetic powder deposited
from a suitable suspending liquid.

• Twinning: Twin boundaries and low angle grain boundaries can often be
observed directly on intersection with the surface. Frequently, the small
tilts associated with internal twinning (as in antiferroelectrics) may be
observed by reflection microscopy or multiple beam interferometry.

• Grain boundaries: In both metals and nonmetals, reflection from a
polished and etched section is a standard method for delineating grain
boundaries. Many methods are available for assessing mean grain size from
measurements on such sections. The technique is also of particular value
in revealing evidence of second phases which frequently segregate at the
grain boundary and are, therefore, very difficult to detect by x-ray methods.

The only equipment necessary for the above studies would be a metal-
lurgical microscope, or a petrographic instrument equipped with objec-
tives for incident illumination. The cost could vary widely depending on
quality and completeness of equipment, ranging from $250 for a basic
system, to $15,000 or more for a complete microphotographic system
with automatic exposure control.

## Special Surface Studies

Beyond the scope of normal microscopic examination, a number of special techniques can be of use in special problems.

a) Multiple and two beam interferometry: Very precise measurement of the surface topology, which can reveal features down to 5Å in height, is possible using the methods of multiple beam interferometry.

b) Ellipsometry: In studies on ultra-clean surfaces, the formation of surface films can be followed by measurement of the azimuth and ellipticity of reflected polarized light (ellipsometry). For thicker films (above 20Å), the method allows a separation of the thickness and refractive index and thickness may be measured for films to a fraction of an Å averaged thickness.

c) Reflectance studies: While it has very recently been shown that modulation of the reflectance of a solid surface by periodic electric[1] and elastic[2] stress fields can give details on surface structure, the principal information deals with the energy band structure and not ionic structures and hence this will not be considered further.

These special techniques are, in general, relatively expensive; and for effective exploitation may require expensive auxiliary equipment, such as ultra-high vacua, sophisticated electronics, or other features. One of the important advantanges is their nondestructive nature.

## Bulk Properties

In transparent solids, precise measurement of the refractive index, the index anisotrophy (birefringence), dispersion, and rotary dispersion may used in the following ways: (details may be found in many excellent text-books).[3]

• Identification: Precise measurement of the refractive index or, more frequently, of the three principal indices of the indicatrix, is frequently

used to characterize minerals. High precision is possible by use of mono-chromatic light with temperature-controlled immersion methods ($\mu \pm 0.0005$). The method is tedious and not completely unequivocal as an identification tool. Routine immersion techniques are capable of determining indices in the higher symmetry systems to $\pm .002$ in a matter of minutes.

•Symmetry: Detailed evaluation of the optical indicatrix can give useful information on the crystal symmetry. These data together with the refractive indices provide one of the most effective structural characterizations of a solid. Optical methods are particularly sensitive in detecting pseudo-symmetric forms of a higher symmetry phase, and, therefore, for detecting phase changes with temperature in ferroelectric, antiferroelectric, and transparent ferrimagnetic crystals.[4]

• Twinning: Because of the optical anisotropy in lower symmetry crystals, twinning can frequently be detected immediately in the polarizing microscope. The effects of superposed twinned regions may give rise to very complex and often beautiful optical patterns.

◦Domain studies: Ferroelectric domains are frequently visible in polarized light through the spontaneous Kerr effect, or may be made visible by a superposed electric field. Ferrimagnetic domains in transparent crystals show optical rotation in polarized light, the sign of rotation changing with the direction of the magnetization vector.

• Phase separation: In thin sections of polycrystalline materials, phase separation may be detected optically before there is any evidence in an x-ray powder study. In critical applications, optical study can be quite indispensable.

• Structural information: In certain cases, specific structural questions

may be answered from the bulk property data above. Thus, the orientation of the $CO_3$ groups in calcite can be deduced from the refractive ind ces; the presence of optical activity can indicate something about the internal atomic structure or the asymmetry of the units in the structure.

### Special Bulk Techniques

In the study of bulk properties, special techniques have been develo with applicability over limited ranges of problems:

• Stress optical analysis: Precise measurement of refractive index, birefringence, can give evidence of internal stress in imperfect crysta and an index of the efficacy of annealing techniques. In special cases, c locations may be observed directly from the stress field around the co

• Harmonic generation: In some transparent crystals of lower syn. useful data can be obtained from the detection of harmonic generation matrix of the higher order optical coefficients is similar to that of the piezoelectric constants, and relates in the same manner to the crystal symmetry.

### Scattering Studies

Scattering studies are essentially adapted to the investigation of het geneous systems where there is a distribution of fine particles (the sc terers) in a transparent matrix. Two types of experiment are possible

1) Measurements of total scattered intensity: No effort is made to separate contributions from the individual scattering centers. The tot scattered intensity is measured as a function of angle and of the wavel of incident light. From these measurements, mean particle size and n of scattering centers may be deduced. If there is a preferred orientati of anisotropic scattering centers, some information may be obtained

the particle anisotrophy. Commercial equipment is available for measuring molecular weight in polymers from total scattered intensities.

2) Individual particle scattering: Two techniques are used for investigating scattering from individual centers. One in the ultra-microscope which measures scattering at 90° to the incident beam; the other is the dark field microscope which measures small angle scattering close to the illumination direction. Very recently, ultra-microscopy has been greatly improved with the use of coherent light sources, and it is possible now to detect microheterogeneities on a very small scale. For example, using a 1 milliwatt gas laser, it is possible to detect by eye 900Å latex spheres in water.[5] With currently available high power laser systems and with photographic recording, it would appear that 'resolution' limits of the order of 100Å are possible in many typical solid-state device crystals; e.g., in ruby laser rods.

## C. STRUCTURAL CHARACTERIZATION OF MATERIALS BY X-RAY DIFFRACTION

### Introduction

X-ray diffraction is one of the most important methods for characterizing materials in the solid state, because the results are derived rather directly from the atomic or molecular arrangement of the substance. X-ray methods are used in: research, development, and quality control in metallurgy, ceramics, the mineral, chemical, and pharmaceutical industries; and practically anywhere the chemical and physical properties must be related to the crystal structure. A modern materials program thus requires extensive use of x-ray analysis. This section outlines the use of the method for the study of materials in the form of:

• Polycrystalline specimens for phase identification, lattice parameter

determination, and certain more sophisticated topics (x-ray powder meth.

• Well-crystallized single crystals for structure determination* (x-ray single crystal methods). The capability at room temperature and pressur will be treated first. Later sections deal with the special problem of high and low-temperature work and high-pressure work.

### X-ray Powder Methods

Counter tube detectors were introduced in commercial x-ray apparat. at the end of World War II. This development launched a vast increase in the use of x-ray methods. Although film techniques are still widely use .. bulk of x-ray powder work is now done with counter tube diffractometers. A conservative estimate is that there are now approximately 3500 x-ray powder diffractometers throughout the world (made by about eight major manufacturers), and perhaps 75% are in the U.S.A. A complete apparatus which includes the x-ray generator, x-ray tube, goniometer, counter tube and its circuits, costs under $20,000. If the useful life is limited (very conservatively) to 10 years, an x-ray tube to 1200 hours and the apparatu used 1200 hours per year, the cost is $16 per day or a few dollars per pattern exclusive of labor, overhead, and maintenance. The time require for the interpretation of the pattern varies over wide limits depending on the experience of the analyst, the quality of the data, and the information required.

While the theory and application of x-ray powder methods is widely known[6,7] and taught in most universities and special courses, the instru mentation and techniques now available are not often used to full advantag

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*The following types of analyses will be omitted, though some are treated elsewhere in this report:
a) Thin film work, b) Microdiffraction, c) Microradiography, d) Thickness gauging, e) X-ray microscopy, f) Stress-strain determination.

because relatively few users take the time to learn and to apply the latest and best methods, including careful specimen preparation.* An example of a recent development that enhances the capability of x-ray methods in complex patterns is illustrated in Fig. 1, which shows the effect of increasing dispersion (by increasing the x-ray wavelength from $CuK\alpha$ to $CrK\alpha$) on line separation. This has been made possible because sufficient intensity can now be obtained using softer x rays.

By present standards, it is possible to define a reasonable standard of a "good" x-ray diffractogram against which performance can be judged. Such a pattern is one of the most important single pieces of physical data for the characterization of a material. "Good" means:

• The resolution is adequate to resolve most of the important lines down to about d=1.5Å ($60°$ $2\theta$ with $CuK\alpha$, $100°$ $2\theta$ with $CrK\alpha$),

• The precision is sufficient to determine the reflection angle to $\pm0.005°$ - $\pm0.01°$ $2\theta$,

• The line profile shape is sufficiently free of instrumental broadening factors to recognize gross lattice imperfections (e.g., disorder stacking, small particle size, etc.),

• The intensities and peak-to-background ratios are adequate for good counting statistics ($\pm5$ to $10\%$ for the principal lines), and the methods of recording the data do not introduce significant errors,

• The pattern has been indexed and all lines related to the crystallography of that substance.**

*The quality of x-ray specimens is often the limiting factor in the accuracy of the x-ray powder data.

**The success of the crystallographic indexing is dependent largely on the precision with which the d spacings are measured. Computer programs have been developed for indexing directly from the powder pattern, and from unit cell dimensions derived from single crystals using x-ray or electron diffraction methods.
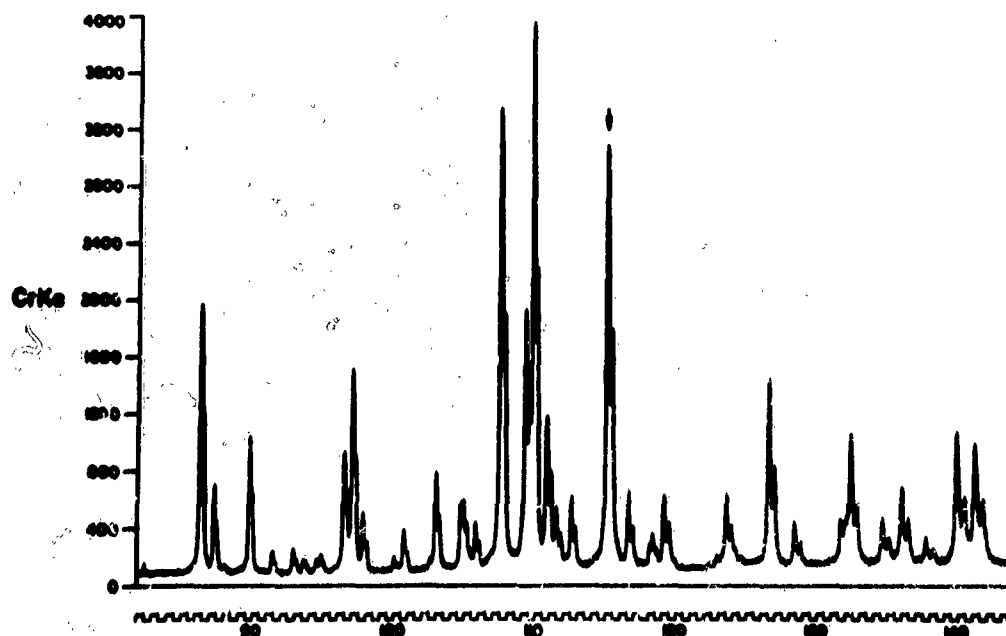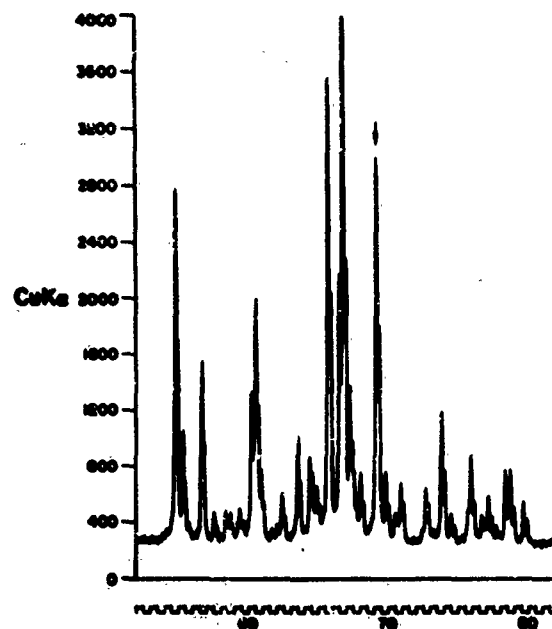
Fig. 1. Portion of topaz powder pattern covering same d-range with CuKα and CrKα radiations. Vacuum diffractometer.

Powder diffractometry can be applied in the following different aspects of materials characterization:

### Phase Identification

Qualitative analysis of polycrystalline materials is the most widely used application of x-ray diffraction. The specimen may be in the form of a fine powder, a solid polycrystalline aggregate, a foil or frozen liquid, etc. The complexity (i.e. number of lines) of a powder pattern increases with increasing unit cell dimensions and decreasing crystallographic symmetry, and is more or less independent of the chemical composition. The use of x-ray diffractograms as a means of "fingerprint" identification is practiced widely, by comparing the spacings and intensities of the lines of the unknown with those of knowns in the A.S.T.M. card files.[8] There is no doubt that this method is the routine, automatable, indispensable minimum, solid-state characterization tool wherever it applies. It is limited only by the number and precision of the "standard" patterns in the card indexes and the precision of the data.

The present A.S.T.M. index has data for about 10,000 substances, and there is a small continuing program for improving and extending the data. For example, there is a project at the National Bureau of Standards to produce high quality standard patterns. There is a great need for expanding the powder standard program by bringing in other groups, but care must be taken to obtain the services of scientists who are well-qualified and well-equipped in this area (see recommendations).

### Quantitative Analysis

The relative amounts of two (or more) phases present in a mixture may also be obtained from powder x-ray data. The accuracy is dependent on the specimen preparation, quality of 'standards,' and the care taken to reduce systematic and random errors. The lower limits of detectability

depend on the complexity of the pattern, the relative x-ray absorption of the phases, and related factors. The range of sensitivity of detection of t second phase is very great; for example, 0.1 weight percent of silicon in tungsten matrix, and 0.01% in a lithium fluoride matrix may be detected with moderate accuracy in reasonable counting times, providing the pro; care and techniques are used. On the other hand, even if the impurity if known, the detection limit is increased when the matrix has a very comp pattern (e.g. to perhaps 10% of magnetite in a granite rock). Amorphous and segregated phases may be missed, and it is advisable to make micr scopic studies of the materials prior to specimen preparation for x-ray analysis.

Lattice Parameter Determination.

The lattice parameters are the averages of millions of unit cell dime sions in the specimen and are important in characterizing materials. A precision of 1% to 0.1% can be obtained rapidly using routine methods. Higher precision measurements of the order of 0.01% or better are requ to determine the coefficients of thermal expansion, the type of isomorphi to locate atomic positions and a variety of other studies. The crystallographic indexing of complex powder patterns requires precise measurements of many reflections in the low-angle region.

There have been many claims in the literature of very high accuracy often exceeding 0.001% based upon the reproducibility of powder camera data, but these measurements may not indicate the real accuracy. The difficulties of reducing and/or properly treating the systematic errors a the various correction factors may limit the accuracy. The observed x-, diffraction profiles recorded with a diffractometer are a convolution of t profiles arising from wavelength and intensity distribution of the inciden x-ray beam, the various instrument factors, diffraction geometry, and

specimen properties. All these factors combine to cause small distortions and shifts of the observed profiles, thereby introducing systematic errors and problems in interpretation when the highest accuracy is sought. Fig. 2 summarizes the results of an international round-robin collaborative study by sixteen laboratories using the same sample of elemental silicon powder.[9] The composite mean value of 25 average values submitted was 5.43054Å at 25° C, standard deviation ±0.00017Å, and the agreement calculated from the highest-lowest/mean was 0.012%. Relative lattice parameter values may be determined with much higher precision. Thus, Bond[10] has described a relatively simple method for single crystal plates in which a precision of a few parts per million was attained. The Kossel technique has been reported to have an accuracy better than 1 part in 50,000 provided certain precautions are taken. The elegant "centroid" method is limited at present to high symmetry substances of small unit cell dimensions, and by the need for better x-ray spectral data.

### Determination of Composition of Solid Solution.

Since there is usually a relatively simple relationship (approaching linearity) between lattice parameter and composition of solid or crystalline solutions, precision measurements of the separation and relative intensities of the lines provide an important and widely used method of materials study and characterization. If proper precautions are observed, one can determine chemical compositions from these structural data. Sensitivities of 0.1% are obtainable in favorable cases.

### Advanced Uses of the Powder Method

The powder method is difficult to apply to the determination of crystal structures except in the most simple cases, because the overlapping reflections prevent unequivocal indexing and measurement of intensities. Although

## THE PRECISION DETERMINATION OF LATTICE PARAMETERS
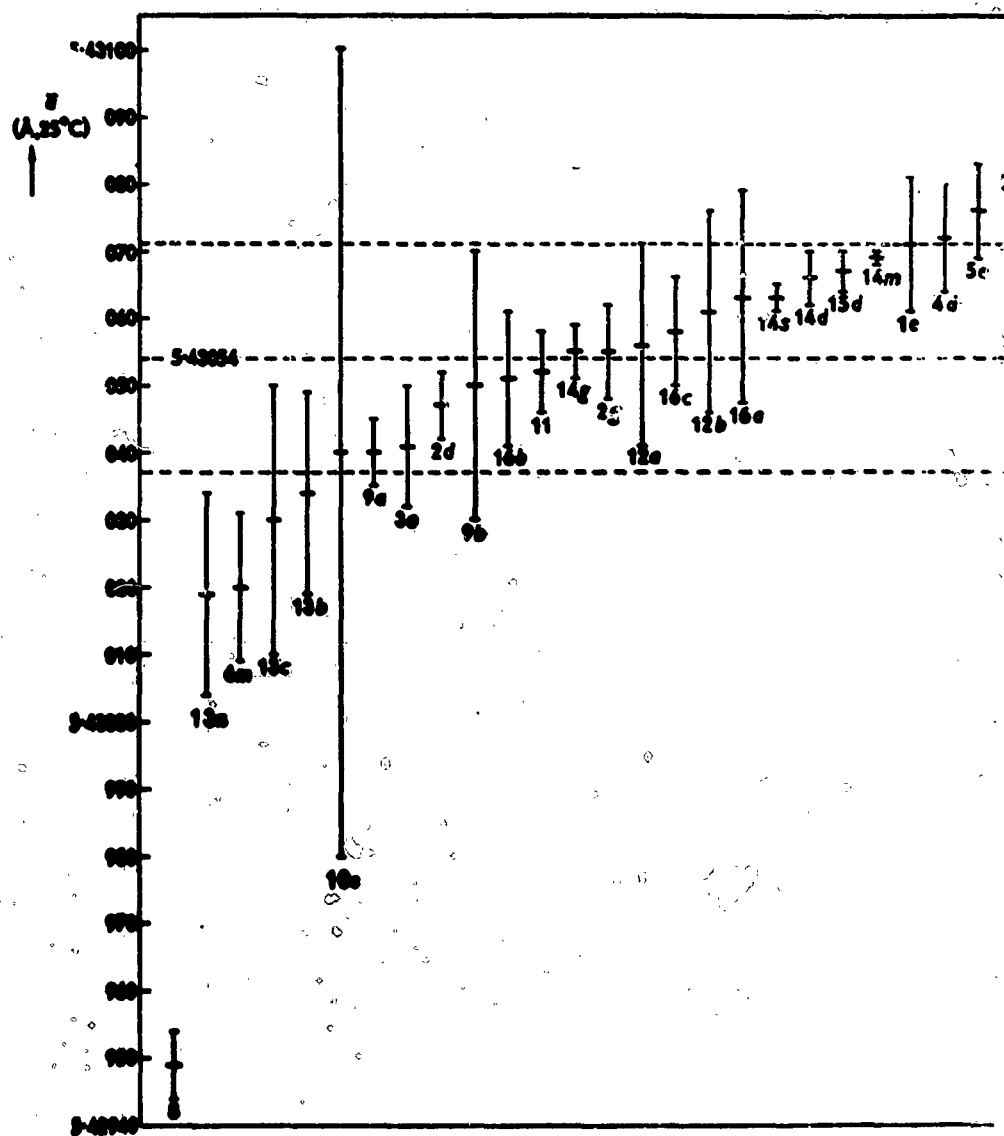


Fig. 2. Distribution of individual mean values (heavy short horizontal lines) of lattice parameter of silicon and ± error limits (vertical lines) reported by various laboratories (Code numbers on bottom). The dotted lines show the composite mean of the mean values and the standard deviation, Code No. 8 omitted.

this is a fundamental limitation that cannot be overcome by better instrumentation, the powder method is, nevertheless, useful for a variety of structure studies, some of which are mentioned below. Since, wherever single crystals are not available, the powder data must be used in any case, the enhancement of this capability is very important.

One of the limitations in precision single crystal diffractometry is the error caused by extinction and absorption. The powder method is useful in determining the magnitude of these corrections by comparing the powder and single crystal data.

The determination of the distribution of unlike atoms over structurally equivalent lattice sites is of considerable importance in solid-state studies as, for example, in the ferrites. If single crystals are not available, the distribution may be determined from accurate intensity measurements of those reflections most sensitive to the variation in composition. By using x-ray wavelengths close to the absorption edge of one of the atoms, it is possible to enhance the difference of the atomic scattering factors for the two atoms (anomalous scattering).

The development of high-precision, counter-tube, intensity measuring techniques makes it possible to apply the x-ray powder method to the study of atomic interactions in crystals. The technique requires accurate, 'absolute,' and relative measurements of the integrated intensities at relatively small diffraction angles, and the determination of the differences of the observed and calculated scattering factors of various structural models. Since the intensities must be measured to an accuracy of the order of 0.1% to 1%, the most careful experimental methods must be used. The results would be used to study such problems as the bonding electron density distributions, radial extension of individual atoms, and electron transfer. It is recommended that support be given to research in this area in order

to learn the effects of the instrumental aberrations, systematic errors, spectral distribution, etc., on the precision of the measurements. The Apparatus Commission of the International Union of Crystallography is currently studying the problem, and collaboration among several laboratories is planned.

### Single Crystal X-ray Methods

The determination of the arrangement of atoms or crystal structure of a substance is one of the outstanding triumphs of 20th-century science and dates back to the discovery of x-ray diffraction in crystals by von Laue in 1912. Hundreds of crystal structures have been worked out, and the results are of inestimable value in our growth of knowledge of the chemistry and physics and, hence, the properties of materials.

Recent developments in the application of high speed, large memory computers to crystal structure analysis, and of semiautomatic and automatic single crystal counter diffractometers for collecting complete three dimensional intensity data with high accuracy, are completely revolutionizing the techniques of structure work and the extension to more complex structures, higher accuracy bond lengths, and electron density maps. Crystal structure determination is not a simple or trivial problem, but with these new developments the availability and cost of a structure determination will improve dramatically. At present, a very large fraction of structure work is carried on at university and government laboratories, but we can look forward (hopefully) to increasing industrial laboratory participation.

It is difficult to estimate the cost of a crystal structure determination because the time required varies over wide limits depending on the complexity of the structure, the accuracy required, the facilities available, and

most important, the experience of the crystallographer. Large biological structures are in a special class and require a very large effort. An attempt to estimate the cost of a determination may be made for a structure of moderate difficulty; e.g., an organic substance in which there are 24 atomic positions or about 200 parameters, including anisotropic temperature factors containing a heavy atom to facilitate phase determination and a bond length accuracy of about 0.008Å. The costs of obtaining an accurate electron density map from a simple known structure such as silicon may be even higher, because the experimental problems are greatly increased and the methods not well established.

Automatic single crystal diffractometers are now being manufactured by several companies and sell for about $75,000. Auxiliary apparatus such as binocular and petrographic microscopes and another x-ray unit, equipped with precession and Weissenberg goniometers, cost an additional $15,000. The field is new and developments are rapid, and assuming a five-year useful life; $3,000 yearly maintenance expense; $2,000 per year for x-ray tubes; and a ten-year useful life for the auxiliary apparatus, the equipment cost is about $21,500 per year. Allowing for vacations, down-time, etc., we assume the equipment is used 75% of the time, and that it takes two weeks of measurements (the apparatus can run day and night) so that the equipment cost is about $1,100 per structure. (If good low-temperature apparatus is added, the cost would be increased by about $650 per structure.) Large-scale computer calculations are then required for data reduction, Patterson and Fourier maps, and least-squares refinements. Assuming efficient programs are available for the computer to be used (and many are), the computer costs may be of the order of $1,500 for the structure. The total costs are thus about $2,600 per structure, or $3,250

if low temperature is used, <u>exclusive</u> of the manpower cost. The cryst lographer would require about six weeks to do the structure and prepa. a report (to which the cost of a technician for about four weeks shoulc added). Using manual methods the time required for the collection of data would be several times longer and would contain subjective error

The replacement of film by automatic counter methods thus provid: potential enormous saving of cost and increase in accuracy. However, is a mistake to assume that all counter data are accurate. There is n; for several good, fundamental, research programs on problems which currently limiting the accuracy and these are indicated below. Presen accuracy of electron density maps, under the most favorable condition using the best techniques, and making all the known corrections, is oi order of 1 to 5% of the atomic number of the atom or, say, 0.1 electro. per cubic angstrom in an organic structure. Genera ly speaking, the accuracy of the map is more or less proportional to the accuracy of t: intensity measurements.

### Present-Day Capability in Precision of Crystal Structure Determir

The results of crystal structure determinations are published in <u>A</u> <u>Crystallographica</u>, <u>Zeitschrift für Kristallographie</u> and, occasionally, a number of other journals such as <u>American Mineralogist</u>, <u>Journal of Metals</u>, etc. Collected reviews of crystal structure determinations ar published in a series of books by International Union of Crystallograph by Wyckoff; efforts are being made to bring these abreast with the cur literature. A review of crystal structure papers published in <u>Acta Cr;</u> <u>lographica</u> from January 1962, to June 1964, shown below, gives some indication of the present state of the field.[11]

TABLE II. ACCURACY OF COUNTER VERSUS FILM X-RAY METHODS

| Type | Method | No. | V/Z $(\text{Å})^3$ | r | $N_p$ | N |
|------|--------|-----|--------------------|---|-------|---|
| Organic | Film | 169 | 100-700 | 0.123 | 80 | 43 |
|  | Counter | 26 | Mean 300 | .090 |  |  |
| Inorganic | Film | 107 | 50-300 | .114 | 30 | 17 |
|  | Counter | 34 | Mean 150 | .076 |  |  |

In this Table, 'V' is the unit cell volume; 'Z' is the number of formula units per unit cell; 'r' = $\Sigma | \Delta F | / \Sigma | F |$; '$N_p$' is the number of parameters (positional, thermal, and scaling); and 'N' is the number of positional parameters. The value of 'r', which has been a traditional measure of the accuracy of a structure determination, is significantly lower for counter-tube measurements than for film.

Results obtained a few years ago with an automatic single crystal diffractometer (used then for the first time) are illustrated by Ladell's work on topaz.[12] They are summarized below, and are _not_ the best that can be obtained if certain corrections and modifications of the technique (now known) are made:

a = 4.6499Å, b = 8.7968Å, c = 8.3909Å: Space group: Pnma

15 levels = 6117 reflections measured with MoKα in 17 days (1° /min). 53 parameters including 15 positional, 36 anisotropic temperature, scale factor and extinction parameter. Using 2230 independence reflections, the calculations gave an r = 0.04; if only those reflections with a counting statistical error < 1.3% are used, r = 0.017 based on 23 reflections per parameter. Positional coordinates ±0.0005Å; bond lengths ±0.0008Å (cf. Alton and West, 1929, ±0.05Å).

The American Crystallographic Association recently sponsored a p ect[13] "to obtain a quantitative comparison of the absolute accuracy, the magnitudes of the various systematic errors...". Seven well-known crystallographers measured the same crystal (a $CaF_2$ sphere sent fro one lab to another) and used all existing types of counter tube apparat and methods. Each lab used $MoK\alpha$ radiation, measured the integrated tensities of every reflection in the (hhl) zone to $\sin\theta/\Lambda = 1.00\text{Å}^{-1}$, m absorption corrections, and calculated the structure factors. Some la also measured other spherical crystals made from the same $CaF_2$ crystal. The agreement between the experiments was stated to be rer ably good, although there was no evidence that any lab obtained $F^2$ valu to better than 2%. The largest systematic error was $\theta$-dependent and probably resulted from extinction.

Limitations in Accuracy

Increased accuracy in structure determination requires good instru tation and methods, as well as the willingness of the crystallographer take the time to explore the various factors which may affect the inter data. Some problems which require further research include:

**Extinction**

**Mosaic spread of the crystal**

**Absorption**

**Methods of handling the background**

**Spectral distribution of the x-ray beam**

**Thermal diffuse scattering corrections**

**Instrument misalignment**

**Mechanical and electronic problems**

**Extinction is an important limiting factor, and the measurement of**

several size crystals and use of different wavelengths, as well as attempts
to treat the crystal to reduce the extinction are being tried. Time also
becomes an important factor in the counting statistical accuracy since
thousands of reflections must be measured. The stability of the x-ray
source and counting circuits and reproducibility of crystal settings also
become limiting factors.

The various methods of overcoming the phase problem are being used
with greater assurance as more experience is gained and experimental
accuracy is increased. There are, however, some problems that require
further study and these may be illustrated by barium titanate.[14] Equally
good explanations of the experimental data were obtained with widely differ-
ent sets of parameters. The neutron diffraction results also led to anom-
alies. The difficulties are caused by a large interaction of the structure
and temperature parameters in the structure factors, and Evans suggests
that this may be a general problem in polar space groups in which the
crystal has a lower symmetry because of small atomic displacements.
Unfortunately, many ferroelectric crystals are of this type: HCN, $PbTiO_3$,
$KH_2PO_4$, etc. It has been recently pointed out, however, that the difficulty
may have been caused in part by antiparallel twinning, and also that
this problem may require taking the imaginary part of the anomalous
scattering into account, which was not done in the barium titanate analysis.

### High- and Low-Temperature X-ray Diffraction

Many materials are used at either high or low temperatures, and their
characterization at those temperatures can be even more important than
the room-temperature study. Since temperature is a variable to which
crystal structures are sensitive, the application of x-ray diffraction to mate-
rials maintained at high and low temperatures is a natural aspect of struc-
ture investigations. Crystalline materials have been studied by x rays

over the temperature range from $1.5^{\circ}$ K to $3000^{\circ}$ C, and recent bibliographie[15] on high-[15] and low-temperature[16] x-ray diffraction have been compiled.

## High Temperature

X-ray diffraction studies at elevated temperatures comprise a major source of data on thermal expansion, high-temperature phase transformations, and reactions such as the oxidation of metals. To obtain such information, it is necessary (1) to maintain the small specimen at high temperatures for extended times without any changes other than the structural ones desired (this may require vacuum conditions or a protective inert atmosphere, and therefore fragile x-ray windows), (2) to measure its temperature accurately, and (3) to observe its change in structure and lattice dimensions (usually over a wide range of diffraction angles) quickly and accurately, using requisite relative motions between source, sample, and film or counter

The two principal instrumental techniques for obtaining high-sample temperatures involve (1) a wire-wound, oven-type resistance heater surrounding the specimen, and (2) a metal-foil resistance heater in direct contact with the sample. Other less prominent methods use (3) induction heating, (4) arc image, solar or electron-beam heating, and (5) self-heating by passing electric current directly through the sample. Typical instrumental details are given in Campbell, et al.,[17] Smith,[18] and Goldschmidt.[19] Data pertinent to the two principal heating methods are given in Table III.

TABLE III. TEMPERATURE CAPABILITY OF
HIGH-TEMPERATURE X-RAY DEVICES

|  | Max. Temp. Used | Sample Temp. Gradient | Temp. Measurement |
|---|---|---|---|
| Oven-type, wound heater | 1400°C (Pt) 2000°C (Mo) | 0.2° at 1000°C | ±1° at 1000°C |
| Ribbon-type, contact heater | 2600°C | large; need auxiliary heaters | ±10° at 1000°C ±50° at 2000°C |

Arc image and direct self-heating (methods 4 and 5 above) have been used
up to 3000°C. Although less common techniques, such as arc image and
electron-beam heating, can involve a cost of $25,000 (excluding normal
x-ray diffraction equipment), the two principal heating methods usually
cost about $5,000 per instrument. However, the total number in use in
laboratories throughout the country probably does not exceed 200.

X-ray diffraction lines (or spots) from a specimen at high temperature
have a lower intensity and higher background than those from specimens
at room or low temperature. One contributing factor, thermal vibration
of the atoms, is intrinsic; it is generally of little consequence for cell
dimension measurements, but limits the accuracy of determining the
atomic positions. The other factor, thermal gradient in the specimen, is
introduced by the experimental procedure. Such high-temperature measure-
ments are normally made on powders, as are most phase transition studies;
a few studies for atomic parameters and phase transitions have been made
on single crystals. High-temperature measurements generally have a lower
accuracy than those made at room temperature because the apparatus is
more complicated; specimen preparation is more difficult; the position
of the specimen is more difficult to locate and to maintain; there may be grain

growth causing poorer crystallite-size statistics; and there may be a thermal gradient in the specimen. Pertinent data for accuracies with powders and single crystals are summarized in Table IV,

TABLE IV. ACCURACY OF HIGH-TEMPERATURE
MEASUREMENT OF:

|  | Cell Dimensions | Atomic Positions |
|---|---|---|
| Powder | .005% to 500° C<br>.01% to 1000° C | No effort |
| Single crystal | Comparable to room-temperature to 1000° C [20] | ±.008Å at 600° C [21] |

For moderately high temperatures (up to ~1300° C), the instrumental problems are not severe; equipment costs are not high; and cell dimension and atomic parameter accuracy are within an order of magnitude of that at room temperature. Modern materials technology, however, requires the extension of structure studies by x-ray diffraction to higher temperatures. Such a development involves difficult experimental problems in the genera tion, maintenance, and precision measurement of higher temperatures; rel ative specimen motion; reduction of temperature gradients; maintenance of specimen surface position; maintenance of high vacuum or gaseous environments; elimination of poor crystallite-size statistics caused by grain growth; and retention of accuracy for cell dimensions and atomic positions by paying heed to x-ray optics and recording techniques (film or counter tube) at higher temperatures. However, it can provide important higher temperature information on thermal expansion, phase changes, and chemical reactions (oxidation, etc.). Further use and development of specializec x-ray geometries; e.g., stationary specimen - movable synchronous x-ray tube and detector; stationary x-ray tube - stationary specimen - multiple counters (Seeman-Bohlin) geometry; etc., may be helpful in solving some of these problems.

## Low Temperature

X-ray diffraction studies are conducted at low temperatures to observe phase transitions; to investigate materials which would be liquids or gases under standard conditions; to obtain coefficients of thermal expansion; and to obtain better atomic positional parameters through increased quantity of diffraction data and improved intensity data afforded by lessening of thermal vibrations.

Low-temperature techniques are applied to powders and to single crystals. Both film and counter methods are used. There are two commonly used basic procedures for obtaining low temperatures. The first normally involves passing a stream of nitrogen, at or near its boiling point, over the sample, which is usually a single crystal mounted on a standard goniometer head, placed in standard cameras or diffractometers. In the second method, powder specimens are placed on a metal block which is in contact with or immersed in the cryogenic medium (e.g., liquid nitrogen or helium). Temperatures are controlled to $\pm 0.1°K$ from 4 to $20°K$ and to better than $\pm 1°K$ at higher temperatures. Control is obtained by admixing warm gas in the cooled stream or by a small heater in or near the metal block. Equipment for liquid nitrogen ($77°K$) and higher temperatures is very common. Liquid helium ($4°K$) facilities are considerably less common and with few exceptions are limited to powder studies by the block technique. A good liquid nitrogen capability can be obtained for $1000 or less (exclusive of x-ray diffraction apparatus), although extremely elaborate feed-back and moisture-free systems may cost $15,000 - $25,000. Liquid helium facilities necessitate an expenditure of $5,000 - $10,000, and are considerably more expensive to operate due to the higher cost of the coolant.

Although low-temperature x-ray diffraction, because of lower thermal

vibrations, permits greater accuracy in the determination of lattice parameters and atomic positions (via intensity measurements); this has not yet been achieved for the latter. Capability data for liquid nitrogen (77° K) and liquid helium (4°K) are summarized in Table V. The entry for atomic positions from single crystals is a projected capability; current achievements fall an order of magnitude short of this. Attempts are underway to increase the accuracy in single-crystal diffractometry at liquid nitrogen temperature. At liquid helium temperature, problems introduced by requisite cryostat instrumentation usually offset potential advantages from still lower thermal vibrations; the net effect is generally a lowering of practical attainable accuracy, particularly for atomic positions via intensities. A new single-crystal technique, however, permits precise cell dimensions at both nitrogen and helium temperatures. There have been little or no atomic position determinations (using intensities) on powder samples.

#### TABLE V. PRECISION OF LOW-TEMPERATURE MEASUREMENT

| | Lattice Parameters | | Atomic Positions | |
|---|---|---|---|---|
| | 78°K | 4°K | 78°K | 4°K |
| Powder | .002%[22] | .01%[23] | prob. ±0.005Å | prob. ±0.05Å |
| Single crystal | .01%[24] | .01%[24] | (±0.0002Å) | no capability |

The situation on cell dimensions at low temperatures appears to be well in hand except for more emphasis on powders at 4°K. Ultimate accuracy in the determination of atomic positions via intensities at 77°K is within reach; for liquid helium temperatures, however, few data have been reported. Current technological interest in the fundamental properties and potential applications of superconductors point to a need for improved structure capability in the range of extremely low temperatures (0° -20° K).

Problems arise with respect to fragile x-ray windows, establishing and maintaining specimen surface position, specimen motion, etc. Special x-ray geometries may be useful.

### High-Pressure X-ray Diffraction

X-ray diffraction studies of substances maintained at high pressures are undertaken to identify new high-pressure phases (unobservable at standard pressure); to determine their crystal structures; and to measure their compressibilities (by determining lattice dimensions vs. pressure). Instrumentally, the problem is to contain a sample in a vessel which is mechanically strong, yet relatively transparent to x rays. Up to approximately 10 kilobars (1 kbar≈1000 atmospheres), the problem is relatively simple. Above such pressures, instrumentation becomes increasingly difficult; at 100 kbars and above, high-pressure x-ray diffraction involves an exceedingly difficult experimental problem. This is a relatively new area of experimental physics, one which requires considerable developmental instrumentation. Crude diffraction patterns however, have been obtained at pressures up to 500 kbars; temperatures up to 1000° C have been applied at 100 kbars.

With very few exceptions, all high-pressure x-ray diffraction studies have involved powder rather than single-crystal specimens. This is due in part to instrumental difficulties (maintenance of quasi-hydrostatic conditions), and in part to the fact that relatively few materials remain as single crystals after passing through a phase transition. The latter circumstance limits such single crystal studies to compressibility measurements where no phase transition is present, and to phase and structure studies of crystals grown within their high-pressure stability fields.

In the range of 10 kbars, a gas-filled bomb with beryllium windows suffices and gives hydrostatic pressures. Since 1949, there has been a

sequence of miniature pressure vessels in which both the bomb and sample are bathed in the x-ray beam. Polycrystalline beryllium, single-crystal beryllium, and single-crystal diamond "containers" have been used for x-ray transparency. More recently, diamond and WC anvils have permitted pressures of 200 and 500 kbars, respectively. Details of such instrumentation have been given by Jamieson and Lawson,[25] Perez-Albuerne, et. al.. and Takahashi and Bassett.[27] Concurrent temperatures to about 350° C are described (this range is now being extended). These techniques employ the Debye-Scherrer geometry and use mostly film recording; counter-tube recording has been used in some of the anvil procedures. Collectively, these procedures suffer to some degree from several disadvantages: large pressure gradients; specimen-preferred orientation; undefined absolute pressures; relatively high-noise level (due to container scattering and x-ra absorption); diffraction lines which are both few and broad, and questionable relative intensities. As a result, no crystal structure determinations (atomic positioning) are possible; except where these are defined by the lattice parameter(s), only the simplest materials can be studied, and cell parameter accuracy is limited to not much better than 0.5%. The latter figure has been improved to at least 0.1% with a technique using Guinier x-ray geometry at pressures up to 200 kbars.[28] Pressure gradient and preferred orientation problems have been virtually eliminated, and meaning ful intensities (permitting atomic positioning) have been obtained with a tetrahedral anvil x-ray diffractometer.[29] The instrument can operate at 100 kbars and 1000°C; its cost, ~ $150,000, however, is prohibitive. Absolute pressures still remain defined to only ± 10% in the 100 kbar range. Table VI summarizes current capabilities in high-pressure powder x-ray diffraction.

## TABLE VI. ESTIMATE OF HIGH-PRESSURE POWDER
### X-RAY DIFFRACTION CAPABILITIES

|  | Lattice Dimensions | Atomic Positions |
|---|---|---|
| Standard pressure | 0.005% | ±.0005Å |
| Approx. 100 kbars | 0.1%[28] | prob. ±0.05Å |

A beginning into high-pressure, single-crystal, x-ray diffraction has been made using a diamond anvil cell to 30 kbars and 250°C in a precession camera,[30] lattice dimension accuracy is in the order of 1%.

Except for the costly tetrahedral apparatus, high-pressure, x-ray diffraction-instrumentation can be set up for $1000 to $10,000, depending on the desired pressure range. The opposed-piston, single-crystal diamond cell, for example, offers an economical means of operation in the 30 kbar range; and is being used not only for x-ray diffraction but also for microscopy and various forms of spectroscopy. Relatively speaking, research using high-pressure x-ray diffraction is not particularly widespread. Along with application of available techniques in the "lower" high-pressure range, considerable effort is called for in instrumental development for the "higher" ranges.

It should be noted that Russian activity in the whole field of high-pressure x-ray work is considerably more extensive than ours, based on first-hand reports of visiting American scientists. It can be said that the Russian effort has succeeded in developing more sophisticated, miniaturized, high-pressure cells for use in a variety of x-ray cameras, including single-crystal arrangements. Our effort has been almost entirely limited to the Debye-Scherrer geometry. Considerably more instrumental development is necessary in this direction, aimed at higher accuracy in lattice dimensions and more meaningful intensities. There is a pronounced need for

refined pressure cells which circumvent problems in pressure gradients,
x-ray beam attenuation, etc.; and which can be used with currently availabl
sophisticated, x-ray geometries.

## D. STRUCTURAL CHARACTERIZATION BY ELECTRON DIFFRACTION AND MICROSCOPY

### Introduction

Electron M and D (microscopy and diffraction) are indicated whenever
one dimension of the particle is 2000Å or less, or when fine surface or
internal structure is in question. It is, therefore, preeminent for thin
films or crystals and for fine-particle characterization where other
methods fail or are of limited utility. Bulk materials can be examined
by thinning down to foils. The chief limitation is that the electron beam
can, in general, give information on materials only less than about 200Å
in thickness by transmission. Where samples are not thinned, informa-
tion on surface structure can be gained by replica techniques and by
reflection diffraction. Several recent books have appeared on the subject
and these provide up-to-date details on the various applications and
capabilities of the technique.[31-34]

There are about 4500 electron microscopes in the world, and of these
2000 are in the U.S., about 1000 in Japan, and 400 in Russia. These
figures reflect Japanese interest and possibly subsidy in E.M.; whereas, th
Russians only recently have made a major effort in E.M., and are now rapi
building up their efforts in E.M. However, over 75% are used for biology,
so that about 300 instruments are used for materials characterization in
this country. Special instruments for electron diffraction only have been
manufactured (e.g., RCA 16 machines) but without much success. Several
individual designs have been described in the literature but they have never
become popular. Electron microscopes can easily be converted to diffracti

but of the 300 machines in use possibly only 100 use electron diffraction for routine problems. An electron microscope with all accessories costs $50,000, and the operating cost per year, including salary and overhead, about $40,000. Cost per sample is about $50, but a specific problem might take several weeks of work. The full benefit of electron microscopy in materials characterization is never gained unless it is done in conjunction with other instruments or techniques, such as x-ray diffraction, emission spectroscopy, light microscopy, electron probe, etc. In each case, independent measurements must be related to the electron microscopy. These costs are not included but must be considered.

Moreover, the purchase of an electron microscope does not solve any problems; it is very unlikely that a technician or graduate will be able to operate the microscope effectively without training. At present, this lack of training is one of the most severe limitations in microscopy.

### Magnification, Precision, Resolution

Most micrographs are taken at from 4000X to 16,000X, but it is possible to work from 300X to about 250,000X. Most magnifications in electron microscopy have an accuracy of about 10%. This is more than satisfactory for over 90% of the problems. At the higher magnification, accuracy may be reduced by 20%.

Most modern microscopes can give a resolution of about 5Å. With a great deal of time and effort, it is possible to show resolution of about 2Å in some few selected specimens. Several Japanese microscopists claim 1.8Å on metals. R.D. Heidenreich has obtained 2.1Å on graphite, and it is possible to generally resolve 2.3Å using fringes. However, there are three different tests for resolution, and there is no agreement as to which method is best. Further, very few materials are suitable for resolution tests. In

more than 95% of problems there is no need for resolutions of better than 5Å, and with most samples it would be difficult to prove resolution of below 10Å. The future need in materials research is not for better resolution in itself but for better use of the present microscopes. Resolution in reflection microscopy is about 100Å at best, but often 200Å or over is more general. In replicas, resolution is about 20Å, at best, with direct replicas. Two stage replicas give about 50Å, and three stage about 100Å resolution. Decoration replicas show, indirectly, faults that may be of unit cell size.

### Accuracy in Electron Diffraction

Electron diffraction is in general done in three ways with commercial electron microscopes:

1. Transmission with a diffraction camera accessory.

2. Selected area diffraction.

3. Reflection diffraction with an accessory.

The precision of the determination of the lattice parameter decreases in the above order as is shown. A = good material; B = normal material; C = poor or amorphous material.

|  | A | B | C |
|---|---|---|---|
| 1. Transmission | .2 - .8% | 1 - 2% | 1% - 8% |
| 2. Selected Area | .3 - 1% | 1 - 3% | 3 - 10% |
| 3. Reflection | .5 - 2% | 2 - 5% | not used |

Only one in several hundred samples gives patterns from which precision measurements can be made. Normally, electron diffraction is a poor second to x-ray diffraction as far as accuracy is concerned. Reduced accuracy may be due to:

particle size line broadening,

refractive doubling,

contamination,

orientation,

defects, twins,

nonstoichiometric samples, and other factors.

For example, in selected area diffraction, removal and reinsertion of a
sample holder can cause an error of 1%. To attain an accuracy of 0.3%,
an internal standard is necessary.

Claims have been made of lattice determinations of 0.1% by electron
diffraction. This is unrealistic and a figure of about 1% is more useful.

### Identification of Phases

Electron diffraction should be used for routine identification only when
the results cannot be obtained with x rays. However, when under certain
conditions it is difficult to obtain reasonable x-ray results, electron micros-
copy can supplement or even exclude x-ray methods; for example, with
thin films, or when very small amounts of second phase are present, or if
the particle size is $\ll 1000\text{Å}$. Thus, EM and ED can identify impurities,
or show that amorphous materials are present at levels well below that
of x rays and should be used for this purpose. Differences in the shape
and habit of crystals in a mixture are readily perceived and each phase can
then be identified by selected area diffraction where x-ray techniques fail.
In favorable cases where a low-level impurity has a distinctive morphology
(i.e., needles in a mixture of cubes), one can detect even 0.1% impurities.
However, although impurities can be found at low levels of even less than
0.1%, it is very difficult to give a percentage figure for the impurity.

In intermediate cases, EM and ED can be used to supplement and
clarify x-ray results. For example, with x-ray powder patterns it is often
difficult or even impossible to index lines in a diffraction pattern if mixtures

are present, whereas, using ED, the problem can be solved by obtaining separate unit cells directly from single crystal data. Likewise, with complex powder patterns of new materials, indexing of x-ray patterns is often difficult, especially if the cell is large. An electron diffraction pattern from a small crystal of this material shows the reciprocal lattice and often gives definite information on the principal axis and symmetry of the crystal. This information when combined with the x-ray powder data can give a rapid solution. As many new materials are often in the form of very small crystals suitable for electron microscopy, the conjunction of ED with x-ray diffraction should be encouraged.

When the crystals are very thin and powder data is insufficient or incomplete, a combination of powder and single-crystal ED can be used alone to identify the material.

### Structure Analysis by Electron Diffraction

It is generally faster and more accurate to have structure done by single crystal x-ray methods than by ED. While Russian workers claim solutions of crystal structure by ED alone, very little of this work is done in the U.S. Most crystallographers consider the Russian claims as exaggerated and point out that in most cases the structure had been solved by x-ray methods before ED solutions were attempted.

However, there is no doubt that the Russian school of ED is at the very least on a level with or ahead of the schools in Australia, Japan, and Great Britain, while there is no equivalent at all in the U.S.

### Low-Energy Electron Diffraction

Low-energy electron diffraction can provide structural information on the first two or three atomic layers. Although it has given important information on the structure of material at surfaces, its use for real materi

characterization is strictly limited, because the method of specimen preparation is so specialized and necessarily alters the nature of the original surface. Further, a strict interpretation is often difficult and as yet not generally accepted. Recent results show that similar effects are produced at the usual high energies used in ED if the surfaces are clean and the vacuum high; this is likely to have a major effect on the LEED field, since it is possible that high energy work will be preferred in many cases.

### High- and Low-Temperature Electron Diffraction

Electron microscope hot- and cold-stages are commercially available as standard items, capable of maintaining temperatures from -180° C to about 1000° C; and some microscopes have been made with liquid helium stages and with hot stages to 2000° C. Several very interesting problems on phase transformations and chemical reactions have been investigated. This field holds great promise for the future and its use is encouraged for dynamic and kinetic problems.

### Special Application to Ferromagnetic and Ferroelectric Methods

Since the electron beam is deflected at ferromagnetic domain boundaries, depending on whether the beam converges or diverges, a light or dark line appears on the micrograph; and the convergent boundaries show interference fringes. Bloch and Néel and hybrid "cross tie" walls can be distinguished. The width of such walls can be measured from micrographs. Fine magnetic ripple is also evident and is orthogonal to the magnetization factor. Thus, the local magnetization vector in various parts of a single domain can be measured. The magnetization configuration within the walls can be shown. By application of an external magnetic field, wall motion can be measured. Films can be made to switch and pinning and reversal can be studied directly. Holes or second phases

rather than dislocations or stacking faults are pinning sites. During these studies the film may be imagined at high magnification, or selected area diffraction patterns taken. By straining, the effect on strain sensitive magnetic materials can be studied. By heating, a rough indication is given of the Curie temperature. The anisotropic dispersion (and field) can be measured. Often these measurements can be made accurately outside the microscope.

Ferroelectric domains have also been observed by electron microscopy in barium titanate; as the domain forms, the lattice constant changes. The is a contrast difference between domains. However, the electron beam can charge the surface and switch domains.

### Some Limitations in Electron Microscopy and Diffraction

Lack of training facilities is the main limitation of electron microscopy in the United States at present. Very few universities have courses in microscopy, and technicians are in general trained while working on the instrument. As a result of this, many microscopes are unused or used we below their potential. Some industrial firms even use the instrument as a showpiece for visitors, but seldom for characterization of materials. This lack has been of concern to the National Society (EMSA), the Nationa Institutes of Health, the ASTM, and the New York Society (NYSEM). The latter made an attempt some time ago to start an institute for microscopy but without success. There are several un. rsities which train microsco: for biological work, but very few for industrial research. As this is the main limitation, it is recommended that the various societies pool their efforts and help several colleges set up appropriate facilities.

### Theory

In electron diffraction, the problem of intensities is much more comple

than for x-ray diffraction. The theoretical treatments are complex and only approximate. In many cases, it is questionable whether crystal structures could have been deduced from electron diffraction intensities if x-ray models were not available. Although Russian workers take a contrary view, it is the general opinion that crystal structure work is more easily and better done by x-ray than by electron diffraction.

Fortunately, the simple kinematic theory is sufficient and semi-quantitative for amorphous and small crystals (below about 100Å). Here it is assumed that the electron has only one interaction and that the scattered and incident beams do not interact.

For thicker crystals, the two-beam dynamic theory gives very reasonable results in image interpretation even though it is approximate. Here the theory considers a single diffracted wave and incident wave, but allows the two beams to interact. However, present theory, although giving a reasonable quantitative picture, is not nearly as well developed as for x rays and so needs further refinement.

For high resolution of the order of 2Å-3Å, contrast is often the limiting factor. The image contrast depends on a phase relationship which is not known with exactitude. At this level of resolution, a compromise has to be made between the various image defects, of which spherical aberration is probably the most serious. However, astigmatism and alignment have to be adjusted exactly to obtain such values. Practice has fortunately led theory in high resolution microscopy and, repeatedly, microscopists have achieved higher resolution than predicted by theory. However, if the theory were better, it might be possible to image atom positions in suitable thin specimens. If the objective can be improved so that the spherical aberration is reduced by a small factor, then it may well be possible to obtain direct

atomic resolution. A superconducting lens offers distinct possibilities for the future.

### Difficulties of Specimen Preparation.

Specimens should be less than 1000Å in thickness for electron microsc‹ and this remains the main experimental difficulty in electron microscopy. In pure materials, specimens can be thinned from the bulk to below this figure by special methods. In materials that have precipitates or, in general, more than one phase, ordinary thinning methods often do not worl There is as yet no general method which can be used for a wide variety of materials. It is possible that ion bombardment at low angles, as some French results suggest, will provide a general method. If such a method were developed, it would give a great impetus to work with many solid materials which have proved difficult or impossible to date. Support for such research should receive high priority.

### Equipment Problems and Possibilities.

High vacuum serious equipment limitation is the poor vacuum present in electron microscopes. Less than $10^{-4}$ mm Hg is common at the specim This means that many problems cannot be attempted or give ambiguous answers.

Sources: At present, point filaments give beams with a double condense of less than $0.5\mu$ spot size; there is a possibility that cold cathode sources would improve resolution. The difficulty is that point sources have a very small emitting surface. It would be best to work at very high magnificatio of about 250,000 for high resolution and at this figure beam intensity is lov A cold cathode may give the high intensity required and a smaller source size than is presently available.

High Voltage Microscopes: Several high voltage machines have been or are being built in the range near $10^6$ volt. They can penetrate much

thicker samples, have less background, and might possibly give higher resolution. They are, however, rather difficult to operate, expensive, and have not given good results so far. Volt machines (500,000) have been built and show resolution of about 2Å. These may well be the best compromise as they are much more easily operated than the $10^6$ volt instruments.

Cryogenic Microscope with Superconducting Lens: Several of these are being built. These solve the vacuum problem and should have much improved objectives. Possibly in the next few years, these machines will resolve atomic positions.

Scanning Electron Microscope.

This machine combines some of the best features of the electron microprobe, the electron microscope, and the optical microscope in an instrument that has been developed into a commercial product of outstanding performance, high reliability, and ease of operation. It is uniquely suited to a large variety of research problems. It may, in the near future, cause a revolution in the study of topographical and electrical features of surfaces and their immediately underlying bulk material. It is the only practical tool for the nondestructive examination of MOS transistors, integrated electronics microdevices as they are working, and for investigating their failures and defects. But it can also be used to examine metal and semiconductor surfaces, phosphor layers, magnetic tape coatings, epitaxial layers, evaporated films; and other surfaces where depth of focus, light scattering, or stereo views are critical. Its application to biology problems is far reaching, and it could also be used in catalysis, surface wear problems, etc. It is very easy to use and does not require a skilled electron microscopist.

In the Scanning Electron Microscope, a beam of electrons 50Å to 100Å
in diameter scans the surface of the specimen. Electrons from the specim
are then detected and amplified. This signal is used to modulate the light
intensity of a cathode-ray tube screen which is scanned in registration
with the electron probe scan. Various types of signal can be used. These
include secondary electron current, the back scatter electron current, the
target current, the electron-beam-induced current, and the electron-
beam-induced target current. Different information is given by each
method of signal collection. Magnification is from 20X to 150,000X, althou
little information is gained above 40,000X. Resolution is routinely 350Å
but can be below 100Å. Depth of field is 1cm at 100X and about 1 $\mu$ at
10,000X. Cost is $85,000. There are about six machines at present in the
U.S. The potential of this machine is not yet evident to electron micros-
copists in general, but this will change in the next year.

The Electron Mirror Microscope is still a research instrument. It has
a rather low resolution (about 800Å), and the electrostatic lens used gives
problems. It is particularly suited for examination of electric and magneti
patterns, but is not yet an instrument of general utility.

## E. NEUTRON DIFFRACTION ANALYSIS OF SOLID STRUCTURES

### Introduction

In comparison with x-ray diffraction methods, the use of neutron dif-
fraction procedures in establishing details of solid structures has develope
along very specialized and restricted lines. Stated very simply, one can
say that applications susceptible to x-ray methods would never be con-
sidered for neutron study and it is only for those cases where the use
of neutron radiation happens to offer additional or unique information that
the power of the neutron technique becomes significant. The following disc
sion will attempt to outline (a) the reasons for this and the limitations of

the technique, (b) the regions of specialized application, and (c) projections of future techniques.

### Neutron Sources

For diffraction applications, it is necessary to use slow (or low energy) neutron radiation, and all known sources are characterized by being continuous spectrum sources; that is, the radiation available over the full wavelength spread of a nearly Maxwellian distribution. Most diffraction techniques utilize a monochromatic beam, and for the neutron case this means a selection of monochromatic band of radiation by crystal reflection or by some alternative mechanical system. This has two implications: (a) a large fraction of the neutron intensity is automatically discarded, and (b) the monochromatic band is of finite width, in no case as sharply defined as the x-ray Ka line. On a quantum intensity comparison, the specific neutron quantum intensity available in such a monochromatic band is many orders of magnitude less than that available from a Ka x-ray tube. Since the absolute scattering amplitudes of an atom for the two types of radiation are quite comparable, this implies that diffracted neutron intensities from samples will be much smaller than equivalent x-ray intensities. Thus, the accuracy of a neutron intensity measurement is practically always limited by statistical considerations.

Nuclear reactors serve as the most intense neutron source and these are notoriously expensive to build (2 to 30 million dollars) and to operate, with annual operating budgets of 15-20% of the capital cost. Accordingly, the expense of supplying neutron radiation to an operating spectrometer is by no means trivial; this may amount to a figure of $50,000 per spectrometer year at an intermediate size reactor. In comparison, an x-ray source operating expense will be only a few percent of this figure even including x-ray tube replacement.

## Spectrometer Facilities

It is estimated that there are about 250 neutron diffraction spectrom-
eters in operation at, perhaps, 100 research reactors distributed through-
out the world. There has been very little commercial development in this
field; 2 or 3 companies will supply semicustom-built units, so that an ove.
whelming fraction of the operating units are individually designed and buil
Naturally, this has meant a wide variety of characteristics in the spectro
eters ranging from minimal to very elegant sophistication. Capital invest
ment in such instruments can vary from $30,000 to $100,000, which is not
incomparable to equivalently designed x-ray units. Because of the slow
rate of neutron data collection, automatic operation of spectrometers is a
necessity; and it is fair to say that the neutron technology is as advanced
here as in x-ray methods. Very elaborate, computer-controlled, neutron
spectrometers have been designed and are in operation at a number of
installations.

## Neutron Properties and Interactions with Matter

Before discussing applications of neutron methods, it is worthwhile to
outline some neutron properties, and the type of interactions that a neutro
can experience in its passage through matter.

a) Nuclear force interaction: Neutrons, being fundamental nuclear
particles, interact with nuclei of atoms through the little-understood
nuclear force interaction. The strength of this is not amenable to calcula-
tion, and recourse must be had to experiment in evaluating its magnitude.
Unlike the x-ray case, there is no regular variation as one proceeds
through the atomic table, with neighboring atoms or nuclei sometimes
exhibiting drastic differences in both magnitude and sign of the scattering
amplitude. Different isotopes of the same atom will sometimes differ

significantly in their scattering characteristics, and there is also observed a dependence upon the spin alignment of a particular isotope. Because of the short range of the nuclear force interaction, nuclear scattering is always isotropic with no form factor dependence, unlike the x-ray case.

b) Magnetic interaction with electrons: Neutrons possess magnetic dipole moments and can interact with electronic magnetic moments or electronic magnetic fields. This can be calculated from first principles, and it turns out to be comparable in magnitude to the above nuclear force interaction. The magnetic scattering amplitude obviously depends upon the electronic structure of the atom and upon the absolute direction of the atomic magnetization. It is characterized with a form factor because of the spatial distribution of the magnetic electrons within the atom.

c) Neutron spin-neutron orbit interaction: In its passage through an atom, the neutron magnetic moment can interact with the electron charge distribution even though the atom is magnetically inert. The resultant scattering amplitude is weak; about two or three orders of magnitude smaller than usual. It is very interesting, however, because it can be described as an imaginary amplitude with scattering phase $90°$ removed from the real nuclear or magnetic amplitude. In principle, it can be used to determine the imaginary part of a crystal structure factor as has been demonstrated in a few cases.

d) Neutron momentum - Energy properties: Slow neutrons, by definition, are those obtained after thermal moderation in a reactor, and hence they possess energy comparable to the thermal energy levels in a solid. At the same time, the momentum that they carry (related to their wavelength) is also quite comparable to that transported in the thermal oscillations or phonons. This favorable relationship can be exploited in obtaining phonon

dispersion curves and frequency distributions. In such experimentation, it is necessary to energy analyze the scattered radiation; and a variety of special spectrometer techniques has been developed to measure this in- elastic scattering.

### Crystal Structure Analysis with Neutrons

Both powder and single crystal procedures have been developed here. As mentioned above, because the cost of a neutron spectrometer is rela- tively high, applications are normally considered only where the use of neutron radiation is clearly advantageous. Two principal areas of investi- tion have grown in the field: (a) studies of hydrogen-containing crystals, and (b) other structures where the neutron amplitudes are favorable. In the former, use is made of the favorable scattering power of a hydrogen center as compared with that of other atom centers so that it becomes entirely feasible to perform complete structure analysis of hydrogenous, organic, or biological crystals. Powder methods are sometimes used in assessing hydrogen atom positions in simple structures but, as with x-ray diffraction, the more complicated structures are handled by single crystal analysis. Representative of the type of hydrogen structures now being studied is the work by Levy and collaborators at Oak Ridge on sucrose which contains 45 nonequivalent atoms in the unit cell. Using a highly developed spectrometer with automatic data collection, Levy studied the intensities of 5000 reflections with data collection over a period of about three months. The resultant structure model showed an agreement factor of 3% considering all reflections. This is as good as has been obtained in x-ray studies. There is some evidence, in these extended structure studie that the agreement factor obtained in neutron studies agrees better with that expected from statistics and reliability of the necessary corrections than is the case for equivalent x-ray studies. An even more complicated

structure study is now reported underway at Harwell on vitamin B-12.

The hydrogen-containing crystal illustration is only one of many, wherein the particular neutron scattering amplitudes may be useful in establishing structural detail. Ordering within the alloy FeCo for instance, can be easily established with neutrons because the scattering amplitudes are very favorable for producing superlattice reflection intensity. Similarly, the Mn and Fe ionic positions in manganese ferrite can be readily studied with neutrons for the same reason. Such applications, of course, depend upon the availability of neutron scattering amplitudes; and a convenient tabulation of these will be found in the review book by Bacon.[35] In this reference book, many specific applications of the neutron technique are discussed.

### Magnetic Structure Analysis

This area has developed into one of great activity because of the unique interaction occurring between neutrons and electrons, and its usefulness in supplying information on electron spin distributions in materials. Since the magnetic scattering depends upon the spin magnetization distribution among the atoms in the unit cell, a new type of magnetic crystallography becomes available, and many ferromagnetic, ferrimagnetic, and antiferro-magnetic substances have been explored by this technique. In addition to the interest in such materials for the application of their physical properties, such magnetic structure studies are of fundamental interest due to their bearing on basic electron interactions among the atoms in the unit cell. The physical properties of materials are to a very large extent dictated by these electron interactions. X-ray methods can and do give us much information on the spatial distribution of electron charge in and between atoms, and the neutron studies supplement this with information on the electron spin distribution.

The magnetic structures that have been studied range from simple ferromagnetic structures to very much more complicated helical-spin structures with periodicities as large as 20-30Å. Both polycrystalline sample and single crystal methods have been utilized, usually with involv temperature and magnetic field control on the scattering sample. In such work it is, of course, necessary to separate the magnetic scattering fro. the nuclear scattering (which is always present), and the auxiliary temperature and field control are very helpful in accomplishing this. Freque the use of polarized neutron radiation in which the neutron spins are all commonly oriented is very helpful. This is particularly true where very weak magnetic scattering is encountered, or where the magnetic scatteri is to be measured very accurately. Recent illustrations of this have occurred in studies of electron spin-pairing in super-conductors, and of the internal magnetization distribution at interatom sites in the simple ferromagnetic elements such as iron and nickel.

Very useful information about magnetic defect structures can be obtai from studies of small angle scattering and magnetic diffuse scattering. T disruption of long range magnetic order, as Curie or Néel temperatures approached, is exhibited as a critical small angle scattering to be found a the (000) or other (hkℓ) reciprocal lattice points; and a number of investi tions have been performed. In the more extreme case of only short range magnetic order being present (at temperatures above the ordering temperature), the small angle scattering is expanded into a distributed diffus scattering. The most complete information is available from a study of both the intensity and energy transfer in the diffuse scattering. This tells not only the spatial correlation of the spins but, as well, it elucidate the time correlations. Along the same line, analysis of the magnetic

diffuse scattering, resulting from the introduction of either magnetic or nonmagnetic impurity atoms into magnetic lattices, has been very rewarding in assessing the spin correlation range. Valuable information supplementing that from nuclear magnetic resonance and Mössbauer measurements has been obtained for a number of such systems.

### Lattice and Spin Dynamics Applications

Because of the favorable energy-momentum relationship with slow neutrons, many details of thermal energy excitations in solids may be studied by neutron scattering. In such experimentation, neutrons of known energy and momentum are scattered by crystals in directions removed from those dictated by Bragg conditions. By energy analysis of the scattered neutrons, the energy and momentum of the thermal atomic oscillation wave (or phonon) responsible for the scattering can be determined. In this way, phonon dispersion curves for the lattice may be obtained; and these may be used in a very fundamental way in assessing interatom force constants, and the range over which the interatom forces act. By similar means, the phonon frequency spectrum may be obtained, and, as well, there have been exploratory studies of phonon lifetimes in some materials. Because of the necessity of energy analysis of the scattered radiation, the measured intensity is low, and work in this field has naturally concentrated at research centers with high-power reactor sources. Nevertheless, there is an increasing research effort being devoted to these problems—perhaps three dozen materials have been studied to date by such methods.

In parallel to such studies of atomic dynamics, equivalent effects of magnetic origin are to be found with magnetic substances. Electron spins are aligned in magnetic materials with interaction energies comparable to atomic bonding, and magnetic inelastic scattering of neutrons can

yield very fundamental information on the strength, directional character, and range of the exchange interaction. It is, of course, necessary to separ the magnetic effects from the phonon effects, and this has been effected by suitable magnetic field application to the specimen, and through use of polarized beams of neutrons. An excellent review of the inelastic scatteri studies which has been performed with slow neutrons has been given by Brockhouse, Hautecler and Stiller,[36] and by Egelstaff.[37]

### Specialized Applications

Because of the great transparency of most materials for neutron radia tion, it is rather easy to obtain diffraction data under conditions where the specimen must be contained in temperature or pressure enclosures. Thus, temperature controlling radiation shields present no particular problem in neutron technology, and both low- and high-temperature appendage apparatus is commonly used. Low temperature cryostats, som in conjunction with simultaneous magnetic or electric field application, have been particularly popular in the field; and it can be said that many more neutron investigations have been carried out in the liquid helium temperature region than have been performed in the x-ray field. Similar technical advantages occur in the high temperature area but have not been particularly exploited by neutron investigators. Likewise, the relatively easy introduction of neutron radiation into and out of high-press sample containers has not been particularly exploited. Two neutron inves tigations of structure modifications at high pressure have been reported to date, and a growing interest in such research should see expanded effort here.

A very useful characteristic of slow neutron sources is the availability of neutron radiation of sufficiently low energy, or sufficiently long wave-length, that Bragg scattering processes from crystals is no longer possibl

This permits a direct study of incoherent, randomly distributed, scattering events such as arise from the presence of impurity centers, vacancies, or other defects. In principle, a study of the differential scattering cross section, or the energy dependence of the total cross section, can yield the "structure factor" of such defect centers. A few studies in this area have been reported; for instance, those dealing with the defects arising from radiation dosage on glass. By way of increasing the intensity of such long wavelength neutron radiation, experimenters in some cases have, with considerable effort and expense, inserted cold moderating regions into the reactor source.

### Future Techniques

Among the new techniques which are being developed in the neutron diffraction field, perhaps the most interesting and potentially useful is the new full-spectrum, pulsed-source method of collecting diffraction data. In the usual diffraction method, a monochromatic portion of the neutron spectrum is selected by a monochromating crystal, and this is scattered by a powder or crystal with intensity measurement at various scattering angle positions. With a pulsed source of neutrons, however, one can use the full spectrum incident on the sample with intensity measurement at a fixed angle with flight-time analysis. Thus, all details in a powder pattern are displayed as a function of neutron wave-length at a fixed scattering angle. In essence, through use of multi-channel analyzers, time resolution replaces angular resolution, and the advantage of this system comes through use of the complete neutron intensity in the beam from the source. Thus, comparing a fixed power neutron source and a pulsed neutron source of the same average power level, it is expected that the former system can supply diffraction data at an improved rate of two

orders of magnitude. Development of such systems has just begun at two centers, one in this country, and one in **Poland-Russia**, and it is expected that there will be much activity here.

Such pulsed systems offer additional technical advantages for some types of investigations. Mentioned above was the usefulness of having a fixed scattering angle system in using high-pressure sample cells. A further advantage comes in high magnetic field studies, where pulsed magnetic fields can be applied to specimens synchronized with the neutron bursts. Short period relaxation phenomena become amenable to study through this technique.

With increased source intensity characteristic of the new high-flux reactors, there should come increased sophistication in the type of experiments being performed. Energy analysis of the inelastically scattered radiation, both magnetic and nonmagnetic, will become increasingly useful and important. A somewhat parallel development is now occurring in polarized beam technology where polarization changes upon scattering are now being studied, and it is expected that there will be increased effort here. In the far future, one can see a complete analysis of the scattering process in a solid by simultaneous polarization and energy analysis.

## F. STRUCTURAL CHARACTERIZATION BY "INDIRECT METHODS"

### Introduction

In the previous sections, we have dealt with those methods - polarizing microscopy, and x-ray, electron, and neutron diffraction - that have traditionally served as the tools of the scientist determining 'crystal structure' or the position of the atoms in a solid. Increasingly, during the last decade or two, physicists have studied various properties of solid

that have, with more or less certainty, been correlated with the structure or relative positions of atoms in a solid. While many of these methods, though specialized, are extremely powerful aids, their usefulness and function in structure determination is not widely appreciated. We have grouped such methods together in this section and, because of the last named circumstance, present here a somewhat more didactic treatment than in the rest of the report.

Structural characterization of a solid begins with the classification into either a crystalline solid, having long-range atomic order, or of a glass, having only short-range atomic order. Of course, there is the simultaneous need to determine whether the material in question is a single phase or contains multiple phases. If it is a single phase, there is still the more subtle need to know whether there are chemical inhomogeneities within a single crystallographic phase, or whether there are ordered defects present that have a size scale intermediate between point (or line or surface) defects and clusters that are large enough to be identified and characterized as a second phase. In the case of glasses, it is much more difficult to obtain information about these more subtle questions, and it is usually necessary to be content with information about the local symmetry in the regions of short-range order.

Given a single phase, crystalline solid, there are several levels of structural information that can be obtained as a function of temperature and pressure. These are listed in Table VII. In the case of crystals containing spontaneous atomic moments, it is necessary to determine the magnetic as well as the atomic symmetry. Identification of the space group provides the maximum amount of information. The atomic space group can be obtained by x-ray, electron, or neutron diffraction.

Nonunique solutions for the magnetic space group can be obtained from n

tron-diffraction data. Supplementary information is often required to obt:

reliable, most probable, magnetic space group.

TABLE VII. CRYSTAL AND MAGNETIC SYMMETRIES
OBTAINED FROM VARIOUS PHYSICAL MEASUREMENTS

| Symmetry | Crystal | Magnetic |
|---|---|---|
| Space Group | X-ray, Electron, Neutron Diff. | Neutron Diff. (not unique) |
| Point Group | Property Tensors* | Magneto-electric $\underset{\approx}{?}$ |
| Local Point Group | ESR, NMR, Mössbauer, dc Magnetism,** Absorption spectra | |
| Atomic moments (magnitude, distribution, orientation) | | d.c. Magnetism,** NMR, Mössbauer, Transport, Bitter Pa terns, Kerr and Far day Effects |

* Optical dielectric constants, elastic constants, charge-mobility tensor, magnetostriction and electrostriction constants.

** Magnetic susceptibility, spontaneous magnetization $M_s$ (T), magnetic anisotropy (crystalline and induced by magnetic anneal, stress, or cold work), magnetostriction.

Since property tensors give information about the rotational symmetri

of a crystal, they can only provide the point group. There are several

property tensors that can be used conveniently: charge-carrier mobility

dielectric constant, magnetostriction or electrostriction, piezo-optical ar

elastic constants. There is only one physical property that, to the best of

our knowledge, provides magnetic point symmetry: this is the magneto-

electric tensor. (Magnetic-point symmetry is a concept that is useful

only for the case of collinear or canted atomic spins.) Unfortunately, this property can only be obtained in crystals that are good insulators and have magnetic ions in a crystal-field potential containing odd terms. Optical techniques are the most straightforward methods of obtaining point symmetries from the dielectric constants. These techniques and the various diffraction techniques are discussed in previous sections of this report.

The magnitudes of atomic magnetic moments and the directions of easy magnetization can be obtained from dc magnetic susceptibilities, magnetic resonance data, magnetostriction constants, and the Mössbauer effect. The distribution and character of magnetic domains is obtained from Bitter patterns and magneto-optics. (In the case of films, electron microscopy is also a successful tool.)

Local atomic symmetries, whether in crystals or glasses, or at point defects, are obtained by a variety of techniques. Optical absorption, Mössbauer effect, and nuclear magnetic resonance (NMR) are general techniques. If there are electrons with unpaired spins, either at atoms having a spontaneous atomic moment or trapped at impurities, electron-spin resonance (ESR) and magnetic susceptibilities are powerful tools. In this section, the problem of local symmetry at crystalline defects is not discussed in general. However, some examples of this type are mentioned.

Although structural characterization does not include the structure of the Fermi surface of collective electrons, it is concerned with the magnetic structure and, therefore, with the magnitude and order of spontaneous atomic moments. In most cases, spontaneous magnetism is associated with localized electrons, for which crystal-field theory

provides a fairly complete theoretical description. However, spontaneous band magnetism may occur if special conditions are present. A combination of susceptibility and transport data can frequently distinguish between band electrons and localized electrons, between superconducting and normal-conducting band electrons.

Finally, much labor and expense can be saved if it is possible to determine the critical temperatures and pressures at which crystallographic, magnetic, and/or electronic phase changes occur. Some supplementary measurements that have proven convenient are listed in Table VIII.

### TABLE VIII. SOME METHODS FOR OBTAINING CRITICAL TEMPERATURES AND PRESSURES

1. Calorimetry: DTA and Specific heat.
2. Diffraction.
3. Susceptibilities: Magnetic for magnetic phase changes (including superconducting $\rightleftarrows$ normal conducting); dielectric for ferroelectric phase changes.
4. Transport: **Resistivity and Seebeck** voltage.
5. Dilatation and Elastic **Constants**.
6. ESR.
7. NMR and Mössbauer.
8. FMR and AFMR.

Note that thermogravimetric measurements should be made to determine whether the chemistry has remained constant on passing through any critical temperature.

**Glossary**: DTA = Differential Thermal Analysis; ESR = Electron Spin Resonance; NMR = Nuclear Magnetic Resonance; FMR = Ferromagnetic or Ferrimagnetic Resonance; and AFMR = Antiferromagnetic Resonance

Because several of the techniques discussed may not be familiar to those usually concerned with structural characterization, a brief statement of the principle of each measurement is followed by specific exampl

that illustrate the type of structural information that can be obtained.

### Point Group Symmetries

#### The Magnetic Effect[38]

Two distinct magnetoelectric effects may occur in certain materials:

One is the appearance of an induced magnetic moment that is proportional

to an applied electric field, $\underset{\sim}{M} = -\underset{\approx}{\alpha} \cdot \underset{\sim}{E}$, and the other is the appearance

of an induced electric moment that is proportional to an applied magnetic

field, $\underset{\sim}{P} = -\underset{\approx}{\alpha} \cdot \underset{\sim}{H}$. The coupling energy is

$$W = \underset{\sim}{E} \cdot \underset{\approx}{\alpha} \cdot \underset{\sim}{M} = \underset{\sim}{M} \cdot \underset{\approx}{\alpha} \cdot \underset{\sim}{E} \tag{1}$$

where the tensor $\underset{\approx}{\alpha}$ transforms according to elements of the magnetic point

group, as defined for the case of collinear or canted spins.

In order that the magnetoelectric effect exist, it is necessary to have

a finite perturbation term of the form

$$< \Psi^{(e)}, H' \Psi^{(o)} >< \Psi^{(o)}, V_{cf} \Psi^{(e)} > / (E^{(e)} - E^{(o)}) \tag{2}$$

where the perturbation energy $H' \propto eE_a z$ is odd in the direction $\underset{\sim}{z}$ along

the applied field $\underset{\sim}{E} = E_a \hat{z}$. This means that the excited state $\Psi^{(e)}$ and the

ground state $\Psi^{(o)}$ are connected by an energy that is odd, and therefore that

the crystal-field potential $V_{cf}$ must contain an odd term. If a cation is lo-

cated at the center of its anion interstice, the crystal-field potential contains

only even terms. However, there are structures, such as corundum $(Al_2O_3)$,

in which the cations are displaced from the centers of symmetry of their

interstices, and in these $V_{cf}$ contains odd terms.

In order to either observe a small induced $\underset{\sim}{P}$ or to apply a large $\underset{\sim}{E}$, it is also necessary to have a crystal that is a good insulator. The first observation of a magnetoelectric effect was in $Cr_2O_3$, which is an insulator having the corundum structure. In this structure, the existence of a threefold-rotation axis eliminates all of the off-diagonal terms in the tensor $\underset{\approx}{\alpha}$. However, the magnetic order found in $Cr_2O_3$ may be distinguished from that found in $\alpha Fe_2O_3$, since the diagonal terms $\alpha_{xx} = \alpha_{yy} = \alpha_\perp$ and $\alpha_{zz} = \alpha_{||}$ exist in the first case and vanish in the second. In $Cr_2O_3$, $|\alpha| \sim 10^{-4} - 10^{-5}$ have been found. (In orthorhombic $Ga_x Fe_{2-x}O_3$, the diagonal terms vanish and the off-diagonal terms exist.)

## Transport Properties.[39]

The electronic current density $\underset{\sim}{J}$ induced by an applied electric field $\underset{\sim}{E}$ is

$$\underset{\sim}{J} = \underset{\approx}{\sigma} \cdot \underset{\sim}{E} = ne\underset{\approx}{\mu} \cdot \underset{\sim}{E} \tag{3}$$

where the mobility tensor $\underset{\approx}{\mu}$ transforms according to elements of the crystal point group.

The mobility components of a band electron are $\overset{\wedge}{\mu}_{ij} = e(\tau/m^*)_{ij}$, where $\tau$ is the mean time between scattering collisions and $m^*$ is the effective mass of the carrier of charge e. From measurements of the temperature dependence of the $\mu_{ij}$, it is possible to determine whether the dominant scattering centers are atomic vacancies, optical phonons, acoustical

phonons, neutral impurities, or ionic impurities. The mobility components

of a small polaron (an electron or hole that is localized to a discrete

atom and its nearest neighbors because of atomic relaxations that trap it),

on the other hand, are given by diffusion theory: $\mu_{ij} = eD_{ij}/kT$, where

$D = D_o \exp(-\epsilon_a/kT)$ and $\epsilon_a$ is the activation energy required for an electron

to hop from one atomic position to another. Since this mobility increases

with increasing temperature, whereas the band-electron mobility decreases,

it is possible to distinguish whether the mobile electrons are localized or

collective. However, this requires a simultaneous knowledge of the

electrical conductivity and the number of carriers as a function of tem-

perature. The number of carriers n is obtained from **Hall-effect** measure-

ments. These latter measurements require extremely high magnetic fields

if the charge-carrier mobility is $\leq 1$ $cm^2/V$-sec. In the case of semi-

conductors, a knowledge of the number of charge carriers is often the

most sensitive and simplest method of obtaining the stoichiometry of the

compound.

The Seebeck voltage is an important supplementary measurement. The

sign of the Seebeck voltage indicates the sign of the dominant charge

carriers, holes or electrons, and its magnitude can often be used as a

qualitative guide to the character of the mobile electrons, whether

localized or collective. With a nearly integral number of electrons per

molecule, collective electrons generally give a Seebeck voltage < 100 $\mu V/^\circ C$, whereas localized electrons may give Seebeck voltages that are much greater than 100 $\mu V/^\circ C$. Anomalous changes in the Seebeck voltage as a function of temperature are also found at magnetic-ordering temperatures. This is particularly important for antiferromagnetic ordering of dilute concentrations of magnetic impurities (localized-electron atomic moments at the impurity atoms) due to coupling via collective electrons. This phenomenon usually occurs at low ($\leq 10^\circ K$) temperatures, but if the collective electrons form a spin-density wave, the magnetic-ordering temperature may approach room temperature. Spontaneous band ferro-magnetism is easily detected by magnetic-susceptibility measurements, but spontaneous band antiferromagnetism (the formation of a spin-density wave) may occur, as in chromium, with no measurable change in a temperature-independent (Pauli) paramagnetism. Therefore, an anomalou increase in the Seebeck voltage at the ordering temperature may provide a useful tool for the detection of spontaneous band antiferromagnetism.

Anomalous changes with temperature or pressure in the electrical conductivity are also a convenient indicator of magnetic and crystallograp phase changes. This is particularly true for high-pressure work. Semi-conducting $\rightleftharpoons$ metallic transitions ($\rho_-/\rho_+ \sim 10^6$, where $\rho_-$ and $\rho_+$ are resistivities below and above the transition temperature, have been found

in $V_2O_3$ and $VO_2$) indicate changes in the translational symmetry either as
a result of magnetic ordering, in which case the transition is second-
order; or as a result of atomic displacements, in which case the transi-
tion is usually first-order. Comparison of isoelectronic $VO_2$ and $NbO_2$
shows that the discontinuity in resistivity between the low-temperature
and high-temperature phases is pronounced in $VO_2$, small in $NbO_2$.
Although both compounds, in the low-temperature phase, show pairing
within the cationic c-axis chains of the rutile structure, the axis of the
V-V pairs is tilted so as to provide a short-V-O bond in low-temperature
$VO_2$, whereas similar tilting does not occur in $NbO_2$. This represents
an example of how structural details may have important consequences
for macroscopic properties.

From measurements of the sign and the number of charge carriers
in an ionic semiconductor, it is possible to infer the valence states in
mixed systems.

Finally, changes in transport properties, as a function of temperature
for different crystallographic directions (for different components of the
mobility tensor), may also give important information about magnetic or
crystallographic structure, if changes in magnetic susceptibility or
magnetization vs. temperature are simultaneously known. For example,
MnP undergoes an antiferromagnetic $\rightleftarrows$ ferromagnetic phase change at $50°$ K.
Since the electrical conductivity only shows an anomaly at this tempera-
ture along the longest orthorhombic axis (the a-axis), it indicates that
the antiferromagnetic order consists of a spiral-spin configuration with
a wavelength that introduces an energy discontinuity at the Fermi surface
in the direction $k_a$. In the case of ferromagnetic FeS, there is a crystal-
lographic transformation below the Curie temperature; the conductivity

parallel to the hexagonal c-axis is not anomalous, but that in the basal plane shows a large change $(\rho_- / \rho_+ \sim 10^3)$. Since the magnetic order does not change, this indicates changes in the translational symmetry within the basal plane that preserve the hexagonal symmetry. X-ray measurements have demonstrated that within the basal planes the close-packed cation planes form triangular clusters.

Elastic Constants. [40-42]

The strain energy $V_e$ and the stress energy $V_\sigma$ are

$$V_e = -\frac{1}{2} \sum_i^6 \sum_j^6 c_{ij} x_i x_j \tag{4}$$

$$V_\sigma = \frac{1}{2} \sum_i^6 \sum_j^6 s_{ij} X_i X_j \tag{5}$$

where the $x_i$ are the six independent components of the total symmetric strain tensor $\underset{\approx}{S}$, and the $X_i$ are the six independent components of a symmetric stress tensor describing an externally applied, mechanical stress. The 21 elastic (stiffness) coefficients are

$$c_{ij} = \partial^2 V_e / \partial x_i \partial x_j \tag{6}$$

and the corresponding compliance coefficients are

$$s_{ij} = \partial^2 V_\sigma / \partial X_i \partial X_j . \tag{7}$$

The components of the strain tensor $\underset{\approx}{S}$ and stress tensor $\underset{\approx}{T}$ are

$$x_i = \partial V_\sigma / \partial X_i \text{ and } X_i = \partial V_e / \partial x_i$$

and the two types of elastic constants are related by

$$\sum_h^6 c_{ih} s_{kh} = \delta_{ik} \tag{8}$$

where $\delta_{ik} = 1$ if $i = k$, $\delta_{ik} = 0$ if $i \neq k$. From symmetry considerations, it is possible to reduce the number of independent elastic constants. In

cubic symmetry, for example, there are only three: $c_{11}$, $c_{12}$, and $c_{44}$.

In general, four different methods are used for measuring the elastic constants of solids:

1) Mechanical and/or optical measurements of static deformations of specimens cut in various orientations. The relationship between the measured deformations and the applied force can be obtained for special geometries from a solution of the general equations of equilibrium subject to the boundary conditions.

2) Observations of frequency, dimensions, and density of resonating devices made of or containing the material to be tested. Frequencies are usually so high that the elastic conditions are essentially adiabatic. Care must be taken to avoid or allow for coupling between various vibrational modes. Evaporated ferromagnetic or piezoelectric films are excellent transducers with good coupling. The two principal problems with this technique are:

a) power and impedance matching, and

b) detection, which requires that the elastic wave have the same phase over an entire surface of the crystal. The latter requirement sets a practical limit to the frequency of $\nu \approx 10^{11}$ cycles/sec.

3) Observation of changes in the refractive indices in the presence of ultrasonic waves (piezo-optic effect). Although the method is indirect and complicated, it appears to be capable of precisions comparable to the other two methods (some uncertainty in third significant figure).

4) Measurement of sound velocity with CW or pulse techniques.

## Local Symmetry

General Principles: Measurements of local symmetry are all based on the strategy of obtaining energy differences between different states of

atoms or complexes. In most instances these states are electronic states but they may also be vibrational states. In contrast to molecules, rotational states are not generally excited in a solid. Since there are, in general, many excited states, these measurements provide a spectrum of many resonant energies. A successful experiment requires not only the resolution of these energies, each of which has a finite linewidth, but also the identification of these energies with a particular transition. The identification is accomplished by starting with a theoretical model for the possible local symmetries, a knowledge of selection rules for coupling between states, and the ability to alter the experimental conditions (vari- ation of applied magnetic, elastic, or stress fields and/or of the plane of polarization of radiant energy), in order to remove degeneracies and/ or to change the selection rules. Because the vibrational modes of the molecular units of a glass or the energy levels of localized electrons in a crystal are determined by the local symmetry, successful matching of a theoretical model with an observed spectrum of resonant energies provides positive identification of the local symmetry. Localized electron crystals are most commonly associated with transition-metal or rare- earth atoms, but they may also occur in defect traps or at impurity atoms

There are two important restrictions for this type of measurement:

1) The sample must be transparent to the radiant energy used to ex- cite the system.

2) It must be possible to both resolve and identify all the resonant energies. If there are too many types of symmetry centers simultaneously present, the energy spectrum becomes too complex.

Absorption and Emission Spectra in Visible Regime.[43-45] Electr magnetic radiation in the visible (and near infrared) regions may be

dispersed (sweep of frequency, and therefore of energy $\hbar\omega$) into monochro-
matic components by commercially available monochromators utilizing
either prisms or diffraction gratings. Detection of the radiation may be
accomplished either photoelectrically or photographically. The total cost
of an installation is about $10,000.

If a sample is placed in the beam of radiant energy, then absorption
maxima occur at resonant energies $\hbar\omega_R$ corresponding to allowed energy
transitions. It is possible to resolve energy separations as small as
$\sim 1 \text{ cm}^{-1}$. If the incident radiation is polarized and its plane of polariza-
tion is variable relative to the crystal orientation, it is sometimes pos-
sible to alter the selection rules, which greatly aids in the identification
of the observed resonant energies. Emission spectra are obtained by
pumping with a high-energy radiation and observing the emitted radiation.
This is a useful supplement to absorption spectroscopy.

Some examples of the type of structural information that can be obtained
are the following:

a) The local site symmetry and ionization for transition-metal or rare-
earth ions as dilute impurities in optically transparent host crystals: This
type of study is important not only as a measure of the strength and symme-
tries of the internal crystalline fields and their influence on multiplet split-
tings, but also as a measure of the broadening of certain transitions as a re-
sult of excitations to orbitals of different mean radial extension. Such infor-
mation has an immediate practical application in the evaluation of host crys-
tals for optically pumped lasers. It has also been used to identify transitions
from static to dynamic Jahn-Teller distortions of the local-site symmetry.

b) Distribution and local symmetries of impurities in semiconductors:
In these experiments, stress is applied to remove degeneracies, and the
plane of polarization of radiant energy is rotated with respect to the stress

vectors in order to vary the selection rules.

c) Orientations of F centers: Aspherical potentials for the trapped electrons in F centers could be detected by observing the change in resonant absorption with rotation of the plane of polarization of radiant energy.

d) Surface-state energies relative to the edge of the conduction band in semiconductors: Large electric fields, which are obtained by placing the semiconducting sample in an electrolyte between the plates of a condense change the curvature of $E_b$ vs. x, where $E_b$ is the bottom of the conductio band, and x is the distance from the surface. If electrons are injected into a p-type region (or vice-versa), direct electron-hole recombination gives rise to luminescence. However, the presence of surface states within the gap of forbidden energies offers an alternative, nonradiative path for hole-electron recombination. Therefore, the amplitude of the luminescence varies with the position of the surface states relative to the band edge, which can be altered by the application of an external field.

e) Symmetry of molecular subunits from vibrational energy spectrum obtained at infrared frequencies.

f) Phonon and spin-wave spectra, which are structure sensitive, from Raman scattering: Advantage is taken of the intense, coherent sources of radiant energy now available in laser beams. Raman scattering by phono or spin waves is inelastic and, therefore, shifts the wavelength of the scattered light. In these experiments, the frequency of the radiant energy is fixed, and the spectrum of energies of the Raman-scattered light is obtained.

### Electron Spin Resonance.

If one or more electrons of unpaired spin are localized, either on a para magnetic ion or in an F center or other trap, then information about the

local symmetry can be obtained by using radiant energy of microwave frequencies and subjecting the sample to a variable magnetic field. The energies that are resolved by this technique cover the range $0.001 < \hbar\omega < 3 \text{ cm}^{-1}$. The fact that microwave measurements are generally done in cavities forces them to be done at a fixed frequency. Therefore, in order to obtain an energy spectrum, it is necessary to sweep the applied field $H_a$. As shown schematically in Fig. 1, this sweeps the magnitudes of the energy splittings, and resonant absorption is observed wherever the splittings of allowed transitions match the fixed frequency corresponding to $\hbar\omega$.

From Fig. 3, it is clear that the observed splittings are influenced not only by $H_a$, but also by the crystal-field and spin-orbit splittings. With good resolution of the resonance lines, it is also possible to observe hyperfine splittings due to interactions between the electron spin $\underset{\sim}{S}$ and the nuclear spin $\underset{\sim}{I}$, or even superhyperfine splittings due to interactions of $\underset{\sim}{S}$ and the nuclear spins on neighboring atoms $\underset{\sim}{I}_n$. There are also quadrupole effects that influence the hyperfine splittings. The general spin Hamiltonian that reflects the local point symmetry has the form

$$H_{spin} = \underset{\sim}{H}_a \cdot \underset{\approx}{g} \cdot \underset{\sim}{S}\mu_B + D(\underset{\sim}{S}) + A(\underset{\sim}{I} \cdot \underset{\sim}{S}) + \Sigma a \underset{\sim}{I}_n \cdot \underset{\sim}{S} + Q \tag{9}$$

where $\underset{\approx}{g}$ is the spectroscopic splitting tensor, $\mu_B$ is the Bohr magneton, $D(S)$ includes the crystal-field and spin-orbit splitting, and $Q$ is the quadrupole term.

Although the fundamental theory is known so that only computational difficulties remain for the matching of the observed spectrum with a given mathematical model, nevertheless, the technique is generally restricted to single crystals ($\sim 1 \text{mm}^3$) that contain only a dilute concentration of paramagnetic ions. This restriction is due to the line broadening that otherwise occurs as a result of internal anisotropy fields, which differ from site to site
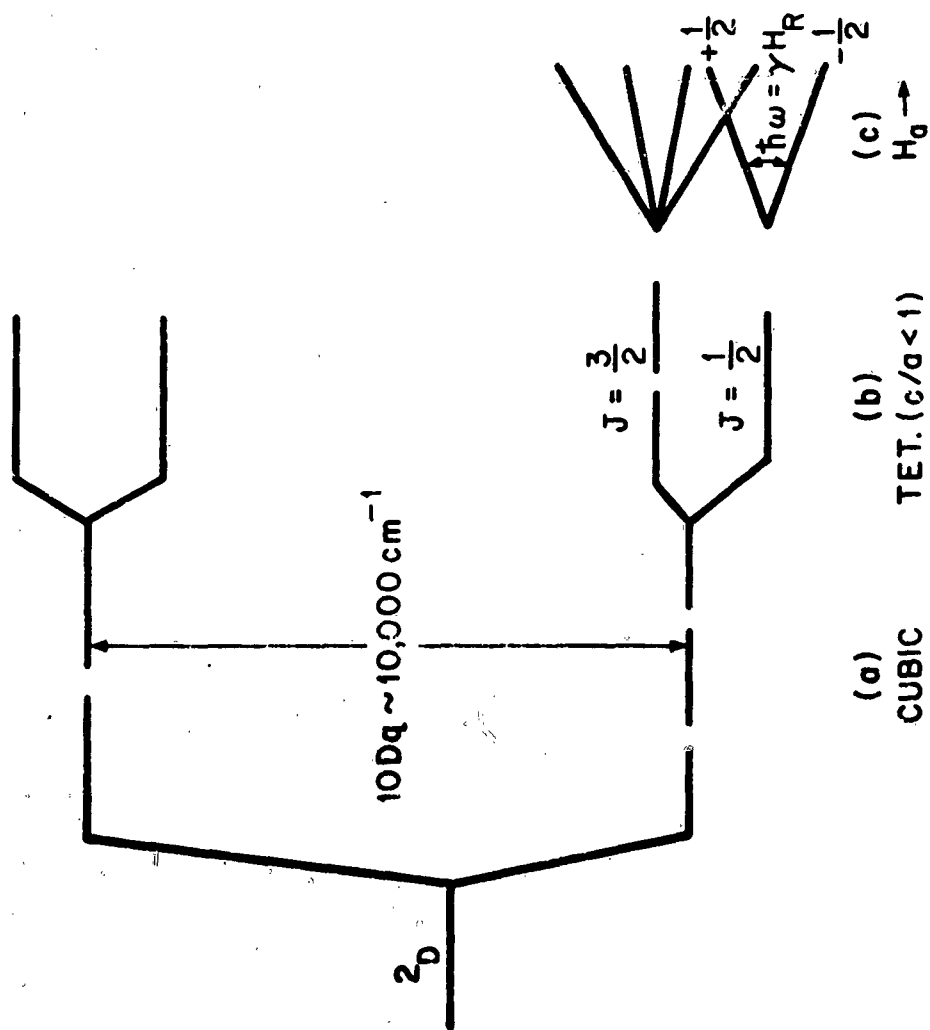
Fig. 3. Schematic energy diagram for a single electron in (a) a cubic, octahedral site; (b) and (c) a tetragonally distorted (c/a < 1) octahedral site

in amorphous or powdered materials and dipole-dipole interactions. Thermal line broadening, which is primarily due to spin-lattice interaction, usually requires the use of low temperature (liquid nitrogen or lower). Although the technique is limited to crystals that are transparent to microwaves, it is applicable to all insulators that have low dielectric loss. Cost of commercial instrumentation is about $50,000 for simple ESR; about $100,000 for equipment capable of resolving hyperfine and super-hyperfine splittings with extreme accuracy. (This cost could be reduced considerably.) There is a definite trend toward more and more automation in the recording and processing of the data.

Some examples of the type of structural information that can be obtained are the following:

a) Orientations of the planar rings in a diphenyl single crystal: A molecule of phenanthrene, which can be excited by light to a triplet state, is similar to a diphenyl molecule in both size and shape differing only in the addition of two coplanar carbon atoms. If a trace of phenanthrene is added to a diphenyl crystal, it substitutes for diphenyl molecules. If these molecules are excited by light to the triplet state, measurement of the absorption of plane-polarized radiant energy as a function of crystal orientation provides a measure of the orientations of the planar molecules within a precision of $\sim 1°$.

b) Identification of location and ionization of chromium in CdS:Cr: CdS has the wurtzite structure. The problem was to distinguish the chromium ionization, and whether the chromium impurities substitute at tetrahedral sites or enter interstitially. It was determined that the chromium is present as $Cr^{2+}$ in interstitial (slightly distorted, octahedral) positions. Measurement of resonant fields at a single fixed frequency gives an ambiguous result, because there are several alternative models

with unknown splittings as a result of possible local, Jahn-Teller distortions. However, the problem was resolved by making measurements at a number of fixed frequencies.

c) .· servation of transition temperatures with an S-state-ion probe: Pressure transforms CdS to the rocksalt structure, and this high-pressure phase can be maintained at atmospheric pressure if kept at liquid-nitrogen temperatures. $Mn^{2+}$ probes can be substituted for the $Cd^{2+}$ ions. This ion is in a $^6S$ state, which is not split by crystalline fields or spin-orbit couplings. However, the hyperfine splitting (~75 guass) is sensitive to the amount of covalence, and, therefore, to whether the $Mn^{2+}$ ions are in octahedral or tetrahedral sites. In the case of CdS with rocksalt structure, formation of the new phase under pressure produces a powder specimen, so that the details of the hyperfine structure are not resolved (the relative amplitudes of the resolved lines would be different for different symmetries). Nevertheless, it is possible to observe a transition from the rocksalt to the wurtzite and sphalerite structures at about $-80^\circ C$.

$Gd^{3+}$ ($^8S$) has been substituted into the perovskites $SrTiO_3$ and $BaTiO_3$ to provide a similar probe for the ferroelectric transitions in these compounds.

d) Superhyperfine splittings: Resolution of the superhyperfine splittings requires highly symmetric and uniform sites for the localized electrons in order to reduce the number of possible lines. A double resonance (ENDOR) technique, which is discussed in the section on double resonance, may be used to obtain a fine resolution. However, the superhyperfine splittings may occasionally be large. For example, $SnO_2:V^{4+}$ and $SnO_2$ $Nb^{4+}$ exhibit splittings of 170 and 400 guass, respectively, whereas in $K_2Pt$ Ir and $CdS:Mn^{2+}$, the splittings are only 2 and 4 guass, respectively. The single d electron at $V^{4+}$ and $Nb^{4+}$ interact symmetrically with the spins of

the near-neighbor tin nuclei, indicating that these ions enter substitution-
ally for the tin in $SnO_2$. The anomalously large splittings indicate that the
singly occupied d orbitals have an anomalously large radial extension,
which is compatible with the fact that transition-metal oxides with rutile
structure tend to be metallic.

### Nuclear Magnetic Resonance

In a nuclear-magnetic-resonance (NMR) experiment, the radiant energy
couples directly to a nuclear spin $\underset{\sim}{I}$. In this case, the resonant energies are
given by

$$\hbar\omega_R = \gamma_n H_n$$

$$\underset{\sim}{H}_n = (\underset{\sim}{H}_a - N\underset{\sim}{M})(1 - \sigma) + (A/\gamma_n)\overline{\underset{\sim}{S}} + \sum_n a\overline{\underset{\sim}{I}}_n \tag{10}$$

$$+ q[m_I^2 - \frac{1}{3}I(I+1)]$$

and $\gamma_n = ge/2Mc = (m/M)\gamma$ is responsible for a resonant frequency that
is smaller than that found in ESR experiments by roughly the ratio of the
electron to nuclear mass. In an applied field $H_a \sim 5$ K guass, the resonant
frequencies for protons are in the Mc/sec range, and it is convenient to
sweep frequency in a fixed $H_a$. For transition-metal atoms, the resonant
frequencies are usually in the more awkward VHF or UHF range, but it is
still possible to instrument for a variable frequency in the desired range.
The first term in $H_n$ represents reduction of the applied field at the nucleus
by the demagnetizing factor NM and a chemical screening factor $\sigma$ that
arises from induced spin density at the nucleus (core polarization, cova-
lency, or conduction-electron polarization). In ionic compounds, the shift
in the resonant frequency due to $\sigma \neq 0$ is called the chemical shift. In
metals it is generally larger and is called the Knight shift. The second
term in $H_n$ arises from the coupling $A\underset{\sim}{I} \cdot \underset{\sim}{S}$ between the nuclear spin and
any unpaired electron spin. This term vanishes in the paramagnetic range

of temperature. The third term represents coupling with the spins of neighboring nuclei, and the last term is the quadrupole term.

This technique, which has an installation cost of about $30,000, including the magnet and power supply, has three general restrictions.

1) The sample must be transparent to radio frequencies, which restricts it to nonmetals, powdered metals (or metal sponge), and metallic films.

2) There must be a large number of identical sites to get sufficient signal without broadening of the lines. Sensitivity depends upon a homogeneous field and the absence of paramagnetic impurities, as well as of nuclear species being measured.

3) The atomic nucleus must have a spin. Further, not only must the frequency range swept overlap the resonant frequencies, but also the power must be correct since too much power saturates the system.

Some examples of the type of structural information that can be obtained are the following:

a) Determination of valence state and local environment: The chemic shift differs for the same atom in different valence states and local environments. In addition, the third term gives a different fine structure for different environments. This method may be particularly useful for the identification of many, like molecular clusters in amorphous materials.

b) Determination of low-temperature spin configurations: From the second term in $H_n$, the resonant frequency $\omega_R$ depends upon $\underset{\sim}{\bar{S}}$ below a magnetic-ordering temperature. This permits a determination of the angle between noncollinear ordered spins. For example, in the spinel $Mn^{2+}[Cr_2^{3+}]O_4$, the spin configuration at low temperatures is a complex magnetic spiral. Neutron diffraction does not provide a unique solution,

and it would be helpful to have the angle $\theta$ between the B-site spins. This can be obtained from the fact that $\bar{\bar{\text{S}}}$ varies with the angle between $\underset{\sim}{\text{H}}_a$ and the spin $\underset{\sim}{\text{S}}$.

c) Line narrowing with increasing temperature may signal onset of additional vibrational or rotational degrees of freedom: In a rigid structure, dipole-dipole interactions introduce variations in $\text{H}_i$ that broaden the resonance lines. The dipole-dipole interactions are proportional to $3<\cos^2\theta_{ij}> - 1$. If increasing temperature introduces additional degrees of freedom and the motions are rapid enough, then the average value $<\cos^2\theta_{ij}> \to 1/3$ and the contribution to line broadening from dipole-dipole interactions disappears.

d) Presence of a quadrupole term gives information on crystal-field gradients at the nucleus: The quadrupole term is zero if $I \leq 1/2$ or if the nucleus is in a cubic field. The presence of unlike near neighbors, or the displacement of an ion from the center of symmetry of its interstice, may create a gradient at the nucleus and, hence, a quadrupole term if $I > 1/2$. This can provide information on the near-neighbor distribution of unlike atoms or on the existence of unique crystal-field axes. Measurements of relative intensity vs. orientation of a single crystal relative to plane-polarized radiation gives the orientations of the unique axes. However, the quadrupole term usually, because of the presence of crystal defects, only contributes to the line broadening.

### Double Resonance

Double resonance (ENDOR) is a combination of ESR and NMR that permits better resolution of the hyperfine or superhyperfine structure present in ESR measurements, but retains the much greater sensitivity of the ESR measurement. The technique is to pump at an ESR frequency with sufficient

power to saturate the population of the upper state. If this is done, there i
no resonant absorption, since nearly as much energy is being emitted as
absorbed. If the populations, within the two main energy levels responsib
for ESR, are altered by the additional application of an RF excitation that
is frequency swept so as to introduce NMR between the fine-structure le
it is possible to remove the saturation condition and cause the ESR line t
reappear. Moderate NMR power levels are used to saturate the NMR s g,
thus maximizing the effect. This technique has been used successfully to
resolve the superhyperfine structure of the ESR of electrons trapped at F
centers and at donor atoms in semiconductors. The superhyperfine stru
gives information about the point symmetry of the near neighbors to a
trapping site, as has already been pointed out.

### Resonance in Exchange Coupled Systems

Ferromagnetic, ferrimagnetic, and antiferromagnetic resonance are
ilar to paramagnetic resonance (ESR), and an experimental installation,
cluding magnet and power supplies, is about $30,000. The main differenc
the presence of strong exchange forces. As a result, the atomic moment
tend to precess <u>coherently</u> about their equilibrium orientation in the pres
of an applied field $\underset{\sim}{H}_a$. If $\underset{\sim}{H}_a$ is large enough to remove the domain struct
the process can be viewed as the precession of the total moment of a fer
magnet, or of the total sublattice moments of a ferrimagnet or an anti-
ferromagnet. Since the smallest change in angular momentum correspor
to the reversal of a single electronic spin, the difference in energy betw
adjacent states is

$$\hbar\omega_R = -g\mu_B H_e \tag{11}$$

where $H_e$ is an effective magnetic field. In the case of a ferromagnet, H
depends upon $H_a$, the demagnetizing fields due to sample shape, and the

crystalline anisotropy. A fixed microwave frequency is used, and the applied field is swept through the resonance condition. The g-factor is the component of a tensor that depends upon spin-orbit coupling and, hence, upon the symmetry and strength of the crystalline fields via their influence on the multiplet splittings.

In a collinear ferrimagnet, the g-factor becomes

$$g_{eff} = (M_{As} - M_{Bs}) / [(M_{As}/g_A) - (M_{Bs}/g_B)] \tag{12}$$

where the subscripts A and B refer to the two sublattices. This fact allows determination of the angular-momentum compensation temperature. In a ferrimagnet, the spontaneous sublattice magnetizations $M_{As}$ and $M_{Bs}$ and the sublattice angular moments $\Sigma S_A = M_{As}/\gamma_A$ and $\Sigma S_B = M_{Bs}/\gamma_B$ usually have different temperature dependences. As a result, it is possible, in a few materials, to have the net magnetization $M_s = (M_{As} - M_{Bs})$ and the net spin angular momentum $\Sigma S = (M_{As}/\gamma_A) - (M_{Bs}/\gamma_B)$ pass through zero and change sign at some temperature below the Curie temperature. This compensation temperature $T_{cm}$ for the magnetization is usually slightly different from the compensation temperature $T_{cs}$ for the spin angular momentum. It is clear from Eq. (12) that $g_{eff}$ becomes negatively infinite on one side of $T_{cs}$ and positively infinite on the other. In ferrimagnetism, there is also an <u>exchange-resonance</u> mode which represents precession about the intersublattice exchange field.

Antiferromagnetism corresponds to ferrimagnetism in which $g_A = g_B$ and the anisotropy fields are $H_{KA} - H_{KB} = H_K$. In this case the effective field, in the absence of an applied field ($H_a = 0$), reduces to

$$H_e = [H_K(H_K + H_E)]^{1/2} \approx (H_K H_E)^{1/2} \tag{13}$$

where $H_E$ is the intersublattice exchange field. This measurement is useful, in conjunction with d.c. magnetic measurements, for the

determination of the strength of the intersublattice exchange, magnetic a[?] ropy, and the g tensor. Since AFMR is usually done with $H_a = 0$, it is possible to use powder specimens.

Mössbauer Effect.[46]

The Mössbauer effect is a resonant fluorescence of $\gamma$-ray with a freq[?] precision $\Delta\omega/\omega \sim 10^{-12}$ corresponding to $\Delta E \approx 10^{-8}$ eV, which is sufficie[?] resolve hyperfine splittings of $10^{-4} - 10^{-5}$ eV. Although it involves only [?] relatively simple experimental technique (cost of installation less than $10,000), its application is restricted.

In order to have resonant fluorescence of $\gamma$-rays, the energy of the radiant $\gamma$-ray, which comes from an emitter atom, must equal the energ[?] of the absorbed $\gamma$-ray. A free-atom emitter or absorber suffers a recoi[?] energy $R = E_{12}^2/2Mc$, where M is the mass of the emitting (or absorbing) nucleus, and $E_{12}$ is the energy difference between two nuclear states. T[?] means that the emitted $\gamma$-ray has an energy $E_{12} - R$, whereas the absorb[?] $\gamma$-ray has the energy $E_{12} + R$. In order to have resonant fluorescence, it is necessary to have $R \approx 0$; and this condition is realized for a certain fraction of events if the absorber and emitter are bound in a solid, cryst[?] line or amorphous.

From the uncertainty principle, $\Delta E \approx \hbar/\tau \sim 10^{-8}$ eV for a relaxation t[?] $\tau \sim 10^{-7}$ sec. If $E_{12} \sim 10$ KeV, then $\Delta\omega/\omega = \Delta E/E \sim 10^{-12}$ and $\Delta E \sim 10^{-8}$

The experimental problem is to obtain a monochromatic source and t[?] sweep the frequency. The frequency is changed by moving the emitter relative to the absorber. Relative motions of $\sim$ 1cm/sec provide sufficie[?] Doppler shift to sweep through the desired frequency range. The isotope $Fe^{57}$ has a $\gamma$-ray energy $E_{12} = 14.4$ KeV with $\tau \sim 10^{-7}$ sec and is therefore convenient. Cubic paramagnetic salts, which have no quadrupole

splitting, give a time-averaged $\langle H_n \rangle = 0$, since $\tau_e \ell \ll \tau_n$ where $\tau_e \ell$ and $\tau_n$ are the electronic and nuclear relaxation times. $H_n$ is defined by Eq. (10). $Co^{57}$ in stainless steel, where there is no magnetic order and no quadrupole splitting, makes a <u>monochromatic</u> source, since it decays to excited-state $Fe^{57}$, which in turn decays to ground-state $Fe^{57}$ with the emission of a $\gamma$-ray of the proper frequency to excite an $Fe^{57}$ nucleus in the absorber. Fig. 4 illustrates how the nuclear energy levels $E_1$ and $E_2$ are split by the field at the nucleus $H_n$. From the selection rule $\Delta m_I = 0, \pm 1$, a characteristic six-finger spectrum is obtained if there is an internal field $(A/\gamma_n)\bar{\underset{\sim}{S}}$ due to magnetic ordering.

Some examples of the type of structural information that can be obtained are the following:

a) Determination of valence state and local symmetry: Because there is a different nuclear size for the excited-state vs. ground-state nucleus, the contact terms contributing to $H_n$ are different for $E_1$ and $E_2$. Therefore, these terms enter the energy difference $E_{12}$ to produce an <u>isomer</u> <u>shift</u> that is analogous to the chemical shift of NMR. This shift is sensitive to the valence state and local environment of the atom. For example, the garnet structure of $Y_3Fe_5O_{12}$ contains tetrahedral and octahedral $Fe^{3+}$ ions, which give two different isomer shifts; the spinel $Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$ gives three different isomer shifts, corresponding to tetrahedral and octahedral $Fe^{3+}$ ions and octahedral $Fe^{2+}$ ions. Positive identification of $Fe^{3+}V^{3+}O_3$ vs. $Fe^{2+}V^{4+}O_3$ was possible with this technique. Some work has been initiated on the determination of lattice dynamics from this effect.

b) Determination of crystal-field gradients: For noncubic symmetry, such as is found in $\alpha Fe_2O_3$, there is a quadrupole contribution to $H_n$. It
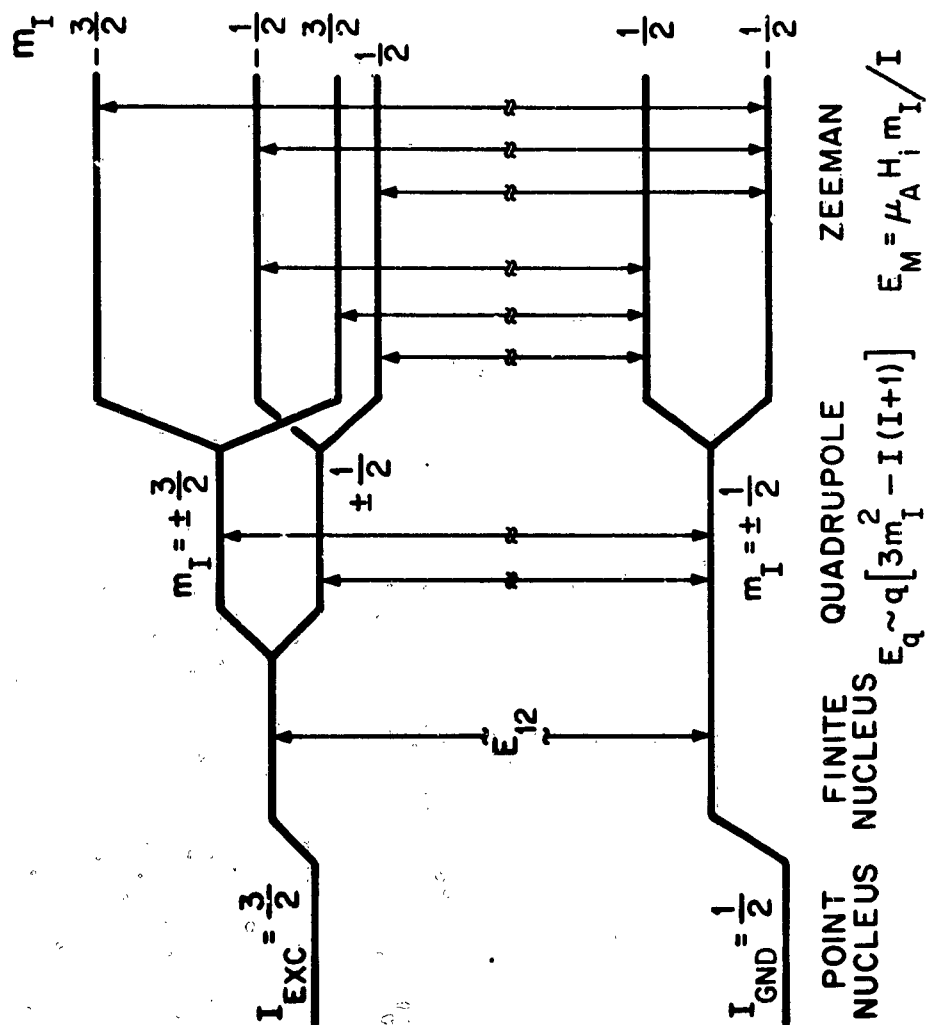
Fig. 4. Nuclear hyperfine interaction for $Fe^{57}$. Effect of finite nucleus in absorber is different from that in source, so that $E_{12}$ (absorber) $\neq$

has been possible to determine the quadrupole moment for this axial-field case. This permits the determination of field-gradient tensors in more complicated systems. Also, variations in intensities of lines as a function of angle of incidence on a single crystal give orientations of crystal-field axes and, hence, of complexes, in a crystal.

c) Determination of directions of magnetization: In magnetized samples, the intensities of the Mössbauer lines depend upon the angle between the net field at the nucleus $\underset{\sim n}{H}$ and the incident $\gamma$-ray. Monitoring the intensity vs. angle of incidence on a single crystal provides the direction of spontaneous magnetization $\underset{\sim s}{M}$.

Stimulated Brillouin Scattering.[47]

Elastic waves have an advantage over optical waves, in that they can traverse opague media and may be more strongly coupled to atomic spins. Because there is strong coupling to the atomic array, even quite mild imperfections of any kind can produce severe scattering of the elastic wave, scattering which is easily detected. If elastic waves of sufficiently high frequency can be generated, it is possible to excite a paramagnetic ion from one electronic state to another via spin-phonon interactions (especially if strong spin-orbit coupling is present as in octahedral-site $Fe^{2+}$ ions). If the elastic-wave frequency approaches the frequency of an allowed spin transition, the elastic wave suffers strong attentuation and dispersion. In the case of $Fe^{2+}$ ions, the coupling of sound waves (phonons) to spins is stronger and of a different type than the coupling of electromagnetic waves to spins. This has two consequences: (1) It may be easier to observe such resonances by sound waves than by electromagnetic waves. (2) Transitions that are forbidden to electromagnetic waves may be allowed to ultrasonic waves.

Piezoelectric and magnetoelastic transducers have been the conventional method of generating ultrasonic waves. However, it is also possible

to generate sound by nonlinear electrostrictive coupling via the intense electromagnetic excitation of a laser beam. Such intense interaction is known as stimulated Brillouin scattering.

Because mechanical radiation is sensitive to any electronic or structural inhomogeneities, it is a particularly useful tool for examining defects and dynamic processes in condensed matter. However, it has limit application to the study of the symmetry properties of crystals. (The us of ultrasonics for the determination of elastic constants was mentione earlier.)

DC Magnetic Measurements.[48-53]

Paramagnetic Susceptibilities: The magnetic susceptibility $\chi_m = dM$ and the spontaneous magnetization $M_s$ below a Curie temperature $T_c$ ar obtained by measuring the moment $\underset{\sim}{M}$ of a sample in an applied field $\underset{\sim a}{H}$. The advent of superconducting magnets places dc fields of about $6\bigcirc$ guass at the disposal of any moderately equipped laboratory. (About \$9,000 for 3/2 in. bore with 0.01% homogeneity over a 1 in. sphere.) For several years pulsed fields capable of 250 K guass have been availab in a few laboratories. Vibrating-sample magnetometers can now be purchased commercially, and with a little care in alignment these are capable of a sensitivity of $10^{-7}$ emu/gm. More sensitive instruments can be constructed. In the case of localized-electron atomic moments, the internal field is

$$\underset{\sim i}{H} = (\underset{\sim a}{H} - N\underset{\sim}{M}) + \underset{\sim A}{H} + \underset{\sim ex}{H} \tag{14}$$

where $\underset{\sim a}{H}$ is the applied field, $\underset{\sim A}{H}$ is an anisotropy field due to both spin-lattice interactions and dipole-dipole interactions, and $\underset{\sim ex}{H}$ is the Weiss molecular field or the interatomic-exchange field. In the paramagnetic range of temperature, $NM << H_a$ and $H_A << H_{ex}$ so that

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$$\underset{\sim}{H}_i \text{ (paramagnetic)} \approx \underset{\sim}{H}_a + \underset{\sim}{H}_{ex} \qquad (15)$$

The induced moment is

$$M = N <\mu_{||}> \qquad (16)$$

where $<\mu_{||}>$ is the average atomic-moment component parallel to $\underset{\sim}{H}_a$ for a unit valence containing N atoms. In general, there are two contributions to $<\mu_{||}>$, one arising from the localized, permanent moments that are aligned by $\underset{\sim}{H}_a$, and one from an $\underset{\sim}{H}_a$-induced atomic moment that is opposed to $\underset{\sim}{H}_a$. These represent the <u>paramagnetic</u> and <u>diamagnetic</u> contributions, respectively. Although the diamagnetic contribution is generally small, unless the sample is superconducting, it is necessary to estimate it and subtract it away from the observed susceptibility before interpreting the paramagnetic contribution. The theory for $<\mu_{||}>$ vs. T has been worked out for localized electrons, so that from a knowledge of $\chi_m$ vs. T it is possible to determine the magnitude of the localized moment and, for energy-level splittings $\Delta \sim kT$, the magnitudes of these energy splittings. Measurements can be performed on polycrystalline samples.

In the case of broad-band (bandwidth >> kT) collective electrons, there is an induced, paramagnetic spin contribution to $<\mu_{||}>$ if the bands are partially filled. This paramagnetism is temperature-independent, like the diamagnetic contribution. It is reduced because of an induced, diamagnetic, orbital contribution. There is also a diamagnetic contribution from the atomic-core electrons that may be of comparable magnitude in heavy metals.

Narrow-band electrons (bandwidth $\leq$ kT) have induced, paramagnetic spin contributions to $<\mu_{||}>$ that are temperature-dependent, and in the narrow-band limit this temperature dependence approaches that for localized electrons. It is not, however, interpretable on the basis of localized-electron theory.

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Some examples of the type of structural information that can be infer from these measurements are the following:

a) Local symmetry about paramagnetic ions: Localized atomic moments contain two contributions, a spin and an orbital contribution. The orbital contribution is strongly influenced by the crystalline fields, and therefore a knowledge of the atomic moment from $X_m$ vs. T measur ments provides information about the local symmetry of the ions. For example, $Co^{2+}$ ions have a nearly spin only atomic moment of $3\mu_B$ if in a tetrahedral interstice, whereas octahedral-site $Co^{2+}$ has a moment of $\sim 3.7\mu_B$.

b) High-spin vs. low-spin ions: If intra-atomic exchange splitting is $\Delta_{ex} > \Delta_{cf}$, where $\Delta_{cf}$ is the crystal-field splitting, then the ion is in a high-spin state in accordance with Hund's highest-multiplicity rule for the free atom. However, if $\Delta_{ex} < \Delta_{cf}$, then the ion may be in a low-spin state. Octehedral-site $Co^{3+}$, for example, has a spin moment of $4\mu_B$ if $\Delta_{ex} > \Delta_{cf}$, but is diamagnetic (spin contribution of $O\mu_B$) if $\Delta_{ex} < \Delta_{cf}$. Therefore, it is possible to determine the relative magnitudes of $\Delta_{cf}$ an $\Delta_{ex}$ from $X_m$ vs. T curves. In $LaCoO_3$, for example, the high-spin and low-spin states have energies within kT of each other, and a plateau in inverse susceptibility vs. temperature in the interval $125 < T < 370°$ K signals an ordering, at higher temperatures, of the two types of ions, th is reflected structurally only in a subtle change in symmetry from $R\bar{3}c$ to $R\bar{3}$.

MnAs is a metallic compound that exhibits a pronounced anomaly in $X_m$ vs. T about $100°$ C above a ferromagnetic Curie temperature, which first order. It has been possible to show that this anomaly is due to a change in the spin state of the manganese atoms. Within the anomalous

temperature interval, there is a small distortion from the hexagonal $B8_1$ structure to the orthorhombic B31 structure.

c) Magnetic ordering temperature and types of magnetic order: The Néel temperature, below which an antiferromagnetic compound contains long-range antiferromagnetic order, is manifest as a sharp maximum (discontinuous change in slope) in $\chi_m$ vs. T, or a sharp minimum in $\chi_m^{-1}$ vs. T. The intercept of the high-temperature, straight-line portion of $\chi_m^{-1}$ vs. $T$ the temperature axis is $\theta_p < 0$. In the case of a ferro-magnet, $\theta_p \lesssim T_c$ and the susceptibility increases abruptly below the Curie temperature $T_c$. (The permeability $\mu = B/H$, which is relatively simple to measure, may show a discontinuous change at the ferromagnetic or ferrimagnetic $T_c$.) In the case of a ferrimagnet, the susceptibility in-creases abruptly below $T_c$, but $\theta_p < T_c$ and the curvature of $\chi_m^{-1}$ vs. T just above $T_c$ is toward rather than away from the temperature axis. A first-order phase change at $T_N$ or $T_c$ signals a structural change accompanying a long-range magnetic ordering.

d) Localized vs. collective d electrons: Once the relative magnitudes of $\Delta_{ex}$ and $\Delta_{cf}$ are known, the spin contribution to the atomic moment is known for localized electrons. Collective electrons. on the other hand, usually exhibit no spontaneous atomic moment. Thus, where covalent mixing with near-neighbor anions is not too strong to break down the localized-electron condition in octahedral-site $Ni^{2+}$, the nickel ions have a spin moment of $2u_B$. Where the covalent mixing is larger, the ion is diamagnetic. Compounds or complexes containing diamagnetic $Ni^{2+}$ do not have octahedral-site nickel ions: a narrow-band Jahn-Teller distortion stabilizes square-coplanar symmetry about the $Ni^{2+}$ ions.

Another example is $Ni^{3+}$. Isolated $Ni^{3+}$ ions in oxides are paramagnetic with a spin moment of $1\mu_B$, and they induce Jahn-Teller distortions of the

local site symmetry at low temperatures. The rhombohedral perovskite $LaNiO_3$, on the other hand, is metallic and Pauli (temperature-independ paramagnetic.

e) Changes in interatomic exchange interactions reflect changes in structure: The orthorhombic perovskite $LaMnO_3$ exhibits a cooperative Jahn-Teller distortion of the local-site symmetry about the $Mn^{3+}$ ions below $850°K$. The resulting electronic order introduces ferromagnetic coupling between $Mn^{3+}$ ions in a pseudo-tetragonal basal plane, antiferr magnetic coupling between planes. At high temperatures, all magnetic interactions are ferromagnetic. The intercept $\theta_p$ on the temperature axis of the $\chi_m^{-1}$ vs. T curve reflects the magnitude and sign of the interatomic-exchange interactions, so that there is a distinct anomaly in $\chi_m^{-1}$ vs. T curve where the phase-change occurs.

f) Disproportionation: $PdF_3$ has been reported to have the $ReO_3$ stru ture. Were this so, the compound would contain $Pd^{3+}$ ions with a spin contribution of either $3u_B$ (high-spin state), or $1u_B$ (low-spin state), or $0u_B$ (metallic state). These could all be distinguished by $\chi_m$ vs. T data from the actual situation: $Pd^{4+}$ $(0u_B) + Pd^{2+}$ $(2u_B)$.

g) Detection of magnetic impurities or chemical inhomogeneities: P magnetic impurities or chemical inhomogeneities in a diamagnetic or P paramagnetic host can be detected with low-temperature $\chi_m$ vs. T curve The ordered compound FeAl, for example, is a Pauli paramagnetic met However, every disordered iron atom has a localized atomic moment, a in $\alpha$-Fe, and the character of the low-temperature $\chi_m$ vs. T curve indi- cates how much disorder is present. In some compounds, such as sinter $LaCoO_3$, the chemical inhomogeneities and/or impurities segregate into microphases that are magnetically ordered at low temperatures. The moment of a microphase cluster may be much larger than an atomic mo

and in a diamagnetic host this gives rise to <u>superparamagnetism.</u>

The location of phase boundaries between a ferromagnetic phase and another phase is greatly aided by $\chi_m$ vs. T data. Within the solid region, the Curie temperature $T_c$ varies with the composition.

<u>Magnetic Order Below a Critical Temperature</u>

Magnetic order below a critical temperature more often has collinear atomic spins, but frequently the spins are not collinear. Measurements of spontaneous magnetization, magnetic anisotropy, magnetostriction, and magnetic susceptibility provide information about the magnetic order and, sometimes, about the magnitude of the spontaneous atomic moments. Except for the determination of spontaneous magnetization in collinear ferromagnetism or ferrimagnetism, or in the identification of antiferromagnetic $\rightleftharpoons$ ferromagnetic phase transformations, single-crystal measurements are required. This is to be contrasted with measurements of paramagnetic or diamagnetic susceptibility, where polycrystalline or powder samples are adequate.

Some examples of the type of structural information that can be inferred from these measurements are the following:

a) Magnitude of spontaneous atomic moment in ferromagnets: If the atomic moment is due to localized electrons, it is possible to obtain the magnitude of the spontaneous atomic moment from $\chi_m$ vs. T data above the magnetic-ordering temperature. If the spontaneous moment is due to collective electrons in narrow bands, the $\chi_m$ vs. T data cannot be interpreted from a conventional Curie-Weiss plot. However, if the sample is a collinear ferromagnet at low temperatures, the magnitude of the average atomic moment can be measured directly. If a polycrystalline or powder specimen is used, it is necessary to use applied fields that are large enough to overcome the anisotropy fields. <u>Example:</u> The perovskite

$SrRuO_3$ is metallic and ferromagnetic below $160°$K. Although the high-temperature $\chi_m$ vs. T data appear to obey a Curie-Weiss law, the atom moment deduced from the slope of the curve is larger than the $\sim 1\mu_B/$cule that is obtained from the saturation magnetization. The isoelectr perovskite $CaRuO_3$ is also metallic and appears to obey a Curie-Weis law with similar Curie constant at high temperatures; but there is no spontaneous magnetization at low temperature, which indicates that th is no spontaneous atomic moment.

b) Direction of easy magnetization: This measurement requires a single crystal. A ferromagnet or collinear-spin ferrimagnet contains crystalline directions of easy magnetization, in which the magnetic m are stabilized in the absence of an applied field. Where sample shape not important (spherical sample), this is due to crystalline anisotropy In a one-component system, the crystalline anisotropy reflects princi, crystallographic directions. In a multicomponent system, it may refle preferential local ordering of one constituent relative to another. In fi this local ordering can often be modified by annealing just below the C temperature in the presence of a magnetic field. This technique has i portant practical applications where such heat treatment may cause a polycrystalline material to act magnetically like a single crystal. Con versely, the ability to perform a magnetic anneal indicates that the lo structure is influenced by the local direction of spontaneous magnetiz, just below the magnetic-ordering temperature.

An antiferromagnetic compound generally carries no net moment. (However, see the discussion of parasitic ferromagnetism below.) Ne theless, information about the direction of the atomic moments can be obtained from low-temperature $\chi_m$ vs. T data. A collinear antiferrom

has a susceptibility for applied field perpendicular to the direction of the atomic moments $\chi_\perp$ that is nearly temperature-independent, whereas $\chi_{||}$ falls to zero at $T = 0°K$.

Frequently, the two sublattice moments of an antiferromagnet are canted from a collinear axis so as to give a net ferromagnetic component. Small cant angles ($\sim 1°$) may be induced by the local symmetry, if the atomic moments are due to localized electrons, as in the orthorhombic perovskite $LaCrO_3$. They may also occur as a result of anisotropic exchange. In either case, the parasitic ferromagnetism due to small cant angles is only compatible with a restricted set of symmetry conditions. For example, $\alpha Fe_2O_3$ has the corundum structure and is antiferromagnetic. Just below the Néel temperature the spins lie in the basal plane, and the symmetry conditions permit spin canting, which produces a parasitic ferromagnetism. Below a spin-flip temperature, the spins are all parallel to the c-axis, and this orientation is not compatible with spin canting. Therefore, the spin-flip temperature marks an antiferromagnetic $\rightleftharpoons$ parasitic-ferromagnetic transition.

If a compound contains the same atom in two valence states, and is consequently a fairly good conductor, as in the case of the perovskite $La_{1-x}Ca_xMnO_3$, interatomic interactions via $n_c$ hopping electrons per molecule are ferromagnetic (double exchange), and vary as $n_c \cos \theta/2$, where $\theta$ is the angle between neighboring spins. Simultaneous interactions via the localized electrons may be antiferromagnetic. These vary as $\cos \theta$, so that the optimum configuration may be some large cant angle $\varphi$, where $2\varphi + \theta = \pi$, that increases with $n_c$ from zero (antiferromagnetism) to $\pi/2$ (ferromagnetism). The existence, in $La_{1-x}Ca_xMnO_3$ having $0.1 < x < 0.25$, of a cant angle rather than collinear ferrimagnetism was verified by measurements of the moment in very high pulsed fields. The

moment of a collinear ferromagnet or ferrimagnet saturates, whereas the canted-spin moment increases with increasing applied field.

c) Determination of ionic distribution in collinear ferrimagnets: Since the spontaneous atomic moments of different ions in different environments are now known experimentally and theoretically, provided the outer d or f electrons are localized, it is possible to determine the ionic distribution in a collinear ferrimagnet from the spontaneous moment at lowest temperatures. For example, the ferrospinels have tetrahedral-site ionic moments aligned antiparallel to the octahedral-site ionic moments. The simplest ferrospinels have the chemical formula $M_x^{2+} Fe_{1-x}^{3+} [M_{1-x}^{2+} Fe_{1+x}^{3+}]C$ where the octahedral-site ions are within the brackets and are twice as numerous as the tetrahedral-site ions. A net moment results that is a function of x. Other ferrimagnets, such as the chromium spinels, do not have collinear spins, so that this measurement is not applicable. Measur ment of the susceptibility in high-pulsed fields has been used to test whether the spins are collinear or have a complex configuration.

d) Critical temperatures separating two magnetic phases: Antiferromagnetic $\rightleftharpoons$ ferromagnetic or antiferromagnetic $\rightleftharpoons$ ferrimagnetic phase changes, as in MnP and $Mn_{2-x} Cr_x Sb$, are readily detected and usually ar accompanied by significant crystal-parameter changes as a result of cha in exchange striction.

e) Determination of a compensation temperature in a ferrimagnet: Th spontaneous magnetization of a collinear ferrimagnet is $M_s = M_{As} - M_{Bs}$ where $M_{As}$ and $M_{Bs}$ are the spontaneous magnetizations of the two sublattices that are coupled antiparallel. Since the temperature dependences of $M_{As}$ and $M_{Bs}$ may be different, it is possible to have a compensation temperature for the magnetization $T_{cm} < T_c$ at which $M_s = 0$. Since $M_s$

changes sign on passing through $T_{cm}$, it is possible to demonstrate the effect directly by suspending a sample by a fiber in a magnetic field and varying the temperature. As the temperature passes through $T_{cm}$, the sample rotates $180°$.

f) Detection of simultaneous presence of antiferromagnetic and ferromagnetic phases: A ferromagnetic phase in an antiferromagnetic host, especially if the two regions have similar crystal structures, are coupled to one another by exchange interactions. An applied magnetic field may reverse the moments in the ferromagnetic phase, which has a net moment, without reversing the moments in the antiferromagnetic phase, which has no net moment. Exchange coupling between phases makes it easier to return the ferromagnetic phase to its original position, which causes a shift in the B-H hysteresis loop along the H-axis. This phenomenon is known as unidirectional anisotropy, as opposed to uniaxial anisotropy. It was first observed in small Co particles that had an oxidized CoO layer over the surface. Since then the phenomenon has proven useful in interpreting the magnetization of many partially disordered alloys, such as disordered $Ni_3Mn$.

g) Crystal point symmetry from magnetostriction: Magnetostriction can be readily measured with the aid of a strain gauge. It reflects the coupling of the magnetic moment to the crystal structure, and the coupling tensor for a ferromagnet, therefore, reflects the point symmetry of the crystal.

h) Macroscopic, structural features of polycrystalline materials: The magnetization processes in ferromagnets and ferrimagnets are extremely structure sensitive. This is primarily due to the fact that any discontinuity in the lines of magnetic flux creates internal demagnetizing fields, and there may be a complex configuration of magnetic domains (separated by

relatively narrow transition regions called domain boundaries or walls)
that minimizes the energy associated with these demagnetizing fields.

There are four methods of directly observing magnetic domains:
(1) Bitter patterns: A magnetic colloid ($Fe_3O_4$) is placed on a polished
and etched (to remove surface stains) surface. If the surface contains a
easy direction of magnetization, magnetic flux emerges from it only at
the domain boundaries, and the magnetic colloid is attracted to the emd
flux. In bulk material, the magnetization within a boundary rotates with
a plane that makes equal (or nearly so) angles with the magnetization d
tion in the domains on either side. This is called a Bloch wall. In films
that are thinner than a boundary thickness, the magnetization direction
a boundary rotates within the plane of the film. This is known as a Née
wall. Films with thickness comparable to a boundary thickness have cc
plex rotations within the boundary, and the Bitter pattern shows short
cross walls periodically along the principal boundary, the cross walls
fading away as they penetrate the domains. These are known as cross-
walls.

2) Kerr effect: Since the rotation of reflected plane-polarized light
depends upon the angle between the magnetization and the H-vector of t
incident light, it is possible to distinguish different domains by viewing
crystal through an analyzer. This technique can be used to observe dyr
processes, but intense light sources are required. Laser sources coul
profitably be developed for this type of study.

3) Faraday rotation can be used for those few ferromagnetic compo
that are transparent. This provides a three-dimensional view of the
domains in the bulk.

4) Electron microscopy has been used for magnetic films.

An indirect way to obtain information about magnetization processes is to investigate the B-H hysteresis loop. Coercivity and remanance are both extremely structure sensitive.

In polycrystalline materials, the grain boundary is an important surface of discontinuity in the magnetization vector, unless it is possible to align the directions of easy magnetization in the two neighboring grains. This alignment can be accomplished in three ways: (1) rolling metallic sheets in order to align a crystallographic easy axis along the rolling direction, (2) magnetic annealing, and (3) subjecting magnetostrictive materials to tensile stress.

A second phase offers a surface of discontinuity in $\underset{\sim}{M}_s$, and the magnetic processes are sensitive to the existence of a second phase.

Chemical inhomogeneities that have the same crystallographic structure, but a slightly different magnitude for $\underset{\sim}{M}_s$, also offer a surface of discontinuity in $\underset{\sim}{M}_s$. Undetectable by x rays, they may be observed as intragranular nucleation centers for domains of reverse magnetization. It is thought that these may be a necessary imperfection for creation of square hysteresis loops in the polycrystalline ceramics used as memory cores in digital computers.

### Calorimetric Measurements.[54,55]

Calorimetric measurements provide a rapid and accurate determination of (1) the existence of a transition and its order, (2) the temperature, or temperature range, over which it occurs. These measurements may be dynamic, as in differential thermal analysis (DTA), or adiabatic. The two types of instruments are commercially available, and the best ones (sensitivity better than $10^{-3}$ cal/mole-deg) cost about $9,000 each.

If the transition temperature depends upon the rate of heating in a

dynamic measurement, it involves an atomic diffusion process; if it d
not, it is diffusionless and involves only electronic ordering.

If a transition is second-order, then the Landau-Lifshitz theorem
applies. This theorem states that the density (charge or spin) below a
close to the transition transforms like a single, irreducible represent
of the symmetry groups that pertains above the transition temperature
In general, this means that the space group below the transition is a s
group of that above the transition.

### Dielectric Measurements.[56-58]

Ionic crystals may be ferroelectric, antiferroelectric, or paraelect
If a crystal has two stable states (different in polarization) at zero el.
field and is capable of alternating between these states in an a.c. elect
field, the crystal is said to be ferroelectric. Any ferroelectric crystal
longs, therefore, to a noncentrosymmetric point group. A regular ferr
electric crystal belongs to a polar group, and the space lattice in one
two stable states of a crystal plate is parallel to the space lattice in th
There are fourteen kinds of regular ferroelectrics, in accordance with
point groups, space lattices, and types of state transition. A ferroelect
crystal is said to be irregular if it is not regular, and there are eleven
of irregular ferroelectrics. If the kind of ferroelectric is known, it is
ble to deduce the crystal character of one state from information about
other and, moreover, to make predictions about the ferroelectric $\rightleftarrows$ par
tric phase transformation.

If it is possible to transform a crystal to another phase having the
structure of the first as a superlattice, the first phase is called antifer
electric.

A crystal is paraelectric if it is neither ferroelectric nor antiferro-
electric.

A convenient method for determining the phase-transition temperatures is to measure the dielectric constant $\epsilon$ vs. temperature, where $\epsilon = C/C_0$ is the ratio of the capacitances of an electrical condenser with and without the dielectric between the condenser plates. The d. c. dielectric constant approaches a maximum above the transition temperature and changes discontinuously at the transition.

### Local Symmetry and Long-Range Order by Spectroscopic Methods.

Soft x rays (wave length 5-500Å) have not as yet been widely used for the characterization of solids. Soft x-ray spectroscopy techniques can be used to measure the wavelength and shapes of emission bands, which are related to the electron distribution and the transition probability of electrons in the valence bands of solids. However, physicists have been interested in the emission bands primarily from the standpoint of checking various aspects of theory. Unfortunately, they have not been concerned with a variety of materials and, perhaps as a consequence, the present theory cannot utilize the observable fine structure of soft x-ray spectra.

Moreover, recent technological improvements in electron microprobe and x-ray spectrographic instrumentation have made generally available a capability of recording the x-ray spectrum for all elements, from boron to the end of the periodic table. There are at least 100 electron micro-probes (costing between $75,000 to $125,000) and a comparable number of commercially-built x-ray fluorescence spectrometers (cost near $20,000) presently in use in the U.S. which are perfectly suitable for crystal chemi-cal characterization of materials by soft x-ray spectroscopy. The fact that so few are being used indicates both the difficulties with theory and a general lack of information about the potential usefulness of this method.

Since these x-ray emission bands contain electrons involved in chemical

bonding, it follows that one should be able to correlate them with other measurements which depend on how an element is chemically combined in a material. Very recently, several investigators have attempted to establish empirically the correlation in changes in soft x-ray spectra with the major crystal chemical parameters such as valence, coordination number, bond-type, interatomic distance, and changes in coordinating anion species and next neighbor cation species. Although most of the results are preliminary, it does now appear that one can predict a great deal about the crystal chemistry of an unknown substance from these relatively simple measurements. Thus, for example, one can distinguish the valence states of Cl or S (ranging from +7 to -1 and +6 to -2 respectively). The first sphere coordination number of, say, Al or Si can be determined in minutes. Furthermore, even the cation-anion distance in silicates and aluminates can be predicted with a precision comparable to that of the best x-ray, single-crystal, structure determinations from the measured shift in position of the K peak.

An important aspect of the soft x-ray spectra is that they do not appear affected by the degree of long-range order; thus, one can apply this technique to the study of noncrystalline, highly disordered, and well-crystallized materials with equal facility.

### X-ray Absorption-Edge Spectroscopy.

X-ray absorption methods are used for routine chemical analysis in a few establishments. For most cases, the x-ray fluorescence method is to be preferred for accuracy and convenience. Measurements of the absorption coefficient in the region of the absorption edge have, however, also shown that certain features can be used as means of structural characterization. For example:

a) The oxygen content of chromium can be predicted with a 5-10% precision from the height of a small peak at the leading edge.

b) The valence of iron can be estimated from the shift in energy of the half-height of the main edge. The precision is about 10% of the amount present, but a change in coordination number will invalidate the estimate.

c) Some information about the bond type can be qualitatively derived from the similarity in over-all shape of spectra from covalent and metallic materials and their differences from that of ionic compounds.

As in the case of soft x-ray emission spectroscopy, commercially available equipment can be readily adapted for measurement of the structures of absorption edge. It is too early to predict accurately the extent to which the technique can be adopted for routine characterization of the crystal chemistry of materials.

A need exists for both theoretical explanations of the observed results and additional instrumentation of maximum resolution capability, but chiefly for the publicizing of the possibilities of these methods so that it is studied more extensively.

### Infrared Absorption Spectroscopy

Infrared spectroscopy is a useful tool for the characterization of solids because of the ease of sample handling, the ability to work with polycrystalline materials, and the wide availability of first rate commercial spectrometers. A spectral range from the 2 to 200 microns is available commercially.

At the lowest level of sophistication, infrared offers a method to recognize molecular entities in solid materials. For example, hydroxyl ions or residual carbonate and sulfate in glasses are easy to recognize because of their characteristic spectra. The hydroxyl ion, in particular, can best be characterized by infrared and, because of a systematic frequency shift, the lengths of the hydrogen bonds and thus the location of the OH group can be determined.

The primary coordination number of a cation is strongly reflected in the IR spectrum. In simple structure-type materials (one cation), coordination numbers can be determined quite accurately for low atomic weight anions (oxides, fluorides). Where cations are present on several coordination sites, the interpretation becomes more equivocal, and only the smallest coordination numbers can be determined with certainty. Characteristic frequency ranges for most of the common cations in 4 and 6 coordination have been determined. There is a general relationship between the square of the vibrational frequency and the inverse cube of the interatomic distance that gives first approximations to these distances.

At the highest present level of sophistication, the behavior of the spectrum during polymorphic and order-disorder transitions can be predicted exactly by a simple group-theoretic argument. Infrared spectroscopy is an unusually powerful tool for order-disorder study, because dramatic changes may occur in the IR spectrum in systems where the ordering reflections in the x-ray diffraction pattern may be weak. For a few very simple structure-type solids, a normal coordinate analysis is possible that permits measurements of force constants and thus provides information about the bonding.

There is a need for additional good experimental data on simple structure-type solids, particularly in the low frequency region of the spectrum. Such data would permit testing the current theoretical models.

## G. STRUCTURAL CHARACTERIZATION OF DISORDERED, POORLY CRYSTALLINE, AND NONCRYSTALLINE SOLIDS

Since solids in the disordered to noncrystalline range still retain varying degrees of periodicity in their atomic distribution, they can be studied by diffraction techniques. The principal tool in such studies has been x-ray diffraction, although supplemental data can be furnished chiefly by electron

(and occasionally neutron) diffraction. Information thus obtained ranges from degree of deformation faulting and/or strain in otherwise well-ordered materials, through crystalline/amorphous ratio, to the structure of noncrystalline (including glassy) materials; i.e., their radial electron density distributions. The contribution of "indirect methods" is treated under Section F., Structural Characterization by "Indirect Methods."

### X-ray Methods

Instrumentation for studies of this nature is basically the same as that used for normal powder x-ray diffractometric research. The very nature of the material limits studies to powders or their equivalents, except for faulting and strain in single crystals, which are better treated as defects. More sophisticated work in the "noncrystalline" area may involve minor, albeit ingenious modifications to normal instrumentation. Equipment cost is equivalent to that of a standard x-ray powder facility with electronic counting.

### Faulting and Strain

X-ray powder patterns of simple metals; e.g., copper and nickel, can be analyzed so as to yield information on particle size, deformation fault probability (i.e., the average number of atomic planes out of position by virtue of stacking faults), mean square strain, and twinning (longer range faulting). Specific features yielding such data include diffraction line broadening, peak shifts, and line profile asymmetry. The theory and techniques have been derived and applied by Warren,[59] and Warren and Averback,[60] and are aptly described therein. To assess faulting probability, certain drastic assumptions are necessary, and the detectability limit is approximately one faulted layer in 200.

### "Percent Crystallinity."

In the case of a crystalline phase in an amorphous matrix, one can obtain

a rough measure of their ratio if the composition of each is the same and is known. This is accomplished basically by summing the powder diffraction line intensities, subtracting the amorphous (background) intensity, and correcting Compton modified scattering. Resultant absolute numbers appear in the form 30:70, 45:55, etc. The fact that there is a continuous transition from well-crystallized through disordered to noncrystalline phases, is an inherent semantic limitation to the accuracy of any such statements.

### Radial Distribution Curves.

Whereas crystalline materials are described by a crystal structure (spatial positioning of atoms), an amorphous (glassy) material has a "structure" defined by a radial distribution curve. This is the probability of finding the centers of atoms at a distance r from the centers of other atoms. The source of such information is a scattering curve (usually x ray) from which the Compton modified component has been subtracted. This is accomplished experimentally by a new technique[61] utilizing monochromated radiation and x-ray fluorescence. Nevertheless, only simple amorphous materials or mixtures thereof (e.g., $Na_2O$-$SiO_2$) can be handled. Mixtures are treated by a combination of x-ray and neutron diffraction (each emphasizing certain interatomic separations), together with a recognition of known spacings (e.g., Si-O) from simple materials. An attempt to so analyze a complex amorphous substance such as neodymium laser glass, which probably also contains segregated phase(s), is beyond the scope of present theory and techniques.

Studies on poorly crystalline and noncrystalline materials to date have not been particularly widespread. This is partly due to difficulties involved in applying suitable theories and techniques and to the "grey areas" of the phenomena involved. Today, with the advent of the whole of thin-film technology and materials such as neodymium laser glass and poorly-crystallized

super-conductors, there is great need and demand for such information. The nature of these studies precludes "precise" results, but the numerical data are no less useful for characterization, for correlation with properties, and for an insight into materials preparation phenomena.

## Electron Methods

Electron diffraction and microscopy can give some information on amorphous materials. Thus, a few materials, among them glass, organic waxes, smokes, clays, etc., which are "amorphous" by normal x-ray diffraction, are sometimes shown by electron microscopy and diffraction to contain very small crystals giving diffraction patterns. Often immediate information on the particle size and crystallinity is given by the diffraction pattern. However, characterization of new crystalline material is very difficult by electron diffraction as only two or three broad rings are present, and "d" values are inaccurate.

## Radial Distribution Curves.

. Analyses of radial distribution curves are seldom done in electron diffraction at present. Randall's book (1934) on the subject is out of print. The bulk of the work was done about ten or twenty years ago. Recently, however, some radial analysis has been done on biological materials and on organic polymers.

## Dark Field Electron Microscopy.

Recently it has been shown that dark field electron microscopy is of tremendous importance in the determination of defects in thin foils, and in the distinguishing of crystalline from noncrystalline regions. In bright field, defects give a subtractive contrast image, and in dark field an additive contrast image. Often the dark field image has better contrast, because in very thin foils only a small fraction of the intensity is diffracted out in the normal image. As yet few microscopes are able to take full advantage of this technique, and it 's taught in only a few schools at present.

### "Percent Crystallinity."

Under special conditions, percentage crystallinity can be evaluated with accuracy by electron microscopy. For example, in a phase transformation from amorphous to crystalline, contrast between the two phases is sufficient for an accurate analysis. Where, however, contrast difference is slight, as with organic materials, the problem is rather difficult and is better done by x-ray methods.

### Particle Size and Line Broadening.

Particle size can be observed directly and more exactly by electron microscopy than by x-ray methods, especially if the particles are single crystals. This is very evident in the size range 500 - 5000$\overset{\circ}{A}$ where x-ray methods are difficult. In the region below 100$\overset{\circ}{A}$, even though electron microscopy can resolve suitable particles of 10$\overset{\circ}{A}$, contrast limits particle size determination. Thus, for good crystalline particles of gold or platinum, particle sizes of 10$\overset{\circ}{A}$ or 20$\overset{\circ}{A}$ can be resolved. Materials which are poorly crystalline or amorphous give low contrast. These may have sizes of 30$\overset{\circ}{A}$ and be unresolved by direct microscopy. Here electron diffraction can give an estimate of crystallite sizes below 100$\overset{\circ}{A}$. In theory, the relation between crystallite size and line broadening is fairly simple in electron diffraction, but often difficult to utilize line broadening in practice. However, in general, particle size is better done by electron microscopy for sizes from 1$\mu$ down to 40$\overset{\circ}{A}$. Below 40$\overset{\circ}{A}$ interpretation may be difficult, as the effect of particle size and poor crystallinity merge. A distinction should always be made between crystals, particles, and aggregates.

### Stacking Fault and Defect Analysis.

As the theory of image contrast has improved, more and more information has been gained by direct observation of foils by electron microscopy. X-ray

topography used in conjunction with electron microscopy has been very valu-
able. Thus, stacking faults can be resolved directly and their nature deter-
mined (e.g., whether they are extrinsic or intrinsic, their size, density,
shear vector, and fault plane, and whether they intersect the top or bottom
of a foil). This is also true of many dislocation problems. A combination
of light and electron microscopy and x-ray topography is required here.
The method is not yet used as widely as it should be, but its use is growing.

### Low Angle X-ray Scattering.

For three or more decades, this technique has been applied to the detec-
tion of inhomogeneities on a scale of $10\text{Å} - 1000\text{Å}$ in liquids, glasses (and
also in crystalline materials). The most favorable cases are those in which
a high atomic number phase separates out in isolated particles from a low
atomic number matrix. Naturally, the calculations require a "model" of the
composition of the two phases, which is almost always a zeroth order approx-
imation. As a characterization tool in the general case, x-ray scattering
can detect the incipience of phase separation but has proved rather disap-
pointing in its quantitative aspects.

### Other Methods.

It can be seen from the above that one of the major limitations in struc-
ture determination lies in the field of the aperiodic structures. Moreover,
it is now apparent that diffraction methods in general are tedious and, even
with refinement, cannot give us adequate information. If we follow the scheme
of Table I we can, however, list the other techniques which are now on the
horizon that are perhaps more effective for doing this job.

Electron microscopy, especially after differential etching, can be used
to detect substructure in glass at the $15\text{-}30\text{Å}$ level when both "components"
are noncrystalline. This partly overlaps the region in which low-angle
x-ray scattering can be utilized for the same information. Light scattering

has been of value in the 100Å range and, especially now with laser sources, may prove efficacious in detecting submicroheterogeneities down to 100Å or lower.

On the atomic scale, it has been noted above that infrared absorption spectroscopy is capable of giving some rather unambiguous answers on the coordination of the major-constituent cations, if they are the common light atoms. X-ray emission spectroscopy provides about the same informa tion and has the advantage that the overlap from different atomic species is absent. Indeed, it appears to be capable of providing some data on second nearest neighbor interactions even in noncrystalline solids.

Magnetic susceptibility measurements appear capable of describing the clustering of paramagnetic phases, while dielectric and mechanical relaxation processes can be related to certain aspects of the structure such as the "movability" of certain cations. Optical absorption and electron spin resonance give fairly clear-cut data on the nearest neighbor environment of paramagnetic ions; whether one can logically use such an ion (e.g., $Ni^{2+}$) as a "tracer" to give us information on the "carrier" diamagnetic species (e.g., $Mg^{2+}$) is still a moot point. NMR studies have provided coordination number information on particular nuclear species such as selected isotopes of Al and B, but such information seems to be no more detailed than the infrared absorption or K-emission data, which can be obtained and interpreted more directly.

## IV. APPLICATION OF PRESENT CAPABILITIES TO
## SELECTED EXEMPLAR MATERIALS

It may perhaps be easiest, at this stage, to return to our earliest pre-
sentation in Table I of the various types of structural information that can
be obtained, and to summarize in tabular form the precision that is attain-
able in each category, given all the instrumentation necessary. This has
been done in Table IX. In this presentation, the assumption has been made
that the sample is present in the form most suitable for the particular
experiment. Wherever this is not the case, there may be considerable loss
of precision. By a coincidence, most of the phases selected (Si, ZnS, KCl,
Cr, $CaF_2$) are quite simple from a structural viewpoint (i.e., atoms are
in special positions), and the limits are those which limit the method at
present. "$MnFe_2O_4$" and Nd-laser glass are seen to be very much more
difficult to characterize structurally, although they represent widely used
materials. Some comments on special problems with the individual phases
are appended:

Chromium serves as a particularly simple illustration of the useful-
ness of the neutron-diffraction technique in assessing the electron spin
distribution in a metal. From the magnetic scattering of neutrons, it
has been established that an antiferromagnetic structure exists below
$311°K$, with a further modification in this structure below $120°K$, in
which the two unique atoms of the b.c.c. cell are characterized by opposite
spin orientation. Furthermore, there is observed a modulation of the
magnitude of the spin moment over distances of about $25Å$ and this case
has served as the strongest evidence to date for the existence of the
Overhauser spin-density-wave in metals.

$MnFe_2O_4$: From neutron diffraction and x-ray diffraction, it is possible

TABLE IX. APPLICATION OF PRESENT CAPABILITY TO EXEMPLAR MATERIALS.

| | Si | ZnS | KCl | Cr | CaF$_2$ | Nd-laser Glass | MnFe$_2$O$_4$ | Anthracene |
|---|---|---|---|---|---|---|---|---|
| Unit cell and space group | .005% S. G. Known | .005% | .005% | .005% | .005% | N/A | .01% S. G. Known | .005% |
| Site symmetry | Trivial | Trivial | Trivial | Trivial | Not unambiguous for traces | Optical; ESR not unambiguous | (See text) | Known |
| Structure Position of atoms | ±0.0005Å | ±0.0005Å | ±0.0005Å | ±0.0005Å | ±0.0005Å | Cannot be handled | Site-distribution determined by neutrons (± 2%) | ±0.0005Å |
| Spin configuration and atomic moments | N/A | N/A | N/A | Complex, but well established (See text) | N/A | N/A | Complex (See text) | N/A |
| Bonding | Electron density to .1/Å³ | | | | Electron density to .1/Å³ | Cannot be handled | .1/Å³ | |
| Special Features | | Stacking faults difficult to determine in small concentrations | | | | | For valence states, see text | |

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to show that a particular $MnFe_2O_4$ crystal is a spinel that is roughly 88% normal:

$$Mn_{0.88}^{2+}Fe_{0.12}^{3+}[Mn_{0.12}^{x+}Fe_{0.12}^{y+}Fe_{1.76}^{3+}]O_4$$
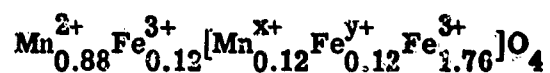
$x = 2$, $y = 3$, or $x = 3$, $y = 2$.

Neutron diffraction also confirms collinear A-site spins antiparallel to collinear B-site spins (Néel ferrimagnetic order). Since both $Mn^{2+}$ and $Fe^{3+}$ have a $^6S$ ground state, the net molecular moment for $x = 2$, $y = 3$ is expected to be $5\mu_B$. Experimentally a moment of 4.5 - $4.6\mu_B$/molecule is found, and the average atomic moment on both A sites and B sites, is, from neutron-diffraction data, about $4.6\mu_B$ rather than $5\mu_B$.

## V. UTILIZATION OF PRESENT CHARACTERIZATION KNOWLEDGE

In considering the degree to which characterization is carried out, one recognizes that there is no absolute standard against which performance can be judged. A small laboratory may be doing a very precise job, utilizing all its capability with microscopes and powder x-ray diffraction, yet having to omit many aspects for lack of apparatus. Contrariwise, many large laboratories with all the facilities including neutron sources may not be performing even the simplest characterization on their solid state materials.

It is difficult, without extensive inquiry, to attempt to be quantitative in estimating the extent of utilization of existing knowledge and instrumentation in the various categories used in the main body of the report. However, in the collective subjective judgment of the Committee, one of the main facets of the materials characterization picture is the fact that neither the knowledge, nor even existing instrumentation in many laboratories, is utilized to anything approaching reasonable levels. Thus, for example, the existing information on the great utility of the polarizing microscope to characterize materials is virtually unknown in most materials laboratories. On the other hand, while the general capabilities of powder x-ray diffraction are more widely known, the instruments are not used to capacity. No effort is made here to tabulate or present in chart form the relative picture in each of the fields. However, this judgment is reflected in our next section on recommendations, since, in certain fields, we have indicated that "education" may be an important need.

## VI. RECOMMENDATIONS

### Educational

Serious gaps have been noted in the training of personnel in the theory and application of characterization methods. Such training as there is at the postgraduate level is concentrated at a few universities. The long-range solution, of interesting the departments of chemistry and new materials science departments in teaching such subject matter, is clearly a decade or two off. More immediate, practical steps include the publicizing and encouragement of existing, and setting up of new, short courses of one- or two-week duration. There is plenty of precedent in this field, and financial support of such "service-courses" would return certain and relatively high dividends in value to the materials characterization field. It is noted, for instance, that the field of x-ray diffraction analysis has been favored in the past by having available a variety of short, concentrated study courses under both university and industrial sponsorship. An extension of this into other areas would be highly desirable and, in particular, it is recommended that sponsorship of one or two regular summer schools for training of specialists in electron microscopy be arranged. Such a summer school could be patterned after the highly successful one held regularly in Cambridge, Great Britain.

It would be of considerable value if some venue were established, for bringing together and publishing at appropriate intervals, lists of all short courses being given which relate directly to materials characterization. Since the normal channels of communication—through a "society for materials science"—do not exist, it is necessary that such extraordinary steps be taken to get reasonably quick results. Perhaps one—or more—

of the new materials science journals could be established as a venue for publication of such information.

As useful as these introductory or "refresher" short courses are, it is appreciated that they do not serve as a replacement for formal university courses or advanced student thesis work. It is beyond question that there is great need for more students to be trained in the tools of structure deter-mination, either as a cultural topic subsidiary to the student's principal interest, or as a concentrated thesis study in itself. Encouragement should be given to universities to expand their course offerings in this field, and research grants should be made available for supporting graduate students and their research activities. It is axiomatic that the latter invariably engenders the former. Specifically, this Committee notes a serious lack of training facilities in the fields of electron microscopy and neutron diffraction, and it is recommended that additional support for student training be instigated in these areas.

Another aspect of the long-range "educational" problem would be to publicize materials characterization to those groups where the manpower situation is less tight, and there is a chance of an increase over and above the national averages. Two such groups are proposed. Several good earth science departments produce well-trained miner. ogists, expert in the application of the polarizing microscope and x-ray methods to (natural) materials. Very frequently this capability is not utilized in their employment, and they are unaware of their potential use in the materials field. The other group consists of the analytical chemists who are in general not introduced to the field of solid-state-structure analysis at all. Recommended action here would be to "educate" chemistry departments to the needs and opportunities in this field.

Finally, there is the "education" of the materials research community to the role of characterization in a sound materials program. This effort must run the gamut from the supporting agencies in Washington and elsewhere, to the research directors in industry and universities, down to the individual worker. Traditional means such as Sigma Xi or ACS lecture tours by senior personnel, together with novel or unorthodox methods such as critical reviews or comment on the absence of characterization in so much published work, should be utilized. A specifically important aspect of structural characterization, which should be repeatedly emphasized, is the fact that a single technique approach is very unlikely to be either rapid or accurate. The complementarity of the various methods is so crucial that a multi-technique approach is quite indispensable.

Editorial

One of the most powerful methods by which we may highlight the importance of characterization would be by "getting the message" through to the editors of the main solid state journals: Phys. Rev., J. Appl. Phys., J. Chem. Phys. Solids, J. Am. Cer. Soc., Acta Met. There is only one fortunate aspect about the six (!!) brand new Materials Science Journals that are being started: that we can get the editors started off on the right foot from the beginning, if all editors can be:

a) sent copies of the report,

b) personally invited to a presentation,

c) asked to insist that every paper reporting physical measurements give a certain minimum characterization of the phases studied.

Naturally, to put force behind our suggestions, it would be a great boost if we could persuade the particular society, through its editorial committee, to endorse the general idea, possibly embodied in a short policy statement which we could help draw up.

## Research Recommendations

### Optical Methods

Optics, long a dormant science, has recently undergone a complete metamorphosis, and research utilizing several of the new optical phenomena (e.g., coherent light sources), promises real rewards in characterization. This is especially true of surface investigations and scattering studies. For example, the dynamics of high-speed magnetization processes should be studied directly by means of the Kerr effect. Manpower in these fields can be drawn from the general physics community and is, therefore, large. (A ten-to-fifteen-man-year effort is feasible.) Optical methods, such as polarizing microscopy, also need a special effort in "education" of the scientific community in order to make their power better known.

### X-ray Methods

There is a definite need for increasing the number and quality of the data in the ASTM powder file by supplementing the ASTM research effort. It is recommended that two to three separate groups be funded at a time, each at about a two-man-year level over a ten-year period. Each group should specialize in different classes of materials; e.g., organics, minerals, intermetallic compounds, etc. The need for separate groups lies in the fact that each group must be familiar with the structures, crystal chemistry, synthesis, etc., of the classes of materials assigned to it. It is likely that over a ten-year period as many as six groups may have been engaged in the program. It is essential that each group have a major sophisticated facility in x-ray powder instrumentation and methods, together with an established capability in sophisticated specimen-preparation techniques for the group of substances being studied.

Support should be given to all promising proposals devoted to optimizing

the theory and methods of extracting structural data from powder patterns. The reasons for this are obvious: The number of new materials that becomes available in powder form is hundreds of times larger than the number of single crystals; we need coordinated programs in basic research and improved instruments and techniques to obtain more detailed information on order-disorder, surface strain, atomic distributions, accurate lattice parameter data, etc.

With the advent of new crystal structure techniques, it is essential that research be initiated on the various factors that presently limit the accuracy of structure determination. At least two groups, at a two-man-year level, should be funded simultaneously for three-to five-year periods. Each team should consist of a crystallographer and a person well-trained in x-ray physics and techniques.

Materials used at low temperatures (e.g., superconductors) and high temperatures (e.g., nose-cone ceramics) require structure studies at these extreme temperatures. It is therefore recommended that experimental techniques be developed for accurate lattice parameter, atomic position, and electron density measurements in the temperature ranges $0-100^\circ K$ and $1000-3500^\circ C$. It is estimated that four one-man-year efforts are required for each of these problems.

Instrumental development is needed in the field of high-pressure x-ray diffraction to achieve (a) refined, miniature pressure cells for use in sophisticated single-crystal, x-ray geometries; and (b) powder techniques suited to the study of more complex materials. It is recommended that competent work in this field be supported.

### Methods of Electron Microscopy and Diffraction

One of the most significant recent developments is scanning electron

microscopy. It may well have a major impact on the study of the topographical and electrical features of surfaces and of complete devices. Sample preparation is easy, and operation does not require a skilled electron microscopist.

It is recommended that support be extended for the purchase, evaluation of, and exploitation of this class of instrument in the characterization field.

Support should be given to <u>electron microscopy instrumentation research</u> designed to improve the vacuum system, source, and the photographic materials, and to investigate superconducting lenses, image intensification, and the use of higher voltages. Much work also remains in working out contrast theory. Considerable research effort should be devoted to better and simpler methods of specimen preparation for transmission work, which would benefit the entire community of microscopists. Several small efforts of one-to-two-man-years each are suitable in this field.

It is recommended that two or three additional <u>0.5 to 1.0 meV electron microscopes</u> be supported within the appropriate laboratory environment, where these methods may be developed to a high degree and, possibly, where they may be made available to others.

### Neutron Techniques

The neutron scattering techniques that have been used for materials structure study have drawn very heavily upon existing x-ray diffraction techniques, without real recognition of the important differences between the sources and radiation characteristics. This has been recognized for a long time, but it has been only recently that really novel techniques of data collection have been explored. It is recommended that financial support (at approximately a seven-to-eight-man-year level) be given to groups interested in developing new techniques of experimentation. Specifically,

the area of pulsed neutron sources with associated flight-time diffractometry has great potential and is worthy of immediate expanded support. Similarly, the advantages of neutrons over x rays for high-pressure characterization of solids has not been exploited sufficiently, and work along these lines should be encouraged.

### Indirect Methods

The correlation of chemical and physical properties with structure has always been central to materials science. The true role of structure in mediating the physical properties of a chemical compound will be elucidated first in those centers where there is an intimate interplay between preparation, structural characterization, and physical measurement. Rather than emphasize the independent application of indirect methods to structural characterization, it is recommended that means be devised to strengthen a few professional centers where solid-state chemistry and physics are already in intimate and creative interaction.

Specific areas where indirect methods offer reasonable hopes and which should be studied further include:

Infrared absorption spectroscopy appears to be at the take-off stage as a definitive, routine characterization tool for describing the nearest neighbor environment. An injection of a ten-man-year effort here is likely to prove very rewarding.

The development of x-ray emission spectroscopy has great potential, since it can be combined with the most sensitive and highest resolution structural and chemical tools. Thus, a combination of high energy grazing incidence diffraction with dispersive or nondispersive analysis of the x rays offers simultaneous chemical and structural information on tenths of a mono-layer. The study of the structural dependence of the emission

wavelength holds much promise. Two or three small specialized efforts would likely prove effective.

Several indirect methods important for structural characterization are being supported for other reasons. For example, stimulated Brillouin scattering and ultrasonics research are promising fields.

### Poorly Crystallized and Noncrystalline Solids

Recent technological application of poorly crystalline and glassy materials (e.g., neodymium-laser glass, zero-thermal-coefficient ceramics, etc.) has pointed up the need for structure studies to supplant present empirical treatments. In this area, a specially focused effort is necessary in addition to the application of individual tools to this problem. The state of the art is such that it would be best to support fairly basic rather than applied or instrumentation work, since we cannot yet be sure which of the general avenues will be most rewarding. For example, theory and techniques for handling such substances by diffraction methods (x-ray and electron) require considerable extension, in addition to the applications of indirect methods. A thirty-man-year effort divided over several units using different methods for a period of three-to-five years could provide the required manpower combination of theory and experiment that appears to be needed here.

### A Proposal for Major Coherent-Program Support of Research in Materials Characterization

It is widely conceded now that characterization of the material is a major bottleneck in materials science. If this judgment is sustained, we believe that the enhanced small-project approach alone will be insufficient to add the kind of impetus that is quite essential, if the field is to obtain the recognition, visibility, and support it deserves. Something must be done in addition, and we propose herein a modest solution that is, we believe, workable without major perturbation of existing structures.

During a 1966 survey of some ARPA - supported IDMRL's, it was found that while the importance of characterization research was now accepted, its actual initiation on a meaningful scale was extremely difficult. Even the largest IDMRL's have committed their budgets in other directions, and materials characterization is such a large field that its incorporation into existing programs at a sophisticated level is not feasible. Moreover, the IDL schools that have the physics strengths do not have any interest or ability from the complementary "chemistry" faculty, without which no good research can get off the ground.

Moreover, the number of laboratories at which there is sufficient existing strength on which a characterization program can be built, is so small that the probability of being able to do this level of characterization at any but a very few locations is remote. "Customer-service"—type laboratories are not the answer, because it would be impossible to justify the basic research which is necessary to keep up-to-date.

It is recommended therefore that four to six major characterization "programs" be initiated in appropriate centers throughout the country. The host institution should be a university, or university-related laboratory, to be selected on the basis of demonstrated competence and capability in genuinely interdisciplinary materials science, emphasizing an awareness of, and commitment to, the appropriate role of materials characterization. The utilization of groups with established and funded programs in research on preparation and properties will avoid unnecessary duplication, as well as provide the essential ingredient of a broad base of competence in materials science into which context every characterization program should be fitted. The level of effort in each group may range from 0.5 to 1.0M/yr (since equipment is very expensive in this field), of which only a part would, of course, be devoted to structural characterization.

### Role of Characterization in DOD Materials R and D

A further recommendation concerns the necessity for the appropriate recognition of the role of characterization in DOD funding structure, both in-house and contract. It is clear to us that the science of characterization cannot attain its proper place in the materials field, unless it is recognized by line-items in the budget and in the administrative structure of the laboratory. Hence, DOD laboratories need to support vigorously the establishment of characterization as an important and separate function, with in-house and contract budgets appropriate to such goals.

A second source of support for this goal is to be found in much end-item research. DOD agencies can easily require that in all such end-item research a specific level of characterization be included.

### Manpower Level of Effort Summary

In Table X, we present a tabular summary of the levels of effort that we believe could be effectively added to the present activity in materials characterization. The cost of the program including the structural - characterization share of the major centers would amount to about $3 million per year, and without the major centers somewhat over half that amount.

TABLE X. RECOMMENDED LEVELS OF EFFORT

| General Area | Program(s) | Man Years/Year Rate of Effort | Total Effort Envisaged (Man-years) |
|---|---|---|---|
| Optical Methods | Ellipsometry Laser scattering Magneto-optics Piezo and Electro reflectance | 3-4 | 16 |
| Electron Microscopy | Scanning microscope evaluation Improved instrumentation High voltage studies | 5 | 30 |
| X rays | Powder File | 5 | 40 |
| | Theory (powder method) for structure analysis | 1-2 | 10 |
| | Single-crystal accuracy | 3 | 12 |
| | High and Low } Temp. x ray | 2-3 | 8 |
| | High-pressure x ray | 2-3 | 10 |
| Neutron Methods | Time of flight spectroscopy High-pressure studies | 7-8 | 20 |
| Indirect Methods | Infrared X-ray emission | 6 | 20 |
| Noncrystalline Solids | Focused efforts | 7-8 | 30 |
| Major Coherent Efforts | Three-Four | 20-25 (in structure only.) | Long range |

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# SECTION IV

# THE REPORT OF THE PANEL ON DEFECTS

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NATIONAL ACADEMY OF ENGINEERING
DIVISION OF ENGINEERING - NATIONAL RESEARCH COUNCIL
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AD HOC COMMITTEE ON CHARACTERIZATION OF MATERIALS

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## FOREWORD

The science and technology of defects in solids is a highly complex and involved area. Moreover, it is one which has occupied the attention of solid state investigators for a long time. With such an extensive background, it is incumbent upon the authors of this report to focus attention on specific aspects and to assume on the part of the reader at least a qualitative understanding of measurement techniques and properties of solids, including familiarity with the specialized language. Otherwise the report would assume an unmanageable size. In addition it has been necessary to deal, in many cases, with illustrative examples representative of groups of materials. It is obviously not possible nor desirable to attempt to present a handbook which covers large numbers of the various materials—either those having application in the electronics category or in the structural area. The point of view adopted in this report is always in the direction of the application of the material, since this is the basis of any practical characterization.

The members of the Panel are indebted to a number of persons for helpful comments and suggestions. In particular, we wish to mention Drs. P. Baltzer, C. Butler, R. Dreyfus, R. Enstrom, H. Frederikse, R. Lee, M. Pope, F. Rosi, G. Schwuttke, M. Seltzer, J. Sharp, W. Sibley, L. Slifkin, E. Sonder, J. Wachtman, and L. Weisberg.

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## SECTION IV. THE REPORT OF THE PANEL ON DEFECTS

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# I. INTRODUCTION

## THE IMPORTANCE OF DEFECT CHARACTERIZATION

As is well known to solid state scientists, the physical properties of inorganic materials and their behavior in solid state reactions depend essentially on structure and composition. More particularly, the pertinent factors may be specified as follows:

(1) Chemical composition

(2) Crystal structure

(3) Defect nature

If the material is not a single crystal, then the microstructure is of importance--as discussed in the section on polycrystals.

In this section we shall be dealing mainly with the third aspect listed above. By the term defects, we shall mean deviations from the otherwise regular atomic array and charge pattern as determined by the crystal structure of the material, and from the energy spectrum as determined by the band structure or the energy level scheme. For thorough characterization we need to know the types and concentrations of imperfections present, their interactions, and their effects on the physical properties. The purpose of characterization is to place limits on the allowable or desirable concentrations of imperfections for a specific use of the material. The importance of adequate characterization and of being able to produce materials within the tolerance limits for certain applications is well known in the case of the so-called "communication" materials--i.e., those which participate actively in electronic devices. Here, for example, the presence of certain defects can introduce various kinds of energy levels within the forbidden gap. These can have a profound influence upon the electrical properties. Defects can in principle affect the long-time operating

stability of a device by facilitating diffusion of dopant materials away from junctions or contact regions. This effect is now observed to be of practical significance under the stringent operating conditions of exposure to high energy radiation. Most semiconductor devices depend for their operation on the existence of well-controlled internal electric fields which are produced by sharp gradients of impurity concentration. They are, therefore, highly nonequilibrium structures, in which any relaxation toward equilibrium properties is potentially ruinous to the device. This tendency to relaxation is either promoted or hindered by the presence of appropriate defect structures.

Structural materials are even more complex from the defect point of view. Optimum properties often depend on the presence of high concentrations of dislocations and various kinds of area defects. In critical applications, many serious difficulties can arise from the complex interactions between point defects, dislocations, stacking faults, and other interfaces. Unfortunately, it has rarely been possible to identify clearly the interaction or series of interactions that are responsible for a particular aspect of the behavior. A large part of the total research effort in physical metallurgy and ceramics is aimed at identifying the factors that affect phenomena such as kinetics of recrystallization, fatigue, brittle fracture, yield strength, rate of strain hardening, creep, and corrosion.

In view of the above considerations, it can be understood that adequate characterization and understanding of the properties of defects is often highly important, both in materials for electronic applications and also in those for structural applications—especially where there may exist unfavorable environments from the standpoint of temperature, stress, corrosive chemicals, or radiation effects. In this connection, interesting findings

exist in regard to dimensional stability. For various space applications, including elements in precision optical equipment, constancy in dimensions of the order of 0.1 microinches per inch or less over appreciable periods of time is desirable. Studies on various structural specimens, however, have revealed long-term drifts—of the order of microinches per inch over a period of years—in certain materials, as well as appreciable changes occurring as a result of even the most careful fabrication techniques.[1] Apparently the question of thermodynamic equilibrium of defects and foreign atoms is becoming a real problem when ultra stability is demanded.

Any characterization of practical value must take into account the use of the material. Clearly, different standards are involved if the objective is a specimen for basic studies on, say fatigue or brittle fracture, a thermo-electric generator, a radiation counter or dosimeter, a p-n junction for an electronic device or a junction laser. In the case of a refractory metal, an illustration of the fact that we must remember the connection between the physical property and the defect is given by tungsten, where the vacancy concentration undoubtedly plays a role in high temperature creep. Yet the usual equilibrium concentration of vacancies has little effect on the electrical conductivity itself. However, vacancies indeed play a vital role in determining the lifetime of tungsten filaments operating under d. c. conditions. In view of the special relationship between defects and properties, one can cite numerous examples in the case of metals where a foreign defect in small concentrations does not have much effect and other cases where it is critical. For example, it is doubtful if $10^{-5}$ Cu in Au changes the tracer diffusion coefficients much (maybe a factor of 2-5 could be expected). On the other hand the same Cu concentration is responsible for the hetero-geneous nucleation of vacancy clusters in gold quenched from high

temperatures, and the presence of this Cu drastically alters the kinetics of clustering.

For thermoelectric cooling or power generation the content of native defects is usually masked by the relatively large concentration of dopants. For transistors, on the other hand, where the minority carrier lifetime is important, the defect concentration is of direct concern. In many alloys, the problem of homogeneity is very real.

In the case of structural elements, regions of which may be subjected to high stress concentrations, careful specification and characterization of materials in order to reduce the possibility of failure by brittle fracture may be highly important. Many examples exist of structures which have failed when subjected to stresses as low as 1/3 their proper design values because of imperfections such as minute corrosion pits, metallurgical defects, or hydrogen absorbed near a defect. Illustrative examples of failure in DOD matériel are given in Appendix A.

## II. RECOMMENDATIONS OF THE PANEL

Three different facets to the problem can be delineated:

(1) Making the technical community more aware of the need for adequate characterization of materials and of the difficulties which might ensue as a result of the use of materials for which the defect nature is not understood.

(2) Improving the availability of well-characterized materials to the average scientific worker or development engineer.

(3) Developing, in certain cases, better methods for characterization and also improved techniques for preparing certain materials with low imperfection contents.

It is believed that the first category above would benefit substantially from more research on the relationship between defects and properties. In addition, an education program is desirable for those who are not aware of the importance of adequate characterization. The recipients of this information should also include editors and referees of journals which publish articles concerned with the properties of materials and with devices exploiting those properties.

The second category concerns a problem which has at one time faced almost every scientific worker—namely that of obtaining specimens of improved quality, well-characterized materials for use in basic or applied research. The problem is severely complicated by the fact that science and technology are dynamic, never static, and that what was good enough yesterday is only marginal today. This means that a good materials activity must always involve research to push back the boundaries—it can never degenerate into routine production. Therefore, associated with a superior materials facility is always a critical size; and because of the complexities

involved in the production of superior materials and the thorough characterization of them, this critical size calls for an expensive activity. In addition, since in most cases the raison d'être for materials development is exploitation of properties, there must be close interaction and collaboration between the materials' producers and characterizers and the users. In view of the complexity and the dynamic nature of materials science and technology, this latter aspect is becoming of increasing importance in many cases.

The third category involves research and related activities specifically adapted to solving some of the more pressing problems, as documented in the present study. The more obvious needs include:

(a) Further development and improvement of measuring techniques for determination of the kind, concentration, and distribution of defects, including: better nondestructive techniques for determining defects in situ-- particularly needed in device technology (Refer to Part XI); specific techniques for the determination of single and clustered point defects (Refer to Parts IV, VIII, X); reliable etch-pit techniques which do not depend upon the presence of chemical segregation at the dislocation (See Appendix F-I-2); techniques, probably involving computerized scanning, for more meaningful dislocation characterization in metals in the $10^{10}$ to $10^{12} cm^{-2}$ range (See Appendix F-III); and more advanced ultrahigh resolution ion microscopy for studies involving large numbers of successive layers, including refinement of ultrahigh resolution ($0.5\text{Å}$) electron transmission microscopy which might be used in conjunction with the Moiré effect to study tiny clusters of defects and atomic distributions around dislocations (Refer to Part XI & Appendix E-I). Refinement of methods for measuring macroscopi dilatation, density, and lattice parameters (See Appendix E-II).

(b) Better information on the equilibrium and kinetic behavior of defects, including: their creation and behavior in hostile environments such as radiation, mechanical and thermal stresses, or thin film deposition conditions (Refer to IX-VIII-XI); determination of thermodynamic parameters for defect formation under equilibrium conditions (VIII, Appendix B), and the rate parameters of kinetic processes (diffusion precipitation), and determination of the effects of electrons and holes on phenomena associated with point defects, for example, diffusion coefficients (III). Investigations on systematically doped material for obtaining binding energies of vacancies with impurities (Appendix E-I, II); and the increased use of pressure as a variable in measurements to assist in providing information on the volume of formation around vacancies and on the atomic relaxation (Appendix E-I).

(c) Better understanding of the interrelationships among measured physical phenomena and among defects, including: radiation effects and their correlation to material composition and primary defect formation (XI); the relationship between defects and electrical, thermal, and other physical properties of solids (IX); and the interpretation and understanding of indirect techniques for characterization, many of which are highly sensitive, but usually require analyses of a multiplicity of phenomena to provide specificity (IX).

(d) Methods of obtaining materials with fewer defects (XI & Appendix E), or with known concentrations of specific defects.

(e) Better characterization of surfaces (IX, XI).

### III. TYPES OF DEFECTS TO BE CONSIDERED

Four principal types of defects and their subgroups are outlined below:

#### A. POINT DEFECTS (OR AGGLOMERATES THEREOF)

(a) Vacancies: Absence of atoms at sites which according to the crysta structure should be occupied.

(b) Intersititial atoms: Atoms present at sites which according to the crystal structure should not be occupied.

(c) Antistructure defects: Atoms present at sites which according to th crystal structure should be occupied by other types of atoms. These can occur only in compounds.

If the concentration of one constituent is at least an order of magnitude lower than that of others—i.e., in low-concentration solid solutions—one usually considers the latter as the basic components and the low-concen-tration type as a foreign component. It is then useful to distinguish betwee defects that may be formed in the pure crystal, to be called native point defects, and those consisting of foreign atoms, to be designated as foreign point defects. Any of these may occur at sites distant from one another, forming what will be called single point defects, or they may occur at neighboring sites, forming pairs, triplets, or, in general, agglomerates or clusters. The agglomerates may involve only native defects, only forei defects, or both native and foreign defects. When point defects can be re-garded as resulting from the addition or subtraction of atoms, the centers formed have no charge relative to the surrounding crystal: their effective charge is zero. Often, however, such imperfections may either split off or accept one or more electrons. They then acquire an effective charge. This effective charge (or its absence) is an essential feature of the point defects and has to be included in their characterization.

Foreign atoms may be present in a material for two reasons. In the first place, they may be present because they were present in the basic chemicals and have not been removed by purification. In this case we shall speak of impurities. In the second place, foreign atoms may be present because they have been added on purpose. In this case we speak of additives or dopants.

Since we only add atoms, the presence of which is favorable with respect to the application of the material, dopants are always atoms whose presence is wanted. Impurities, on the other hand, may either be detrimental, neutral, or favorable with respect to the planned application. In general, the presence of impurities is unwanted and great efforts have been spent (and will be spent in the future) on their removal by appropriate purification techniques.

## B. ELECTRONIC DEFECTS

In crystalline solids, electronic energy states are restricted to more or less sharp levels or bands, the width of which depends on the overlap of the wave functions of adjacent atoms.

At low temperature, the levels are filled up to a certain energy, and empty above that energy. In metals the filled and empty levels touch, but in semiconductors and insulators the occupied and unoccupied states are separated by an energy gap, the so-called band gap. The low temperature situation represents an ordered state. At higher temperature, or after bombardment with high-energy particles or photons of a suitable frequency, electrons are excited to higher states, leaving unoccupied levels at lower energy. If the excitation energy is sufficiently large, the excited electrons and the missing electrons may move in an electric field or a concentration gradient. They may be considered to be defects and are called, respectively, quasi-free electrons and holes.

At low excitation energies, excited states exist in which the electrons and holes are not yet free to move individually, although they may move together. Such an electron-hole pair is called an _exciton_.

Two types of electrons and holes may be distinguished, according to the extent to which they are free to move. In a crystal, an extra charge—as present on an electron or a hole—tends to polarize the surrounding media which lowers the energy. If atom cores are moved in the process, this polarization represents a tendency to localize the free charge (self-trapp) Overlap of wave functions, on the other hand, favors exchange of electrons between neighboring atoms and thus tends to keep charges free. In the exchange, energy is also gained. If the exchange energy is larger than the energy of self-trapping, the charges are free, or quasi-free, and one speak of the collective electron model, or band picture, of conduction and charge migration. This is the case in most elemental crystals and covalently bou compounds.

If the energy of self-trapping is larger, however—as may be expected for ionic crystals which are strongly polarizable—the charges tend to be trapped and can move only occasionally when locally enough energy is assembled to lift the electron or the hole out of its self-inflicted trap. In this content one speaks of the _hopping electron model_.

## C. LINE DEFECTS (DISLOCATIONS)

(a) Perfect dislocations - Burgers vector is a lattice vector.

(b) Imperfect dislocations - The dislocation line forms the boundary of an area defect or stacking fault.

Classification of a line defect involves specification of geometrical aspects such as:

(i) Burgers vector.

(ii) Orientation - angle between the line and its Burgers vector ($90^\circ$, edge dislocation; $0^\circ$, screw dislocation).

(iii) Plane of dissociation, if split into two or more imperfect dislocations and associated stacking fault ribbons.

(iv) Shape of glide surface - jog concentration.

(v) Cut-off radius of its elastic strain field - generally determined by the average distance from another dislocation of opposite sign.

(vi) Core structure - the size of and arrangement of atoms in the region where atom displacements are larger than about 1/10 the atom diameter.

(vii) Impurity atmosphere.

## D. AREA DEFECTS

(a) Gas-solid interfaces.

(b) Solid-solid interfaces - grain boundaries, twin boundaries, stacking faults, interphase boundaries.

(c) Solid-liquid interfaces.

Description of an area defect involves:

(i) Orientation of the mathematical surface relative to the crystal or crystals.

(ii) Coherence or average coordination number for atoms at interface.

(iii) Atomic scale roughness - ledges or steps - kinks - adsorbed atoms.

(iv) Impurity atmosphere—for example, adsorbed layers at the interface.

# IV. TOTAL AND PARTIAL EQUILIBRIUM OF POINT DEFECTS; DEFECT DISTRIBUTIONS

An essential difficulty in materials characterization results from the fact that defects may be formed or annihilated as a result of thermal treatment or handling. Thermodynamics shows that under equilibrium conditions a certain concentration of point defects of any type must be present at all temperatures above absolute zero. Whether or not equilibrium is reached depends on the rate of formation or annihilation of defects, and this in turn depends on the rate of diffusion of lattice constituents. Since atomic diffusion processes depend exponentially on $1/T$, there is in general a critical temperature above which the population of atomic population of atomic point defects reaches equilibrium in a reasonable time. Below this temperature, complete equilibrium is not reached; point defects are frozen in at a concentration dependent on the previous high-temperature treatment. This critical temperature differs not only from material to material, but usually also with the type of atomic defect in a given material. Thus the crystal may be in equilibrium as far as one type of defect is concerned, but not as regards another. The same applies to foreign point defects. Electrons and holes are usually mobile down to extremely low temperatures. Therefore, apart from a few cases in which stable traps are involved or in which recombination is hindered by a potential barrier, or other means, electronic equilibrium is obtained at almost all temperatures.

In cases in which a certain point defect does not reach its equilibrium concentration, it may react to form some intermediate between the state of complete equilibrium and that of complete nonequilibrium. Thus, if equilibrium requires the removal of defects from the crystal, the defect may form smaller or larger clusters inside the crystal—that is, the defects precipitate in the crystal. This often involves dislocations—precipitation

either occurring at dislocations or else the precipitation itself (e.g., in the case of vacancies) forming dislocations (dislocation loops). Since properly dissolved and precipitated defects affect the physical properties of a crystal in a different way, it is obviously necessary to distinguish between them. Thus, if foreign constituents exist, a chemical analysis which merely establishes the presence of the constituent anywhere inside the material, may not be sufficient to characterize the solid.

## V. SPECIAL COMPLICATIONS ARISING FROM THERMAL EQUILIBRIUM IN COMPOUNDS; NONSTOICHIOMETRY AND VARIABILITY OF THE MECHANISMS OF INCORPORATION OF FOREIGN ATOMS

Whereas previous arguments apply to elemental crystals as well as compounds, additional complications arise in the latter:

• Atomic disorder (not accompanied by a change in composition) involves defects of various types in ratios determined by the crystal structure. For instance, in a compound MX one may have disorder processes involving M and X vacancies $V_M$ and $V_X$ (Schottky disorder), interstitial atoms and vacancies (Frenkel disorder) or misplaced atoms of two types $M_X$ and $X_M$ (antistructure disorder)—to mention only the most common types. In all these cases, the product of the concentrations of the defects involved is constant (dependent on temperature).

• Deviations from the single stoichiometric composition as determine by the crystal structure. This generally involves defects of a type formed by atomic disorder. For instance, an excess of M will give rise to $V_X$ if Schottky disorder prevails, but to $M_i$ if Frenkel disorder is dominant.

• In the case of foreign defects, the situation is complicated beyond that encountered in elemental crystals in that, even when properly dissolved the effects caused by a certain foreign constituent are not uniquely determined. In the first place, the foreign atoms may be present at different sites—forming different foreign point defects. In the second place they may, through defect interactions, give rise to different types of native defects. Thus allovalent foreign atoms may give rise to electronic defects in one case and to native atomic defects in another.

The classical example is the formation of silver vacancies in AgBr as a result of the presence of divalent cadmium at silver sites, the concentrations of cadmium and the induced vacancies being equal. Similarly, in many semiconductors, electrons or holes are formed in concentrations equal to those of foreign donors or acceptors present. For example, in germanium and silicon, phosphorus at the germanium or silicon sites gives rise to an equal concentration of electrons.

The differences noted above may even occur in the same material, the prevailing mechanism of incorporation depending on the equilibrium conditions during preparation or anneal. Thus in $CdS^{(2)}$ and $CdTe^{(3)}$, incorporation of higher valent gallium or indium at cadmium sites (or chlorine at sulfur sites) may give rise either to the formation of free electrons, with

$$[In_{Cd}^{\cdot}] = [e']$$

or to the formation of cadmium vacancies, with either

$$[In_{Cd}^{\cdot}] = 2 \cdot [V_{Cd}'']$$

or

$$[In_{Cd}^{\cdot}] = [V_{Cd}']$$

The dots and dashes indicate effective positive and negative charges. As we shall show in greater detail later (Appendix B) this behavior can easily be accounted for. As shown in Appendix B, Fig. 1 (which summarizes the situation for CdTe + In), compensation by electrons occurs for conditions under which cadmium vacancies tend to be filled; i.e., for high cadmium pressure. Compensation by vacancies happens at increasingly lower cadmium pressures (or higher sulfur pressures). Note that the semiconductor properties are markedly affected by the change in compensation. In the first case the crystals are low-resistivity n-type semiconductors; in the latter they are high-resistance, almost-intrinsic semiconductors.

Evidently, for proper characterization of the material it is not enough to give the concentration of foreign constituents—even if we would know the fraction properly dissolved and present at lattice sites; we must know the compensation mechanism or, in other words, the mechanism of incorporation. This mechanism (and also the concentrations and types of defects formed under equilibrium conditions in pure crystals) depends on the activ ities of the components in the ambient atmosphere in combination with the basic thermodynamic parameters of defect formation. For this reason, determination of these parameters is of great importance for the characterization of materials. This is especially so because the change from one mechanism to another may occur at a relatively low temperature. For instance, CdS containing Al at Cd sites, rendered nonconductive by heating in vacuo at $600°C$, becomes conductive again by heating in cadmium vapor at the same temperature. At the same time the luminescence spectrum changes in a significant way, indicating the formation and annihilation of cadmium vacancies.[4] These considerations are developed further in Part VII. (dealing with the impermanence of defect population).

A detailed discussion of defect equilibria in the binary compound CdTe, showing the intricacies of the interactions as well as the effect on the incorporation mechanism of a foreign donor (indium), is given in Appendix

Although we have mentioned AgBr and some II-VI compounds as examples, this does not mean that the validity of the statements made is restrict to these compounds. The statements are quite general and apply, for instan to the alkali halides and to the III-V compounds. Recently the methods of defect chemistry have also been applied to ternary compunds.[5]

## VI. NONEQUILIBRIUM FORMATION OF POINT DEFECTS

In addition to the thermal formation of point defects, such defects may also be formed by nonequilibrium processes; viz., by <u>bombardment</u> by high-energy particles or quanta, and by migration (<u>climb</u>) of dislocations, as may happen in cold work.

## VII. FORMATION OF LINE AND AREA DEFECTS

Dislocations and area defects are not formed in chemical equilibrium Whenever they are present (and as a rule they are), they are formed by nonequilibrium processes, such as plastic deformation, nonlinear tempe ture gradients, bombardment, point defect condensation, etc. Although s defects themselves are not in equilibrium, they may, and usually do, aif the point defect equilibria. We have seen already that they may act as a nucleus for precipitation of point defects and as sources for vacancies i plastic deformation.

They may also take part in the equilibrium proper through elastic or electric interactions. In the alkali halides, for instance, dislocation co. are charged, the charge being compensated by a cloud of point defects v an excess of defects of opposite charge surrounding it. In such cases, t! is a difference in the concentration of point defects in the bulk far away from and near to the dislocation. The same applies to surfaces.

## VIII. IMPERMANENCE OF DEFECT POPULATION

Handling and specimen manipulation may so drastically alter the numbers
and types of defects present in a crystal that the initial characterization
no longer applies. A case in point is a nearly perfect copper crystal.
Stresses of a few $g/mm^2$ due to handling or thermal gradients can multiply
the total length of dislocation line in the crystal several orders of magnitude.
One way of dealing with this problem is to stabilize the dislocation structure
by introducing another type of defect. For example, it has been found con-
venient to use "radiation hardening" by exposure of the crystals to fast
neutrons prior to preparation of specimens for x-ray topography or trans-
mission electron microscopy.[6] Often the only assurance that the defect
population has not been changed can be given by reevaluation after each step.

An important consideration is obviously the temperature dependence of
the equilibrium. For example, if a material is used in connection with a
measurement or to construct a device, and this involves heating (as is
often the case), one cannot in general rely on the characterization of the
material as determined by its composition and previous history. This can
only be done in cases where it has been shown that, for the conditions of
experiment envisaged, all equilibria involving the immigration of atoms
are frozen in.

Thus, for characterization a double standard seems appropriate:

(1) For materials in which, under the conditions of normal employment,
defect equilibria are frozen in, it is sufficient to give the crystal structure,
the chemical composition, and the concentrations of defects.

(2) For materials in which defect equilibria are never completely fro
in, it is necessary to give not only the crystal structure and the chemica
composition, but also the fundamental thermodynamic parameters gover
the formation of defects in chemical equilibrium and the kinetic paramet

Both types of characterization require experimental methods designe(
to indicate the presence of particular defects and their concentrations.

## IX. METHODS OF DEFECT DETERMINATION

In principle, all physical properties dependent on the presence of defects may be used as techniques of defect determination, although wide differences in sensitivity[7] are encountered. Many of the methods, however, are not capable of distinguishing between various kinds of defects—that is, they are nonspecific. Although the measured quantity is in some way sensitive to defects in the crystal, the measurement does not itself show, with a relatively high certainty, the exact type of defect which is affecting the measurement, or the number of such defects present. In a specific method, on the other hand, the observations do, with relative certainty, identify the type of defect and yield its concentration. An example of a specific technique is direct observation; i.e., the reception of an individual signal or image resulting from the defect. Indirect techniques, where various affected physical properties are measured, possess varying degrees of specificity. In many cases it is necessary to obtain information from various property measurements in order to identify unambiguously the natures of the defects. This utilization of the combined information obtained from investigations of several properties is often of substantial importance, and it is an area where additional research might profitably be carried out.

When doing research on materials, it is usually preferable, when possible, to determine first the defect type and concentration in the crystal and then to perform those physical property (indirect) studies that one wishes, relating the physical property to the defect nature of the solid. In this way one relates properties to structure. It is usually less satisfactory to measure only the physical property, and then by theory or otherwise to try to deduce the type of defects present.

Various properties and measurement techniques which can be used for defect determination, their sensitivity, and their specificity, are listed in

Table I. For dislocations, the first four methods correspond to the direct techniques. For point defects, on the other hand, the only method capable of giving direct observation is apparently the field ion microscope, and th is limited in application to only a very few substances. Several of the ind rect techniques, however, possess certain degrees of specificity, as for example, spin resonance, Mössbauer effect, etc. The simultaneous mea.; ment of lattice constant and density is a method which is specific in its ability to distinguish interstitial-type (or mass excess) defects from vaca type (or mass deficient) defects, but it cannot distinguish among differen possibilities within each group. This method is potentially an important and its limitations and possibilities are discussed in Appendix E (Part II, under "Metals", although most of the remarks made there apply equally well to all categories of crystals.

In Table I, the magnitudes listed for the minimum concentrations detec able are to be regarded only as approximate. Furthermore, they are give for the materials or conditions which are most favorable. To illustrate th point by a simple example, we note that a measurement of the electrical conductivity near the limit of present experimental capability will provide a sensitivity to free electron concentration which is $10^5$ greater in a material where the electron mobility is $10^4$ $cm^2$/volt-sec than where it is $0.1$ $cm^2$/volt-sec.

It is seen in the table that a number of techniques are highly sensitive, although specificity is often a problem, even when multiple studies are carried out. As mentioned above, this is an area where considerable furth research is needed.

TABLE I

MEASUREMENT TECHNIQUES OR PHYSICAL PROPERTIES
WHICH MAY BE USED AS METHODS OF DEFECT DETERMINATION

| Measurement Technique or Physical Property | Type of Defect Indicated | Approximate Min. Concentration Detectable ($cm^{-3}$ or $cm^{-2}$) | Specificity | Applicable to | |
|---|---|---|---|---|---|
| | | | | Nonmetals | Metals |
| Optical microscopy | (a) decorated dislocations | 1 | + | + | |
| | (b) etch pits | 1 | + | + | + |
| | (c) decorated defect clusters formed by passing dislocation | (Resolution 1 $\mu$) | + | + | |
| Electron microscopy | (a) clusters of atomic defects | (Resolution 6-10 Å) | + | + | + |
| | (b) dislocations | 1* | + | + | + |
| Field ion or electron emission microscopy | (a) atomic point defects | 1* | + | + | + |
| | (b) dislocations | (Resolution 2-3 Å) 1 | + | + | + |
| X-ray topography (Lang, Borrmann techniques) | dislocations (Burgers vector) | (Resolution 2-5 $\mu$) 1 | + | + | + |
| Chemical analysis (nuclear activation analysis; mass spectrometer) | (a) foreign point defects (type and valence) | $10^{14} - 10^{18}$ | + | + | + |
| | (b) native atomic point defects (deviations from stoichiometry) | | - | + | + |

* Limitations imposed by typical specimen requirements lead to practical values between $10^6$ and $10^{10}$.

## TABLE I (cont'd)

| Measurement Technique or Physical Property | Type of Defect Indicated | Approximate Min. Concentration Detectable ($cm^{-3}$ or $cm^{-2}$) | Specificity | Applicable to | |
|---|---|---|---|---|---|
| | | | | Nonmetals | Metals |
| Chemisorption and Catalysis (Relation of extent of chemical reaction to density of active sites on surface) | (Phenomena still in research stage) | | | | |
| Conductivity, electronic | (a) electrons, holes | $10^8$ | + | + | + |
| | (b) atomic point defects from residual resistivity | $10^7$ | - | | + |
| Hall effect | electrons, holes | $10^8$ | + | + | + |
| Hall effect f(T) | energy levels of donors or acceptors | $10^8$ | - | + | - |
| Electron mobility as f(T) | (a) atomic point defects (charged) | | - | + | + |
| | (b) dislocations | | | + | + |
| Thermoelectric power | (a) electrons, holes | $10^9$ | + | + | + |
| | (b) mobile charged atomic point defects | | - | + | + |
| Thermoelectric power as f(T) | (a) energy levels of donor or acceptor | $10^9$ | - | + | |
| | (b) heats of transport of electrons, holes or charged atomic defects | | - | + | |

TABLE I (cont'd)

| Measurement Technique or Physical Property | Type of Defect Indicated | Approximate Min. Concentration Detectable ($cm^{-3}$ or $cm^{-2}$) | Specificity | Applicable to Nonmetals | Metals |
|---|---|---|---|---|---|
| Conductivity, ionic | charged native point defects | $10^{12}$ | – | + | |
| Conductivity, thermal as f(T) | (a) electrons, holes (b) atomic point defects (c) dislocations | $10^{17}$ | – | + | + |
| Cyclotron Res. | free electrons, holes (effective mass tensor) | $10^{11}$ | + | + | |
| Plasma Res. | free electrons, holes | $10^{11}$ | – | + | + |
| Azbel Kaner Res. | free electrons, holes (eff. mass tensor) | $10^{11}$ | + | + | + |
| Electron spin res. (specific due to fine structure resulting from nuclear moments) | (a) electrons, holes (b) point defects with unpaired spins, single as well as paired or clustered (anisotropy gives symmetry of centers) | $10^{11}$ spins | + + | + + | – – |
| | (c) centers at surfaces or dislocations | " | + | + | + |

TABLE I (cont'd)

| Measurement Technique or Physical Property | Type of Defect Indicated | Approximate Min. Concentration Detectable ($cm^{-3}$ or $cm^{-2}$) | Specificity | Applicable to | |
| --- | --- | --- | --- | --- | --- |
| | | | | Nonmetals | Metals |
| Electron-Nuclear double res. (Endor) | Atomic point defects with unpaired spin, mapping of wave functions over surroundings through interaction with nuclear moments of neighbors | $10^{12}$ spins | + | + | - |
| Nuclear Magnetic Res. | Atomic point defects | | - | + | - |
| Density | (See lattice constant and density) | | | | |
| Dielectric Loss | (a) free electrons, holes | $10^{15}$ | - | + | - |
| | (b) electronic polarization of atomic imperfections | | - | + | - |
| | (c) migration of charged atomic point defects | | - | + | - |
| | (d) reorientation of electric dipole associated with the point defect | | - | + | - |
| Diffusion, self | vacancies, interstitials, or point defects pairs | $10^9$ | - | + | + |
| Diffusion, foreign | (a) foreign interstitials | $10^9$ | - | + | + |
| | (b) foreign substitutional-vacancy pairs | | - | + | + |

## TABLE I (cont'd)

| Measurement Technique or Physical Property | Type of Defect Indicated | Approximate Min. Concentration Detectable (cm⁻³ or cm⁻²) | Specificity | Applicable to Nonmetals | Metals |
|---|---|---|---|---|---|
| Internal Friction | (a) electronic polarization of atomic point defects | | – | + | – |
| | (b) electrons, holes formation | $10^{17}$ | – | + | – |
| | (c) reorientation of point defects | | – | + | + |
| | (d) migration of dislocations | | – | + | + |
| Interphase equilibrium | atomic point defects (charge from slopes) | (reliability subject to question) | | | |
| Lattice constant and density | atomic point defects type and concen. | $10^{18}$ | ± | + | + |
| Magnetic susceptibility (static) | (a) electrons, holes | $10^{15}$ | – | + | |
| | (b) point defects with unpaired spins | | – | + | |
| Mössbauer effect | structure elements (normal or defects), emitting $\gamma$ radiation with a long lifetime | symmetry of crystal field (coordinations) | + | + | + |
| Neutron Elastic Scattering | Atomic point defects and small clusters | $10^{19}$ | ± | + | + |

**TABLE I (cont'd)**

| Measurement Technique or Physical Property | Type of Defect Indicated | Approximate Min. Concentration Detectable ($cm^{-3}$ or $cm^{-2}$) | Specificity | Applicable to Nonmetals | Metals |
|---|---|---|---|---|---|
| Optical abs. (spectral distribution; dichroism) | (a) free electrons, holes (band structure effective masses) | $10^{15}$ | − | + | + |
| | (b) atomic point defects (anisotropy symmetry) and Zeeman effect for interatomic transitions, type and valence of ions; bound exciton absorption | $10^{15}$ | ± | + | − |
| | (c) optically active vibrational modes near atomic point defects (IR isotope effects) | $10^{18}$ | + | + | − |
| Raman effects (use Lasers) | optically inactive vibrational modes involving atomic point defects | $10^{14}$ | − | + | − |
| Luminescence (spectra; polarization) | Atomic imperfections (type, energy levels) | $10^{18}$ | ± | + | − |
| Photoconduction | electrons, holes | $10^{10}$ | − | + | − |
| Excitation spectra of luminescence and photoconductio… | electronic energy levels of atomic point defects | $10^{10}$ | − | + | − |

TABLE I (cont'd)

| Measurement Technique or Physical Property | Type of Defect Indicated | Approximate Min. Concentration Detectable ($cm^{-3}$ or $cm^{-2}$) | Specificity | Applicable to Nonmetals | Metals |
|---|---|---|---|---|---|
| Glow curves of photoconduction or fluorescence | atomic point defects (position of electronic levels) | $10^{10}$ | – | + | – |
| Stimulation and quenching | atomic point defects (position of electronic energy levels) | $10^{13}$ | – | + | – |
| Electron trapping effects (buildup and decay of photoconduction and fluorescence; space charge limited currents) | atomic defects (existence of energy levels in forbidden gap; trapping cross section) | $10^{10}$ | – | + | – |
| Specific heat as f(T) | atomic and electronic disorder | $10^{18}$ | – | + | + |
| "Titration" with electrons or holes from nuclear decay or from defects formed by bombardment | atomic point defects | $10^{14}$ | – | + | – |
| X-ray small angle scattering | (a) vacancies or foreign point defects | $10^{19}$ | – | + | + |
|  | (b) small point defect clusters | $10^{18}$ | – | + | + |

Although the considerations set forth throughout this section are concerned basically with bulk materials, it is desirable at least to mention the importance of surface phenomena in connection with the characterization of materials. It is obviously essential to insure that the interpretation of bulk properties is not clouded by contributions from the surface. In addition, surface characteristics are of primary importance in a large number of a. including, for example, catalysis, kinetics of crystal growth, corrosion, and various electronic devices. Although space limitations preclude a detailed consideration of these areas—with the exception of some later remarks in connection with silicon devices (in XI)—the importance of surface effects should not be overlooked. As a matter of fact, the desirability of techniques with a high degree of specificity is particularly consequential in the characterization of surfaces. For many materials, the chemical and electrical properties of the surface are notably sensitive to very low levels of contamination. In such cases, the results of indirect techniques of defec. determination are easily invalidated by the presence of surface contaminar. For example, it is usually the case that the active sites which are investigated by the chemisorption and catalytic techniques may equally well be defects or adsorbed contaminants. At the present, in situ field ion microscopy and electron microscopy are the only techniques for surface defect determination which have any degree of specificity, and it is clear that reliable determinations for surfaces must be carried out in ultrahigh vacua

Low-energy electron diffraction has recently been applied to the study of ion bombardment induced surface damage. This technique has the advantages that it provides identification of those phenomena which are relate to surface contaminants rather than to defect structure, and is sensitive to surface faceting of small individual facet areas ($100 \text{ Å}^2$). Sensitivity to

other defect structures is low and nonspecific. The present situation is that the characterization of surfaces is in a highly embryonic state, and it represents an area where much more work needs to be done.

## X. ILLUSTRATIVE EXAMPLES OF PRESENT
## STATE OF TECHNOLOGY

An over-all perspective of the present state of technology for prepari
materials of low defect content and for determining the concentration of
certain defects is provided by the data given in Table II. The figures are
order-of-magnitude only, and for more detailed information concerning
the various classes of materials, subsequent sections of the report shoul
be consulted. The quoted values apply only to bulk crystals, not to whise
or platelets. In regard to defects, it is to be noted that clusters of point
defects constitute a special case and cannot conveniently be represented
by a set of numbers. This is an area where further work is needed. The
elusive area lies between a few and several hundred defects in a cluster.

## TABLE II

### ILLUSTRATION OF PRESENT STATE OF TECHNOLOGY

| | Point Defects (inc. pairs, triplets, etc.) $cm^{-3}$ | Line (dislocations) $cm^{-2}$ | | Area (Stacking Faults) $cm^{-1}$ |
|---|---|---|---|---|
| Prepare/Determine | | P / D | D | P/D |
| Si | $<10^{12}$(a)  $10^{12}$ | ? | 1 up to $10^{11}$(d) | 0/1 |
| Ca | $<10^{12}$(a)  $10^{17}$ or $10^{18}$ | 0 | 1 up to $10^{11}$ | 0/1 |
| Fe | $<10^{18}$(a)  $<10^{18}$ | $<10^2$ / $10^6$ or 7 | 1 up to $10^{11}$ | 0/1 |
| KCl | $10^{16}$(b)  $10^{10}$ to $10^{16}$(c) | $10^4$ (or lower) | 1 | (e) |
| ZnS | $<10^{17}$(a)  $10^{10}$ to $10^{16}$  $\geq 10^{17}$(b) | $10^5$ | 1 | $10^3$ |
| CdS | $<10^{16}$(a)  $10^{10}$ to $10^{16}$  $\geq 10^{16}$(b) | $10^7$ | 1 | $0 - 10^3$ |
| Anthracene | ?  $10^{15}$(?) | $10^4$(?) | ? | ? |

(a) Native defects; i.e., those formed in the absence of foreign atoms. Since in the purest crystals available the properties are still determined by foreign constituents, we can only state that the concentration of native defects is smaller than the concentration of foreign defects present in those crystals.

(b) Foreign defects; either the foreign defects themselves or native defects formed under the influence of the (aliovalent) foreign constituents.

(c) Limit depends on sensitivity of technique applicable. An example of a high sensitivity method is electron spin resonance.

(d) Lower limit by x-ray topography, upper limit by transmission electron microscopy.

(e) Low-energy faults probably do not occur.

## XI. DETAILED CONSIDERATION OF REPRESENTATIVE GROUPS OF MATERIALS

In the sections to follow, we shall concentrate on examples belonging to the following classes of materials:

(1) Semiconductors—elemental and compound, as well as certain oxides

(2) Alkali halides

(3) Metals

(4) Organic Materials—anthracene

A division into categories such as those given above is necessitated by the drastically different applications of the various materials, with highly significant differences in the role of defects, and by the necessity of employing individually suitable techniques for characterization.

## A. SEMICONDUCTORS—ELEMENTAL AND COMPOUND, INCLUDING CERTAIN OXIDES

### Silicon — State of the Art

Silicon is one of the most widely studied solids. As was seen in Section IX, and as is discussed in more detail in Appendix C, a variety of techniques of varying but generally high sensitivity exists for the detection of defects in this material. In many instances, several of the techniques can be used in the study of a specific defect, leading to greater confidence in the resulting determination of its concentration and properties. In addition, the silicon lattice has great mechanical strength, even at high temperatures, and all but a few chemical impurities have very low solubilities in it. Thus, a great deal of progress has resulted from the very substantial amount of scientific attention which has been attracted to this material. Both the purity and perfection possible in large silicon crystals are perhaps unique among solids.

Problems:

(1) Most of the techniques listed in Tables I and II should be applied to large volumes of relatively homogeneous material for best results. However, the continuing trend toward smaller and smaller devices places heavy emphasis on the importance of micro-techniques and especially techniques which can be used to characterize materials at or very near to surfaces.

Developments in the field of Schottky barrier (metal-semiconductor) diodes and insulated-gate field-effect transistors (IGFET) make surface control and characterization a prime area of study.

Despite the large volume of work done on surface phenomena there is surprisingly little known. There is a large body of empirical knowledge on the effects of various environments on the production and properties of unidentified surface states. There is a considerable knowledge of the properties of atomically clean silicon surfaces produced by cleavage-in-vacuum techniques. There is, however, virtually nothing known about the properties of silicon surfaces in their most important technological state; i.e., in contact with other solid materials such as metals or dielectric insulators.

Recently, as a result of interest in the oxide IGFET, there have been a number of studies of the influence of radiation and mobile ions in the oxide on the behavior of these devices and related structures. These studies are to a large degree phenomenological. They have indicated that the creation or movement of charge within the oxide produces a necessary change in electrostatic potential in or near the silicon surface. This is described in terms of an equivalent "surface charge density." Further, there have been experiments using insulated-gate structures which attempt to measure the Hall mobility of the mobile surface charges. There is still no really fundamental information about the nature of the silicon surface.

(2) Another need arising out of device technology is for the ability to characterize the defect properties of the completed device. One source of difficulty which has come under control only recently, for example, is the introduction of damage to the crystalline lattice structure during dopant diffusion, alloying contact attachment, and other fabrication steps. Dislocations are introduced at the surface, and their subsequent motion leaves a damaged lattice containing vacancies, interstitials, and aggregates of these defects in various geometries. The subsequent uncontrolled further motion of these defects during the service life of the device can degrade the original impurities' distribution and ruin the device. The issue, clearly, is how to characterize the material after the device has been fabricated, because only then do the materials' characteristics which will be of importance during usefu. fe actually become evident. If the dopants change their location or electrical properties, the device is degraded. This can come about via two principal mechanisms, associated with lattice vacancy defects.

• The diffusion of substitutional foreign atoms in silicon takes place via vacancy migration, perhaps with the bulk of the vacancies present as divacancies. The higher the concentration of vacancies, the more rapid is the migration of substitutional atoms. All the major doping agents for silicon devices, with the important exception of lithium-drifted radiation detectors, are substitutional. Thus, anything which contributes to a shift in the vacancy concentration in the silicon lattice is potentially disruptive to its kinetic behavior.

Because of the fact that minute distances are inherent in silicon devices and also that long operating times are anticipated, the limits on acceptable diffusion coefficients can be surprisingly stringent. For example, in devices where structures of linear dimension $L \sim 10^{-3}$ cm are found in abundance

and device operating life may be expected to extend for ten years, $D \approx L^2/\tau \approx 10^{-14} \, cm^2 \, sec^{-1}$ is a rough upper limit on acceptable diffusion coefficients.

- Close geometric association of dopants and vacancies or dislocations alters the electrical properties of both and can perturb the electrical potential structure associated with the impurity distribution. In this instance, therefore, it is necessary to know not only the concentration of vacancies but also their state of aggregation.

(3) A third challenging area in silicon materials characterization is associated with the use of devices in an environment of high energy radiation. The present state of our understanding of the effects of radiation on silicon is suggested by the fact that it is not safe to extrapolate knowledge gained in one radiation environment to predict materials performance in another. Experience with device degradation in a beam of 0 - 10 MEV electrons at $78^\circ$ K, for example, will be of limited usefulness in predicting the behavior under proton bombardment at the same temperature or even under electron bombardment at a different temperature, say $4^\circ$ K or room temperature. The reason for this is that the electrical behavior, mobility, and binding energy of these defects are highly individual. G. D. Watkins, for example, has established that the diffusion coefficient of an isolated vacancy in silicon has an activation energy of roughly 0.3 electron volts. This is to be compared to estimates which he has made that a divacancy in this same material has an activation energy of approximately 1.3 electron volts for migration, with a divacancy binding energy of about 1.2 electron volts. In exposure to radiation, the primary defect is produced. Relative abundance and relative geometrical distribution of these and aggregate products will all depend upon the conditions of exposure. A more extended treatment of this and related topics may be found in Appendix D.

Recommendations:

Very little is known about the <u>interface</u> between silicon and other solids such as metals and insulators. From the standpoint of future technological growth, the characterization of surfaces is a primary object of research. There are a number of significant questions that should be asked about such/ surfaces. For example,

In what way is the basic crystal structure modified as the surface is approached?

To what extent is a surface atomically flat?

What are the concentrations and distributions of native and foreign point defects near the surface?

What is the nature of structural defects near the surface?

What specific effects does the mating material have on the characteristics of the silicon?

How do the properties of electrical carriers near the surface depend upon its crystallographic and chemical properties?

What are the effects of modification of the mating material on the electrical properties of the surface?

It is not immediately obvious how some of these questions can be answered. For example, to use electron diffraction or microscopy techniques may require the removal of one of the mating materials. This may itself prove a significant perturbation. Perhaps information will always be of an indirect nature. However, the point should be reiterated that this is the area of greatest concern to people active in silicon work today.

Device Characterization:

• The characterization of highly pure bulk silicon for chemical and structural defects does not pose any worthwhile problems.

- A method for convenient nondestructive determination of inhomogeneous distributions is needed.

- Techniques for improved characterization of low-solubility, highly mobile impurities are needed.

- Techniques for improved characterization of inhomogeneous oxygen distributions are needed.

- A broader application of sophisticated/x-ray techniques is indicated.

Radiation-Induced Defects:

It has been found that the observed radiation defects are complexes of primary defects, interstitials, and vacancies with all types of impurities and crystalline defects. The major problem is the understanding of the complex phenomena and their correlation to the material composition and primary defect formation. Studies should be made of the characteristics of the primary defects produced during bombardment with emphasis on the basic properties and mechanisms involved. Also, a program should be set up of practical tests including the effects of composition of the incident radiation beam, rate effects (reciprocity law failure), and temperature cycling upon device characteristics. Studies such as those of Watkins and his collaborators using the combined techniques of electron spin resonance and infrared optical absorption should continue to be highly fruitful in elucidating the nature of the complex radiation damage defects in silicon. Information gained concerning the structure and behavior of vacancy aggregates will be useful in assessing the relaxation to thermal equilibrium of devices which contain them. In short, it is particularly desirable to study the approach to thermal equilibrium of defect structures.

Further information on the nature of radiation damage, including studies on the energy required to displace an atom from its normal site, and the physical properties affected by the damage is presented in Appendix D.

## Semiconducting Compounds

As was discussed in Section V, defects in compounds can be of a higher degree of complexity than in elements inasmuch as several kinds of atoms may be involved. Certain of these considerations will be brought out in the examples to follow.

III-V Compounds:

In many of the III-V compounds, especially those with the higher melting points, the present state of technology is such that foreign atoms appear to be the property-controlling imperfections—at least for most applications—and defects are usually of secondary importance. A possible exception is gallium antimonide, for which evidence has been presented to suggest the likelihood of antistructure-type defects being responsible for slightly over $10^{17}$ residual carriers. Experience with GaSb has shown that it is not possible to prepare this material, using standard techniques, with acceptor concentrations below approximately $2 \times 10^{17}$ cm$^{-3}$, regardless of the degree of purification of the elements and the compound.[8] Careful analysis for chemical impurities, with sensitivities in most cases substantially in excess of those necessary to account for $10^{17}$ carriers/cm$^3$, rules out fairly conclusively the possibility of foreign atoms—save perhaps for half a dozen different elements—being the source of the omnipresent acceptor centers. These remaining elements are rendered improbable as a result of studies involving variations in preparation procedures and because of their known behavior in GaSb and other III-V compounds. Therefore the existence of defects is indicated. As normally grown, gallium antimonide tends to be slightly off stoichiometry inasmuch as the maximum melting temperature in the Ga-Sb system is on the gallium-rich side of the 50-50 composition by perhaps a few parts per million. Of the possible ways in which the

excess gallium might be incorporated, namely; gallium interstitials, antimony vacancies, or antistructure defects, a type of antistructure defect involving gallium atoms at antimony sites appears the more likely possibility. The defect nature of the controlling imperfection is further verified by experiments in which lithium is paired with the center, and more directly by growth of GaSb crystals from a melt containing an antimony to gallium atom ratio of about 3 to 1, which results in material containing the order of $10^{16}$ defects/cm$^3$. This represents about the lowest defect content that has been achieved in GaSb.

In the case of GaAs—a material which is finding use in a variety of applications—evidence indicates the existence of somewhere between $10^{16}$ and $10^{18}$ defects/cm$^3$ in as-grown crystals, depending on the technique of growth. Some evidence suggests that a reduction to perhaps $10^{15}$ or below might be possible in vapor-deposited materials. The influence of the defects in GaAs on electrical properties is somewhat more subtle than in GaSb inasmuch as the associated energy levels lie deeper within the gap.[9] Nevertheless they can act as recombination centers and therefore be of considerable importance in certain types of devices. An effective technique for the determination of these types of defects has been the study of thermally stimulated current peaks. Other methods have included internal friction, lattice thermal conductivity, and precision lattice constant and density measurements.[9] Further discussion of the latter technique is given in Appendix E, II-2.

In summarizing the situation with the III-V materials, we may say that in regard to GaAs and other wide-band-gap III-V compounds, the present state of the art is such that chemical impurities are still more of a problem than are defects—at least for the majority of devices. With GaSb, however,

the opposite situation appears to be true, and in the case of InAs, more information is needed. Finally, InSb seems to be unique in that it appears possible to produce material where the concentration of active chemical impurities and of defects is in the $10^{14}$ region or below.

II-VI Compounds:

There exists very little quantitative information on native defects in the higher band gap II-VI compounds, at least insofar as the defects are not formed under the influence of aliovalent foreign atoms. An over-all indication of the present state of the technology in regard to CdS and ZnS was given in Table II. A more specific listing of characterization techniques and their sensitivities in the case of certain defects in ZnS is given in Table III. A detailed account of defect formation in thermodynamic equilibrium in CdTe + In is given in Appendix B.

Certain Metal Oxides, Ferrites, etc.:

In most cases, the chemical impurity content in oxide crystals, including ferrites, is found to be the controlling imperfection insofar as the principal applications and property studies of the material are concerned. Indirect evidence exists which suggests that flame fusion sapphire may contain the order of $10^{15}$ point defects (vacancies) $cm^{-3}$. Dislocation contents, which may be in the $10^{5}$-$10^{6} cm^{-2}$ range for the Verneuil process crystals, are perhaps typically in the $10^{3} cm^{-2}$ range for pulled or for vapor deposited crystals.

For most practical applications, the ferrites are prepared by compaction techniques and yield about 95% of theoretical density. Single crystals, prepared by flame fusion methods, probably exhibit defect concentrations of less than $10^{19} cm^{-3}$, which correspond to concentrations of less than those represented by 99.9% of theoretical density—a result which begins

## TABLE III

### MEASUREMENT TECHNIQUES APPLICABLE TO ZnS
### AND RELATED MATERIALS

| Defects | Method | Sensitivity |
|---|---|---|
| A. Grain Boundaries | 1. Etching | |
| | 2. Light Reflection | |
| | 3. X ray | |
| | 4. Double Refraction | |
| B. Stacking Faults | 1. Electronmicroscopy | 1 |
| | 2. X-ray Diffraction | |
| | 3. Electroluminescence | 1 |
| | 4. Anisotropic Conductivity | |
| | 5. Photo emf $> E_{gap}$ | $\sim 100$ |
| | 6. Opt abs. ($E_{gap}$ differs per polytype) | 1 |
| C. Dislocations | 1. Etching | $1 \ cm^{-2}$ |
| | 2. Decoration | $1 \ cm^{-2}$ |
| D. Point Defects | | |
| $D_1$ Foreign, general | 1. Chemical analysis | $10^{16}-10^{18} cm^{-3}$ |
| | 2. Neutron bombardment activation analysis | $10^{11}-10^{14} cm^{-3}$ |
| | 3. Magnetic Susceptibility | $10^{15} cm^{-3}$ |
| | 4. Recombination | |
| | 5. Trapping; thermally stimulated luminescence: | $10^{17} cm^{-3}$ |
| | thermally stimulated current | $10^{12} cm^{-3}$ |
| $D_2$ Foreign, interstitial | 1. ESR | $10^{11}$ spins |
| | 2. Donor Activity | $10^{8} cm^{-3}$ |
| | 3. Luminescence | (a) |
| | 4. Absorption | $10^{17} cm^{-3}$ |
| $D_3$ Foreign, substitutional | 1. ESR | $10^{11}$ spins |
| | 2. Donor or acceptor activity | $10^{8} cm^{-3}$ |
| | 3. Formation by transmutation | $10^{12} cm^{-3}$ |
| | 4. Luminescence | $10^{16} cm^{-3}$ |
| | 5. Opt. absorption | $10^{18} cm^{-3}$ |
| | 6. Trap; thermally stimulated conductivity | $10^{12} cm^{-3}$ |
| | thermally stimulated luminescence | $10^{17} cm^{-3}$ |

TABLE III (Cont'd)

| facts | Method | Sensitivity |
|---|---|---|
| D. Native Defects, general | 1. Recombination center<br>2. Trapping; thermally stimulated current; thermally stimulated luminescence | |
| $E_1$ Vacancies | 1. Fluorescence<br>2. Trapping of electrons or holes (glow curves of fluorescence, or conductivity)<br>3. Formation in presence of aliovalent foreign atoms | (a)<br>(b) |
| $E_2$ Interstitials | ? | |
| $E_3$ Antistructure Defects | not found | |
| F. Native-Foreign Defect Pairs | 1. Self-activated lum. (anisotropy)<br>2. ESR (anisotropy)<br>3. Distant donor-acceptor pair fluorescence | $10^{17}\,cm^{-3}$<br>$10^{17}\,cm^{-3}$<br>? |

(a) It is difficult to derive quantitative information on the concentration of defects from luminescence studies. Even if we find that a certain treatment increases the intensity of a certain luminescence, this does not prove that the concentration of defects involved is increased; it may well be that the concentration of other defects, favoring a competing process, is decreased.

(b) Although the methods of stimulating luminescence or current are as sensitive for native as for foreign defects, so far there is no clear assignment of glow peaks to particular centers; for an attempt of such an assignment for CdS see Niekisch, Z. physik. Chem. **217**, 110 (1961).

## COMMENTS

Note that most of the information available concerns impure or foreign atom-doped crystals. Quantitative information concerning native defects can be obtained in principle by:

(a) investigations on purer crystals; this involves further purification of materials;

(b) theoretical analysis of the results of equilibrium studies on crystals doped with known concentrations of foreign donors or acceptors by the methods of imperfection chemistry.

It is recommended that both approaches be followed.

to approach the limit of the ability to analyze, using density measurements
(see Appendix E, II-2). Dislocation densities of between $10^3$ and $10^6$ cm$^{-3}$
are reported for the single crystals.[10] Actually, for practical applications
as well as for most scientific investigations, there is little impetus to achieve
defect concentrations below $10^{19}$ cm$^{-3}$.

## B. ALKALI HALIDES

The alkali halide crystals represent the class of materials for which
point defects were first studied and had begun to be understood as early
as the 1930's. The unique feature of these crystals is the variety of tools
available for their study, most important of which are the optical and elec-
trical properties. The optical properties are of great importance due to
the wide range of transparency of these crystals, from the far infrared
to the ultraviolet region. Many defects are found to produce absorption
bands, which are then easily studied. Most of the bands in the visible range
(the so-called "color centers") are produced only after irradiation of the
crystal with high energy radiation. The study of such color centers is of
great interest in revealing detailed information about defects in alkali
halides and the interactions among them, but is not important for charac-
terizing the as-grown material. On the other hand, it will be seen that
absorptions in the infrared and uv are very significant for characterization.

Electrical measurements have also been important in the study of alkali
halide crystals. Here the unirradiated material is found to conduct by ionic
migration which requires the presence of defects (notably, cation vacancies).
In addition, time dependent changes in the electrical polarization and dielec-
tric loss under an a. c. potential provide further information about point
defects in the material.

In the early history of alkali halide studies, NaCl was by far the most widely investigated. With the more recent use of zone refining techniques for purification of these crystals, KCl was found to be capable of preparation to a higher state of purity. Accordingly, it has rapidly become the prototype alkali halide crystal.

From a theoretical viewpoint, the alkali halides represent the simplest material for which to calculate defect formation energies because of the almost perfect ionic character. Accordingly, theoretical calculations for these crystals have been carried to a relatively high degree of refinement as compared to similar calculations for other crystal types.

Finally, even for the case of dislocation studies, the alkali halides are unique. Aside from the availability of all of the usual methods for detecting dislocations (x-ray techniques, etch pits, electron microscopy, decoration), a completely new set of electrical phenomena has been found due to the fact that a dislocation in these crystals may carry a net charge. Such electrical effects take the form, on the one hand, of a charge flow produced by inhomogeneous plastic deformation, and on the other hand, of polarization phenomena related to the space charge which exists around dislocation lines. Our understanding of these electrical effects has not reached the point where we can utilize them for characterizing the dislocations in the material. However, the very existence of these effects is another example of the rich variety of possibilities for the study of defects in the alkali halides.

A listing of the principal defects in the alkali halides, the major properties affected by their presence, and the techniques for their determination are given in Table IV.

The following remarks best summarize the current situation:

- As an over-all test of the quality of an alkali halide crystal, the sharpness of the fundamental absorption edge is a very sensitive criterion for the presence of impurities and defects.

- The best over-all techniques for characterizing point defects in alkali halide crystals are (a) spark spectroscopy (primarily for the divalent materials), (b) optical absorption, particularly in the ultraviolet and near infrared, and (c) ionic conductivity.

- A statement of the last heat treatment of the crystal is very important, since this treatment determines the state of dispersion of metallic impurities. The best treatment is to "quench" the crystal at a rate not so fast as to strain it. This treatment leaves the crystal in a well-defined initial state; i.e., with the metallic impurities in solution.

- More work is needed in attempting to grow low dislocation alkali halide crystals and to determine the effect of dislocations on properties other than mechanical properties.

It is certainly desirable in closing this section to make some remarks aimed at extending the relatively detailed knowledge of a crystal like KCl to other ionic crystals, which are in fact far more useful in a variety of applications. The next step may take us to such materials as MgO, $Al_2O_3$ and the Ag halides. All of these are essentially ionic crystals, though not as completely ionic as KCl. In the case of MgO and $Al_2O_3$, which are of great importance as electrical insulators and high-temperature materials, our ability to characterize the materials has lagged far behind KCl. It is clear that a stronger effort is needed to close this gap. The silver halides, particularly AgCl and AgBr, are far better understood. Zone refining methods have been able to provide crystals of rather high purity, while

## TABLE IV

### DEFECTS IN ALKALI HALIDES

| Defect | Properties Affected | Technique for Determination | Sensitivity |
|---|---|---|---|
| 1) Cation vacancy, ⊡ | Ionic conductivity; cation diffusion | Low-temperature ionic conductivity (300-400°C range) | Sensitivity greater than required by present growth capabilities |
| 2) $M^{++}$ ⊡ associated pair | Thermal conductivity; ionic thermo-conductivity; dielectric loss; colorability; mechanical properties | Dielectric loss peak, together with trace metal analysis | The dielectric loss peak has a sensitivity $\sim 10^{15} cm^{-3}$ but it doesn't discriminate |
| 2a) Same defect in aggregated form | Optical absorption; mechanical properties | Tyndall scattering; broadened dielectric loss peak | Can detect to diameters of $\lambda/20$ and to concentrations of $\sim 10^{16} cm^{-3}$ |
| 3) Anion vacancies and F centers | Optical absorption; luminescence; thermo-luminescence; photoconductivity; ionic and thermal conductivity; EPR, ENDOR | Optical absorption: $\alpha$ band and F band | |
| 4) $OH^-$ ion | Ionic and thermal conductivity; colorability; UV absorption; dielectric relaxation and dielectric constant at low temperature | Optical band in UV; optical band in infrared | Sensitivity $\sim 10^{14} cm^{-3}$ |
| 5) Interstitial $H_2O$ | EPR following UV illumination; optical absorption | Infrared band | Sensitivity $\sim 10^{16}$ or above |
| 5a) $H_2O$ in aggregated form | Optical absorption | Microscopic examination | |
| 6) $CO_3^=$, $CN^-$, $NO_2^-$ Borate ions (for KCl), cyanate ions | Optical (UV) absorption; thermal conductivity | Strong infrared band | Generally $10^{16}$ or above, for certain ions $\sim 10^{14}$ |
| 7) Dislocations | Mechanical properties (flow stress internal friction); colorability; dielectric breakdown; charge flow effects on deformation | Etch pit counting<br>Decoration techniques<br>Transmission electron microscopy<br>X-ray topography | $0 - 10^7 cm^{-2}$<br>$0 - 10^8$<br>$0 - 10^{11} cm^{-2}$<br>$0 - 10^4 cm^{-2}$ |

electrical conductivity and optical studies have been used to study various point defects. Finally, it has been possible to produce large crystals of silver halides which possess considerably fewer dislocations than the best alkali halide crystals, as well as small crystals which are free of dislocations.

## C. METALS

### Point Defects

Four broad areas in which a knowledge of point defects is essential may be delineated:

(1) Processing of Metals

All of the solid-state processing or heat treatment of metals is intimately connected with point defects (and in some cases with dislocations also). In general, transport of matter is involved which often takes place by a vacancy diffusion mechanism. A few examples are:

- Age or precipitation hardening
- Spinoidal decomposition, eutectoid decomposition
- Recovery and recrystallization
- High temperature plastic forming
- Diffusion forming (e.g., $Nb_3Sn$ by RCA)
- Sintering

A detailed understanding of the behavior of point defects and their aggregates is essential to the understanding and microscopic description of the above processes.

(2) Mechanical Deformation

Almost all aspects of plastic deformation involve point defects in a primary or secondary role, because nonconservative or climb motions of dislocations require formation or absorption of vacancies or interstitial atoms. Much still needs to be learned about the mechanism of nonconservative

dislocation motions before quantitative microscopic theories can evolve. Examples of plastic phenomena in which vacancies probably play an important role are:

- Creep, creep rupture, and static fatigue
- Cyclic fatigue fracture
- Strain hardening and dynamic recovery
- Ductile fracture

(3) Oxidation

A vacancy or interstitial diffusion mechanism is usually involved in the transport of metal or oxygen atoms through the oxide layer.

(4) Radiation damage and annealing

Characterization of Point Defects:

Although many properties of metals are affected by point defects, the specific identification of a defect is not simple. The only direct technique which has afforded the resolution to exhibit a single defect is the field-emission microscope, and this has been used only in isolated cases of refractory metals. Electron transmission microscopy is capable of revealing clusters of defects—perhaps of dimensions of 10 Å. There is a possibility that decoration replica techniques can be used to give some information on point surface defects down to the 2 Å level.[11]

On a grosser scale, at the 20 Å level or somewhat above, direct replica electron microscopy can show details on surface defects. At the 200 Å level, both the reflection and the scanning microscope can resolve details. Of course, at these gross scales, one cannot deal with individual point defects, but rather with agglomerates or second phases.

It appears that, especially in the field of device inspection where secondary electron emission gives added contrast, the scanning electron microscope can make a real contribution to surface studies. Low energy electron diffraction (LEED), although still in the development stage, also appears to possess strong potential for surface studies.

Electron diffraction and microscopy have been used effectively to study precipitates, with resolution of particle sizes down to 40 Å. A discussion on the study of the associated strain fields is given by Hirsch et al.[12]

Many of the techniques discussed above have substantial potential for more extensive applications, and additional research is recommended to improve their resolution and applicability. If, of course, the defects in a solid are of a single type and one has prior knowledge of their nature, then a number of the indirect techniques which were listed in Table I might successfully yield the concentration. A more detailed discussion of various considerations involved in the characterization of point defects in metals is found in Appendix E.

## Dislocations

Properties which are highly sensitive to dislocation substructure include:

- All plastic deformation phenomena
- Ferromagnetism
- Superconductivity

In fact, a high density of dislocations is essential to the achievement of optimum properties in most structural materials. However, the general theory is not at present sufficiently developed so that a description of the defects, chemical impurities, etc.—even if one knew how to describe them in a proper fashion—could be readily related to a property. Thus out of practical necessity, materials for use as mechanical structural members

have been described directly in terms of those properties which are thought to be significant; e.g., yield strength, hardness, ductility, K-factor, Charpy impact strength vs. temperature, fatigue strength, etc. The same is true of the areas of ferromagnetism and superconductivity. However, extensive research is under way in studying the relationship between defect structure and these general properties. It is with this research in mind—and its eventual potentialities in relation to a better understanding of properties— that one proceeds to consider at this time the characterization of various defects.

Characterization of Dislocations:

Description of a dislocation population in a crystal involves such quantities as total line length per unit volume or total intersections per unit planar area. However, a complete characterization would require a knowledge for each dislocation segment of its length, orientation, plane of dissociation if it is split, shape of its glide surface, cut-off radius of its strain field and its impurity atmosphere.

For characterizing dislocations, the direct methods are obviously preferred. A common technique is the observation of etch pits by means of optical microscopy, which can be used in the range 1 to $10^7 \text{cm}^{-2}$ and perhaps up to $10^9 \text{cm}^{-2}$ by replica techniques. X-ray topography is extremely useful in the density range $0-10^4 \text{cm}^{-2}$, while thin-film transmission electron microscopy is available for the region $10^6$ to $10^{11}$. Details concerning the above methods, as well as a discussion of several indirect techniques, are given in Appendix F. For a material which has not already been studied extensively, it is usually desirable to employ several methods.

Techniques for Area Defects:

- Electron transmisssion microscope: can easily see and identify stacking faults ($10^2$ to $10^5 cm^{-1}$), twins, small angle boundaries, phase boundaries ($10^2$ to $10^6 cm^{-1}$); resolution 8-10 Å.

- X-ray topography: similar to above except that resolution is 2-5 microns.

- Field electron or ion microscope: can see crystal surface essentially atom by atom.

- Optical microscope: can only examine intersection of defects with crystal surface; can see and identify twins, boundaries; resolution 1 micron.

## D. ORGANIC MATERIALS—ANTHRACENE

Anthracene was chosen as the example because it is the best known organic crystal. It is often claimed to be prepared with total impurity concentrations in the parts per million range, its structure is known, it is reasonably stable chemically, and there are a variety of measuring techniques available for characterization. Nevertheless, little is known about the nature, concentration, and properties of defects in the material. Therefore, in attempts at characterization, it is extremely difficult to separate those phenomena related simply to defects from those related to defects in interaction with impurities. Some of the more obvious issues involve detection of dislocations, detection of lattice vacancies or vacancy aggregates, interaction of chemical impurities with lattice imperfections, and characterization of the surface. These problems are discussed in more detail in Appendix G.

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### APPENDIX A - EXAMPLES OF FAILURE BY BRITTLE FRACTURE IN DOD MATÉRIEL

Brittle fracture in a metal structure begins with the development of a crack in a region of high stress concentration. When the crack has grown beyond a certain size, it propagates at high speed through the structure. The result is always a catastrophic failure often damaging to men and machines, accompanied by loud noise and fragmentation. Structures have failed in this manner when subjected to stresses as low as 1/3 their proper design values.

In order for failure to occur in this manner, the material must be characterized as brittle rather than tough (as determined by an impact test or notched specimen test) and some type of defect which serves to concentrate the applied stress must be present. Toughness of a metal is a function of temperature, with susceptibility to brittle fracture increasing with lowered temperatures. DOD equipment failures by brittle fracture increase in number during use in polar regions or during cold weather in temperate climates. Gun barrels failing in this manner generally shatter with the first round fired on a cold morning. The defect may be a crack, sharp change in section, weld void, corrosion pit, metallurgical defect, or hydrogen absorbed near defects. Proper design, testing, and handling can prevent the first-mentioned defects from occurring, but the last-mentioned are properties of the metal itself. A large number of failures which have occurred have been corrected simply by specifying the starting material more fully, that is, by characterizing it more completely. Cases involving this type of failure are cited below.

The requirements of DOD and NASA for high strength-to-weight ratio
materials for air- and rocket-borne components have aggravated the brittle
failure picture, since these particular metals, especially in the thin section
employed, are more susceptible to this type of failure, and smaller defects
are needed to initiate failures.

### I. Missile Destruction by Brittle Fracture During Storage

(REF: F. R. Larson, "Metallurgical Examination of Hydraulic Accumulator
Failure," WAL TN 781.1/1, Watertown Arsenal, Mass., March 1961)

In September 1960, a pressure vessel in a missile that was in storage
at Red River Arsenal exploded, completely destroying the weapon. One
month later, a second, similar missile destroyed itself by explosion at
Fort Bliss, Texas, due to a failure of its pressure vessel.

The pressure vessels were hydraulic accumulators, charged with nitrog.
gas at 4000 psi, which provided the motive power for the missile's guidance
system. The vessel is charged at the manufacturer's plant and remains
at that pressure until the missile is fired. The planned storage life for this
system is in the 5-10 year range. The first destruction occurred after 22
weeks of storage.

A thorough investigation of the matter showed that all design, fabrication
and materials procurement procedures had been followed as specified,
except for a clear check of the water content in the pressurizing gas. The
vessels had failed with a hoop stress applied by the internal gas pressure
of only 30% of the yield strength of the material (H-11 die steel) and at
only 50% of the pressure at which they had been tested prior to installation.
The origin of the fractures was readily located at minute corrosion pits
in the inside surfaces of the vessels. However, the origin of the crack was
considered to be of academic interest since it was found that the steel from

which the vessels were made was so brittle in nature that most any defect could have triggered failure. The problem was solved by replacing the vessels with new vessels fabricated from a lower strength material of much greater toughness. If the original material had been more completely characterized, it would not have been employed for this purpose at the outset.

## II. Solid Fuel Rocket Motor Case Failure

(REF: M. E. Shank, C. E. Spaeth, V. W. Cooke, and J. E. Coyne, "Solid Fuel Rocket Chambers for Operation at 240,000 psi and Above," Metal Progress 76, 74-81, No. 5, and 76, 84-92 (1959), No. 6; C. E. Spaeth. "Defects, Surface Finishes, and Hydrogen Embrittlement," Proceedings of the Seventh Sagamore Ordnance Materials Research Conference, August 1960, III-11 to III-20)

As the final step in the development of a solid fuel rocket motor case, a full scale case was fabricated; 6 feet long, 40 inches in diameter, and 0.040 inch thickness, enclosed at both ends. Care was exercised to avoid all known possible causes of weakness in the vessel. The case was fabricated of a high quality, very high strength, vacuum-melted steel, virtually without inclusions, and with the best quality in design and fabrication. Upon completion of fabrication, the case was tested hydrostatically using water in the interior of the case. The steel had a yield strength of 235 thousand psi and the case sustained five successive hydrostatic tests quite successfully reaching 216 thousand psi hoop stress. On the sixth test, the case shattered into more than 50 pieces at the lower hoop stress of 185 thousand psi. This was the culmination of another attempt to make a high strength-to-weight ratio structure demanded by rocket and air transport power capabilities.

The origin of the cracking was located at a small corrosion pit on the inside surface of the case. By electrolytic action, the water used for hydrostatic testing had embrittled the material in the region of the pit through

the diffusion of hydrogen into the metal. The hydrogen content of the starting material was intentionally kept very low (0.7 ppm), yet the case failed from hydrogen embrittlement in this selected area. Thus, although all materials and procedures had been carefully controlled in the fabrication of this item, the susceptibility of the starting material to corrosion and hydrogen embrittlement had not been sufficiently characterized to prevent the occurrence of a failure.

### III. Brittle Failure of Missile Support Hardware

(REF: P. V. Riffin and C. W. Amos, "Hot Work Die Steel (H-13) for High Strength Structural Components," WAL TR 742.3/2, Watertown Arsenal, Mass., October 1961).

Catastrophic brittle fracture occurred in components of heavy support hardware used for static testing of the Saturn missile. A load cell arm fractured across a 12 inch wide, 3 inch thick cross section, and a thrust gear ring fractured across a 3-1/2 inch square cross section. Failure occurred during proof testing at one-half of the design service load.

These components were fabricated from H-13 steel, a medium carbon Cr-Si-Mo-V steel, employed for many years for hot working dies and tools which required high strength at operating temperatures up to 1000° F. This material was selected for the components by the manufacturer for the Army Ballistic Missile Agency because the high design yield strength needed could be reached with a heat treatment cycle that would cause very little distortion.

A thorough analysis of the use of this steel in this application showed that the failure occurred primarily because of the very low toughness of the material employed. Mechanical, handling, and design defects could only have played a minor role in the failure. Heavy grain boundary

precipitates occurred during the heat treatment and the lack of toughness in
the metal was attributed to this cause. The problem was solved through
the use of a lower alloy steel of equal strength but superior toughness.
If the H-13 steel had been better characterized before selection, the failures
would have been prevented.

## APPENDIX B - POINT DEFECT EQUILIBRIA

The principle underlying the formation of point defects and their mutua interaction under equilibrium conditions is the same for metals and non-metals, elemental crystals, and compounds. The theory is due to Wagner and Schottky.[1] It has been extensively discussed in various books and review articles.[2-4]

Expressions for the concentrations of point defects, both native and foreign, can be obtained by:

(1) Writing down quasi-chemical reactions describing the formation of defects, both native and foreign.

(2) Applying the law of mass action to these, taking concentrations (or rather: site fractions) instead of activities. This is tantamount to assuming that the defects are distributed at random over their respective sites.

(3) Writing electroneutrality condition.

In order to do this it is necessary to introduce symbols for the various reaction partners. We shall use the atomic notation introduced by Kröger and Vink.[2,5] Main symbols indicate the nature of the defect (or, in genera the structure element).[5] Subscripts refer to the site occupied by it.

Zero, positive, or negative effective charges are indicated by superscripts x (cross), · (dot), and ' (prime). Thus $V_A^x$ is an effectively neutral vacancy at an A site, $V_i^x$ is an unoccupied interstitial site, $A_B^{\cdot\cdot}$ is an atom A at a B site with a double positive effective charge, and $B_i'$ is an interstiti B atom with a single negative effective charge. Quasi-free electrons and holes are indicated respectively by e' and h·.

The various reactions interact either because they have reactants in common or (if the reactants are charged) because of the necessity to main-tain electroneutrality. If a considerable number of defects is present,

the task of obtaining a complete solution is formidable. In addition, the complication of the mathematics involved prevents us from getting an insight in the underlying physics. For both reasons it is preferable to obtain an approximate solution. A convenient method of achieving this is available.[6] It consists of approximating the neutrality condition by its dominant terms. In doped crystals these correspond to the mechanisms of incorporation of the foreign constituents. If a fixed concentration of dopant is present, a balance equation for this has to be introduced which has also to be approximated.

Below we demonstrate the method for the case of a compound (CdTe) doped with a fixed amount of donors (In).

### Defect Equilibria in CdTe + In

For CdTe, doped with a fixed amount of indium, and brought into equilibrium with a vapor of well-defined cadmium pressure $(p_{Cd})$, the quasi-chemical reactions describing defect formation, and the mass action relations deduced from them are:

$$0 \rightleftharpoons e' + h^{\cdot} \; ; \; E_i \qquad\qquad np = K_i,$$

$$Cd_{Cd}^x + V_i^x \rightleftharpoons V_{Cd}^x + Cd_i^x \; ; \; H_F, \qquad [V_{Cd}^x][Cd_i^x] = K_F,$$

$$Cd_{Cd}^x + V_i^x \rightleftharpoons V_{Cd}' + Cd_i^{\cdot} \; ; \; H_F', \qquad [V_{Cd}'][Cd_i^{\cdot}] = K_F',$$

$$Cd_i^x \rightleftharpoons Cd_i^{\cdot} + e' \; ; \; E_1, \qquad\qquad \frac{n[Cd_i^{\cdot}]}{[Cd_i^x]} = K_1,$$

$$V_{Cd}' \rightleftharpoons V_{Cd}^x + e' \; ; \; E_3, \qquad\qquad \frac{n[V_{Cd}^x]}{[V_{Cd}']} = K_3,$$

$$V_{Cd}'' \rightleftharpoons V_{Cd}' + e' ; \; E_4, \qquad\qquad \frac{n[V_{Cd}']}{[V_{Cd}'']} = K_4,$$

$$In_{Cd}^X \rightleftharpoons In_{Cd}^{\cdot} + e' \; ; \; E_5 \; , \qquad\qquad \frac{n[In_{Cd}^{\cdot}]}{[In_{Cd}^X]} = K_5 \; ,$$

$$Au_{Cd}' \rightleftharpoons Au_{Cd}^X + e' \; ; \; E_6 \; , \qquad\qquad \frac{n[Au_{Cd}^X]}{[Au_{Cd}']} = K_6 \; ,$$
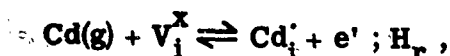
$$Cd(g) + V_i^X \rightleftharpoons Cd_i^{\cdot} + e' \; ; \; H_r \; , \qquad\qquad \frac{n[Cd_i^{\cdot}]}{[V_i^X]} \approx n[Cd_i^{\cdot}] = K_r p_{Cd} \; ,$$

$$[In]_{total} = [In_{Cd}^X] + [In_{Cd}^{\cdot}] \; ,$$

$$n + [V_{Cd}'] + 2[V_{Cd}''] = p + [Cd_i^{\cdot}] + [In_{Cd}^{\cdot}]$$

Values of the constants as determined by de Nobel[7] are tabulated in Table V.

The table demonstrates the amount of data necessary to characterize fully the material thermodynamically. The parameters involved are partly the ones characterizing the material as a semiconductor (e.g., electronic ionization energies), partly parameters for atomic defect formation, and partly those for evaporation of the crystal to atoms or molecules. Concentrations of defects at 700°C calculated from these data, using Brouwer's method[6] are shown in Fig. 1. This represents the situation at high temperature. It can serve as a basis for the determination of the defect concentrations after cooling to low temperature, providing we have some idea of what is to be expected: association and/or precipitation may occur. In any case electrons and holes will recombine, and electrons will tend to occupy low empty levels.

Preparation (equilibration) at a different temperature, say 800°C, must be expected to give rise to similar but slightly different results, as determined by the values of the constants at that temperature. If the indium concentration is not constant, this necessarily involves the transfer of In between the CdTe and an outer or inner second phase. The reaction describing this process then has to be introduced instead of the indium balance equation.

TABLE V

PARAMETERS OF THE FUNDAMENTAL CONSTANTS OF CdTe ACCORDING TO de NOBEL: $K = K^{0*} \exp(-H^*/kT)$

| Reaction | Constant | $K^{0*}$ conc. in cm$^{-3}$ | mole fr. b) | $H^*$ or $E^*$ (eV) | E (eV) | Remarks |
|---|---|---|---|---|---|---|
| $0 \rightleftharpoons e' + h^\cdot$ | $K_i$ | $4.58 \times 10^{40}$ cm$^{-6}$ | $1.9 \times 10^{-4}$ | 1.73 | 1.5 | from optical gap with $m_e^* = 0.11m$, $m_h^* = 0.35m$ |
| Cd$_i^x \rightleftharpoons$ Cd$_i^\cdot$ + e' | n | $10^{20}$ cm$^{-3}$ | $6.5 \times 10^{-3}$ | 0.14 | 0.02 | Hall data |
| In$_{Cd}^x \rightleftharpoons$ In$_{Cd}^\cdot$ + e' | $K_5$ | $2.5 \times 10^{19}$ cm$^{-3}$ | $1.5 \times 10^{-3}$ | 0.14 | 0.02 | Hall data |
| V$_{Cd}' \rightleftharpoons$ V$_{Cd}^x$ + e' | $K_3$ | $2.5 \times 10^{21}$ cm$^{-3}$ | $1.5 \times 10^{-1}$ | 1.56 | 1.43 | |
| V$_{Cd}'' \rightleftharpoons$ V$_{Cd}'$ + e' | $K_4$ | $1.4 \times 10^{19}$ cm$^{-3}$ | $9 \times 10^{-4}$ | 0.57 | 0.6 | |
| Au$_{Cd}' \rightleftharpoons$ Au$_{Cd}^x$ + e' | $K_6$ | $2.5 \times 10^{19}$ cm$^{-3}$ | $1.5 \times 10^{-3}$ | 1.04 | 1.25 | |
| Cd$_{Cd}^x$ + V$_i^x \rightleftharpoons$ Cd$_i^\cdot$ + V$_{Cd}'$ | $K_F'$ | $7.8 \times 10^{36}$ cm$^{-6}$ | $3.1 \times 10^{-8}$ | 1.04 | | $K_F^x = K_F' K_3 K_1$ |
| Cd$_{Cd}^x$ + V$_i^x \rightleftharpoons$ Cd$_i^x$ + V$_{Cd}^x$ | $K_F$ | $1.9 \times 10^{38}$ cm$^{-6}$ | $8 \times 10^{-9}$ | 2.37 | | |
| Cd(g) + V$_i^x \rightleftharpoons$ Cd$_i^\cdot$ + e' | $K_r$ | $10^{30}$ cm$^{-6}$ atm$^{-1}$ | $4 \times 10^{-15}$ atm$^{-1}$ | -0.81 | | |
| Cd(g) + V$_i^x \rightleftharpoons$ Cd$_i^x$ | $K_{Cd_i}$ | $10^{10}$ cm$^{-3}$ atm$^{-1}$ | $6.2 \times 10^{-13}$ atm$^{-1}$ | -0.95 | | $K_{Cd_i} = K_r K_1^{-1}$ |
| Cd(g) + V$_{Cd}^x \rightleftharpoons$ Cd$_{Cd}^x$ | $K_{Cd}$ | | $7.7 \times 10^{-5}$ | -3.32 | | $K_{Cd} = K_{Cd_i}/K_F$ |
| $0 \rightleftharpoons$ V$_{Cd}^x$ + V$_{Te}^x$ | $K_S$ | | $\approx 3.7 \times 10^{-6}$ | >2.37 | | $< K_F; (K_{Cd} X_{Te} K_{CdTe})^{-1}$ |
| CdTe(s) $\rightleftharpoons$ Cd(g) + ½Te$_2$(g) | $K_{CdTe}$ | | $5.8 \times 10^{10}$ atm$^{3/2}$ | 3.11 | | |
| Te$_2$(g) $\rightleftharpoons$ 2Te(g) | $K_D$ | | $6.3 \times 10^5$ atm | 2.3 | | |
| CdTe(s) $\rightleftharpoons$ Cd(g) + Te(g) | $K_{Cd,Te}$ | | $4.6 \times 10^{13}$ atm$^2$ | 4.26 | | |
| V$_{Cd}''$ + In$_{Cd}^\cdot \rightleftharpoons$ (V$_{Cd}$ In$_{Cd}$)' | $K_P'$ | | | $\leq 0.7$ | | |

a) The concentrations of Cd$_i^x$ and V$_i^x$ are not contained in the constant.

b) There are $1.55 \times 10^{22}$ mol CdTe per cm$^3$.
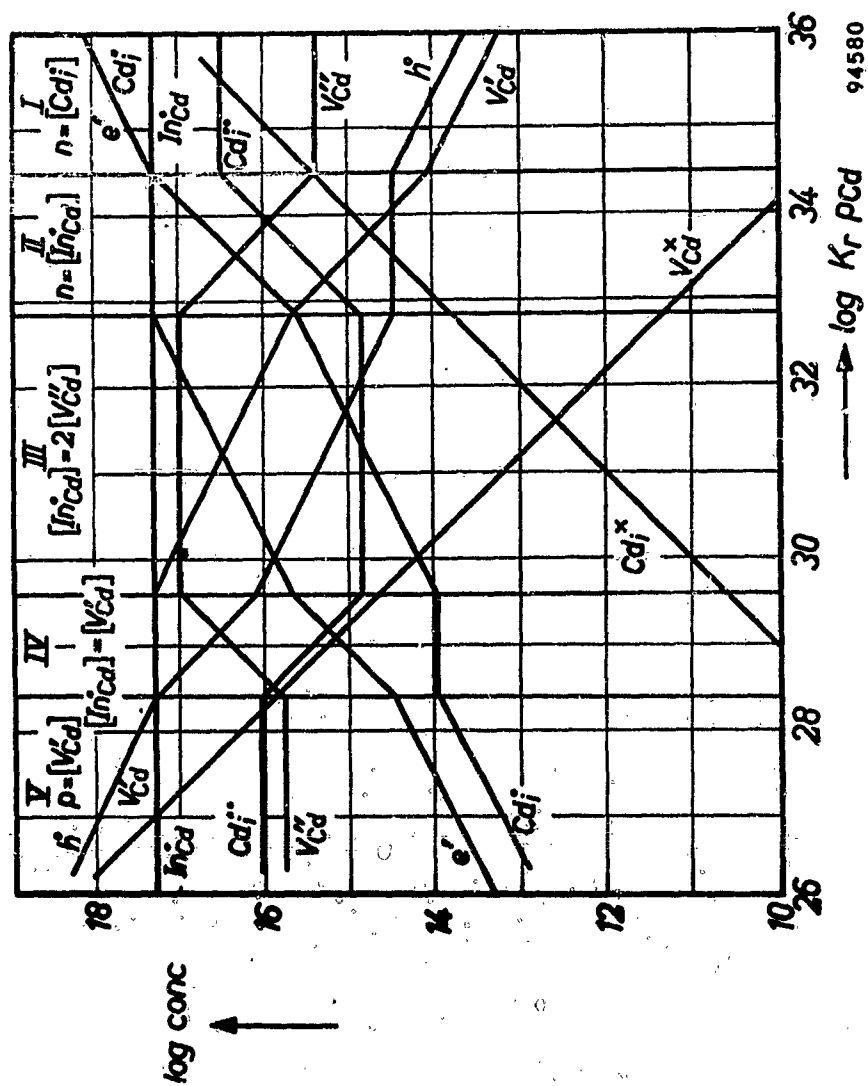
Fig. 1   Isotherms of defect concentrations in CdTe + 2 x 10$^{17}$
In cm$^{-3}$ according to de Nobel.[7]

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### APPENDIX C - IMPURITY DEFECTS IN SILICON

In general, impurities in silicon are made manifest by their effects on the technologically important electrical properties of the material. These properties may be described in terms of such parameters as the type, mobility, and concentration of electrical carriers (and temperature dependence thereof), the lifetime of nonequilibrium carrier concentrations, and the spectral response of photoconductivity. In certain special circumstances, the nature and concentration of impurities may be detected by special methods, such as optical absorption or spin resonance, even for situations wherein no electrical effects are discernible. Finally, for sufficiently large concentrations of impurities, various chemical analytic techniques of varying sensitivity may be employed. These range in novelty from classic wet chemical methods to such very modern techniques as the electron microprobe and neutron activation analysis. In the discussion which follows, we will first consider the current status of "pure" silicon and then consider methods whereby impurities are introduced and the product characterized.

### "Pure" Silicon

The purest bulk silicon is currently prepared by float-zone crystal growth. This step is the final one in a series which is initiated by purification of silicon-containing compounds (e.g., $SiBr_4$), the pyrolysis of these compounds to form polycrystalline silicon, and the zone refining of this silicon prior to final crystal growth.

In terms of its electrical behavior, the best material may be characterized by an impurity density between $10^{12}$ and $10^{13}/cm^3$. The electrically active impurities are either boron, phosphorus, or both. (Usually there is some compensation of these oppositely behaving impurities.) The concentration

of impurities can be determined from the resistivity and Hall coefficient and its temperature dependence. The nature of the impurities can be confirmed (at least for the major impurity) by spin resonance or low temperature optical absorption measurements.

In addition to the directly active impurities, "pure" silicon contains oxygen dispersed monotonically and as very small agglomerates of silicon dioxide. The relative proportions of these forms depend upon the total oxygen content and the treatment the crystal received subsequent to growth. Historically, oxygen in silicon was detected by its infrared absorption and its presence confirmed by direct chemical methods. Subsequently, certain heat treatment and radiation effects were shown to be related directly to the presence of oxygen. These methods of characterizing oxygen in silicon become insensitive at gross oxygen concentration below about $10^{17}/cm^3$. It is believed that the oxygen concentration in the purest silicon is of the order $10^{16}$ to $10^{17}/cm^3$.

From the standpoint of technological application present, "pure" silicon is in general adequately pure and adequately characterized. For most purposes it is necessary to dope the silicon in controlled ways to obtain the desired range of electrical properties. A possible exception to this statement is that for certain nuclear counters, higher purity material may be desirable.

### Device Grade Silicon

As indicated above, for almost all applications, it is necessary to introduce various impurities in order to produce the desired properties and semiconductor structure. It will be convenient to consider the impurities in three separate categories: carrier-controlling impurities, lifetime-controlling impurities, and oxygen.

## Carrier-controlling impurities

Impurities such as boron or phosphorus are intentionally introduced into silicon crystal ingots in concentrations from about $10^{13}$ to $10^{19}/cm^3$, for purposes of controlling the carrier density and type. Since the segregation coefficients of boron and phosphorus are close to unity, crystals will have substantially uniform properties over most of their length and cross section. Accurate data exist for the correlation of impurity density with resistivity and mobility. There does not appear to be any further effort justified in improving on this method of characterization for uniform bulk material.

The addition of boron or phosphorus is usually done by means of a diffusion from the surface although, recently, more sophisticated techniques such as ion implantation have been explored. A continual problem has existed in the control and characterization of the inhomogeneous region resulting from the diffusion process. An important consideration is that of control and characterization of the diffusion source conditions at the silicon surface. That is, while the diffusion coefficients are well known and universal, the source conditions are, in general, poorly known and critically dependent upon the details of the diffusion apparatus and techniques. This situation often necessitated many trial diffusions in device development, and can result in production failure in volume manufacture. Present methods for characterizing inhomogeneous dopant distributions involve such measurements (where applicable) as sheet resistivity, p-n junction location by chemical staining and p-n junction capacitance. These are, in the main, after-the-fact techniques. What is needed is an a priori characterization technique. Clearly, a method for rapid nondestructive characterization of inhomogeneous dopant concentrations would be a boon to all phases of semiconductor work.

## Lifetime-controlling impurities

There are additives such as gold and various transition metals which are used to control the carrier lifetime in various semiconductor devices. These additives form, in general, carrier-trapping centers and thereby also serve as a means for increasing resistivity and increasing its temperature dependence. These dopants usually have strong temperature-dependence and relatively low limiting solubilities and high-diffusion coefficients.[*] These factors give rise to a number of problems in characterization and control, which can be illustrated by the following example. An additive (e. g., copper) is introduced in silicon by diffusion at an elevated temperature (e.g., 1000°C) from a surface film source. After the diffusion, the silicon is rapidly quenched to room temperature to minimize precipitation resulting from supersaturation effects. An electrically active copper concentration of approximately $10^{17}/cm^3$ may result. Subsequent heat treatment at some low temperature (e.g., 500°C) can result in the precipitation of the copper as a dispersion of microscopic clusters. From the viewpoint of the electrical characteristics, the copper is largely no longer present. From the viewpoint of a chemical analysis, the copper content of the silicon is unchanged. From the standpoint of an adequate characterization, a technique that readily determines both the total copper content and its state of dispersion (i.e., activity) is necessary.

## Oxygen

As indicated previously, it is possible to prepare bulk silicon crystals in which the oxygen content is reduced to inconsequential levels. However, in subsequent processing of the crystal by surface oxidization and diffusion,

[*] It was noted in Section XI that for certain silicon devices, a "high" diffusion coefficient could actually be one as low as $10^{-14} cm^2 sec$.

the introduction of oxygen becomes a problem of varying severity. For example, it is well known from studies of oxygen-containing bulk silicon that certain heat treatments give rise to donor centers. In the case of an oxidized wafer of silicon, there will be a large concentration of oxygen near the surface. For this reason, it would be expected that this surface would, under certain sets of processing conditions, have a tendency to show this donor action. If the wafer were p-type there would be the possibility of the formation of an n-type surface channel. This type of behavior has been observed and has given rise to a number of serious problems in device yield and failure. In a similar vein, there is a group of radiation effects which result from the presence of oxygen. It may be the case that some of the failure and instability mechanisms of devices in a radiation environment are due to these oxygen-dependent processes.

At present there does not seem to be any detailed knowledge of the concentration and dispersion state of oxygen near the surface of oxidized silicon. The various factors that may influence its depth of penetration and detailed distributions are largely unknown. The importance of oxidization in the silicon process technology certainly justifies a deeper look at the characterization of the attendant oxygenation of the silicon.

## APPENDIX D - RADIATION DEFECTS IN SILICON

### I. Nature of Damage

As a result of the excellent electron spin resonance (ESR) investigation
of G. D. Watkins[1] and his co-workers at the G. E. Research Laboratory,
we understand the nature of radiation damage and the types of lattice imperfections
created by energetic radiation better in Si than in any other semiconductor
conductor and, perhaps, even better than in any other crystalline solid.
Even so, there are important gaps in our knowledge and we are far from
the point of being able to claim that all radiation-induced defects have been
identified. The major contribution of this work is the discovery that the
stable defects remaining after irradiation at temperatures above that of
liquid nitrogen are almost invariably composite imperfections composed
of vacancies combined with other imperfections, or any impurity whose
state has been altered by the irradiation. Such a wealth of resonances has
been found that one is forced to the conclusion that primary radiation defects
(interstitials and vacancies) readily form complexes with every type of
impurity present in the crystal. The interstitial is even more unstable than
the vacancy since it cannot be retained for irradiation temperatures as low
as $4°$ K, and it leaves a trace of its transitory existence in the form of
interstitial impurity, such as $Al^{++}$ ions, which presumably mark the termi-
nation of a replacement chain reaction. We can only conclude that impurities
present in very small concentrations ($10^{-4}$ to $10^{-9}$ mole fraction) have a
profound effect on the extent and type of radiation response of silicon crysta
In fact, except for the thermally stable divacancies which are created
ab initio, no effect would be expected for room temperature irradiation of
a perfectly pure crystal where no impurities are present to trap the com-
ponents of the Frenkel pairs. These remarks of course apply to the

relatively simple damage produced by MeV electrons and gamma rays.
More complex structures with much greater thermal stability can be ex-
pected for bombardment with energetic ions or fast neutrons (see below).
The defect states identified by ESR investigations are summarized in Fig. 2.*
Also shown for comparison are energy levels determined from other electronic
property measurements.

## II. Energy Threshold for Displacement of Atoms
### in Silicon and Distribution of Damage

To a first approximation, the energy required to displace an atom from
its normal lattice site may be readily determined from the minimum energy
of an electron to produce a measurable effect in a radiation sensitive
property. Such measurements on Si by Loferski and Rappaport,[2] employing
the change in short-circuit current of an Si solar cell as the damage index,
yielded a displacement energy of 12.9 ± 0.6 eV. According to simple, two-
body damage theory this is the energy which must be transferred in an elastic
collision between an energetic (relativistic) electron and a silicon atom to
eject it from its normal lattice site. More recent experiments reveal that
the displacement process is rather complex and that both the lattice struc-
ture and relaxation processes must be taken into account. For example,
Gunnersen and George[3] find that the threshold for displacement is lowest
for ejection in the <111> direction, next lowest for <110>, and highest for
<100>. In addition, the yield of defects for incident electrons with energies
near the threshold value is found to depend markedly upon temperature and
Fermi level. Novak[4] finds that the displacement energy is ~ 14 eV in
n-type and ~ 21 eV in p-type silicon specimens, suggesting that the stability
of defects after creation may play an important role in these measurements.

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* Placed at the end of Appendix D, Section IV.

The spatial distribution of damage and, hence, the nature of effects on physical behavior depends upon the nature and energy of the bombarding particle. Electrons near the MeV range are sufficiently near the displacement threshold that complication due to displacement cascades created through secondary and higher order displacements are avoided. On the other hand, energetic ions (protons, deuterons, and $\alpha$-particles) and fast neutrons transfer energies much in excess of the displacement energy to the lattice atoms, with the result that the primary recoil creates many additional closely spaced defects. The influence of such disordered regions is more important in Ge where the greater atomic mass leads to a shorter mean free path between successive secondary displacements than in Si. Nevertheless, the complex damage produced by energetic heavy particles can play a significant role in Si as well, particularly with respect to effect on structure.

## III. Physical Properties Affected

### A. Electronic Properties

The importance of ESR in determining the nature of radiation defects has already been mentioned. Obviously, only those imperfections possessing unbalanced spins may contribute resonances. In addition, nearly all other electronic properties are affected in a greater or lesser degree. Irradiation induces optical absorption bands at wavelengths greater than the fundamental cutoff which are associated with excitation and ionization of radiation defects. [5] The latter process is responsible for an enhanced photoconductivity in the infrared. [6] The defects also act as acceptors, donors, minority carrier traps, and recombination centers, thereby affecting the carrier concentrations in both steady state [7] (conductivity and Hall effect), and transient mode [8] (minority carrier lifetime, decay of photoconductivity,

etc.). Since they usually bear an excess charge, these radiation defects scatter carriers as manifested by a change in carrier mobility and magneto-resistance.[9] Dilational strains associated with the imperfections influence the band gap through the deformation potential and this can be seen in a shift of the absorption edge.[5] Since the latter effect requires appreciable defect densities, fast neutron bombardment with the accompanying large concentration of complex damage is usually required to produce an appreciable effect. Finally, one might mention magnetic susceptibility[10] which is influenced both through the loss of carrier diamagnetism as carriers are removed by the defects and through the paramagnetic contribution of defects with excess spin.

B. Other Properties

1. Stored energy—A natural consequence of introducing defects into a crystal lattice is the increase of the internal energy of the system. Mayer and Lecomte[11] have measured the stored energy of neutron-bombarded silicon by differential thermal analysis, and find two energy release peaks—one at 230°C and one at 350°C. After an exposure of $3.7 \times 10^{19}$ neutrons/$\text{cm}^2$, 2.1 cal/gm of energy was released in the first peak and 0.3 cal/gm in the second. Analysis of kinetics revealed that a second order process with an activation energy of 1.09 eV governed the 230°C peak. These authors also measured elastic constants and found a perceptible change in $S_{11}$, $S_{12}$, and $S_{44}$ with the largest effect exhibited by $S_{11}$ (1.8%) after the above exposure.

2. Thermal conductivity—The effect of both fast neutron and 2 MeV electron irradiation on the thermal conductivity k of Si has been investigated. Albany and Vandevyver[12] have measured the temperature dependence k after irradiation at 70°C to a dose of $10^{18}$ fast neutrons/$\text{cm}^2$, and find a general decrease in k over the range 80° to 300°K with the largest effect

(a factor of three decrease) at 80°K. Analysis of the results suggests that
the increase in thermal resistivity is associated with phonon scattering
from both point scatterers and boundaries, the latter presumably being
associated with large clusters of defects or damage regions produced by
neutron bombardment. Annealing of the effect proceeded by a bimolecular
process with an activation energy of $\sim$ 1 eV in good accord with the recover
of stored energy reported by Mayer and Lecomte.[11]

Vook,[13] on the other hand, has determined the effect of electron irradi
ation on the thermal conductivity curve of p-type Si to temperatures as low
as 8°K. He finds that the incremental thermal resistivity caused by the
irradiation can be described by $1/k = 3.75 \times 10^{-13} \phi^{0.61}$ cm-deg/W at 47°
where $\phi$ is the integrated dose of electrons. The partial power dependence
on flux is attributed to a radiation induced change in electron-phonon scat-
tering rather than scattering by point defects which would be expected to
depend linearly upon exposure. Upon annealing, both a minor recovery
stage at 80°K and an important one at 140°K are observed. Since a 140°K
stage is associated with the migration and annealing of vacancies, the alter-
ation of charge distribution by these defects seems to be the predominant
cause of the decrease in thermal conductivity in these studies.

3. Structural changes—Virtually no density nor lattice dimension change
are produced by prolonged exposure to MeV electrons at 80°K. However,
0.7 MeV protons, which are expected to produce a more complex damage
by virtue of a large displacement cascade, produce dimensional effects
which are detectable by x-ray topographic techniques. Small dimensional
changes have been observed in neutron-bombarded silicon as well. Wittels(
reports a lattice expansion of 0.017% after an exposure of $4 \times 10^{20}$ neutrons
as determined by x-ray diffraction.

### IV. Summary of Well-Identified Radiation Defects in Silicon

**A. The Vacancy and Vacancy Impurity Complexes**

    1. Isolated vacancy - V

      (a) Method of detection and study: ESR after low temperature (20°K or less) irradiation.[1]

      (b) Electronic behavior: Amphoteric defects, charge states of $V^=$, $V^-$, $V^0$, and $V^+$ possible. (Position of states shown in chart.)

      (c) Stability: Activation energy for motion $E_M$ depends on charge state. V disappears (a) in 15 min at 170°K in p-type Si $[E_M(V^0) = 0.33 \pm 0.03 \text{ eV}]$, and (b) in 15 min at 60°K in n-type Si $[E_M(V^-) < 0.16 \text{ eV}]$.

      (d) Other manifestations: None well established.

    2. Vacancy-donor complex - D-V

      (a) Methods of detection and study: ESR,[1] Hall effect R,[15] photoconductivity,[6] and excess carrier lifetime.[8,16]

      (b) Electronic behavior: Single acceptor level ~ 0.4 eV below conduction band. Also an important recombination center. Evidence that position of level depends on donor identity[15] (0.43 eV for Sb and 0.47 eV for P).

      (c) Stability: Disappears on annealing above 100°C. Activation energy depends on donor identity[15,16] $E_A(P) = 0.94$ eV; $E_A(As) = 1.27$ eV; $E_A(Sb) = 1.84$ eV; and $E_A(Bi) = 2.22$ eV.

      (d) Other manifestations: D-V's form very effective excess carrier recombination centers.[8]

    3. Vacancy-oxygen complex - O-V

      (a) Methods of detection and study: ESR,[1] R,[17] photoconductivity,[6] optical absorption due to vibrational bands.[18]

      (b) Electronic behavior: Possesses an acceptor state 0.17 eV below the conduction band. Also evidence of an associated donor state 0.27 eV above the valence band.[19]

(c) Stability: Disappers on annealing with an activation energy[1] of 1.3 eV. Mechanism in doubt but may migrate is a pair to an appropriate sink. Energy of reorientation[1] (switching of Si-O valence bonds) $0.38 \pm 0$.

(d) Other manifestations: None well established.

**4. Divacancies - $V_2$**

(a) Methods of detection and study: ESR.[1]

(b) Electronic behavior: Amphoteric defect. Charge states $V_2^+$, $V_2^o$, $V_2^-$, and $V_2^=$ are possible (level positions shown in chart).

(c) Stability: Disappears on annealing by migration as a pair with $E_M(V_2) = 1.3$ eV. The binding energy of the pair is $> 1.6$ eV.

(d) Other manifestations: None well established.

**5. Vacancy-acceptor pairs - A-V (observed for Al only).**

(a) Methods of detection and study: ESR.[1]

(b) Electronic behavior: Uncertain. Resonance observed at low temperature for the state $(Al-V)^-$. It is presently unknown whether the further ionization of this defect on warming corresponds to acceptor or donor activity.

(c) Stability: A-V defects are formed in p-type Si upon vacancy migration. The stability against annealing has not been established.

(d) Other manifestations: None well established.

**B. Interstitial Defects**

**1. Interstitial Si atoms:** Do not exist in a form identifiable by ESR[1] subsequent to irradiation in the temperature range thus far investigated (down to 4°K).

**2. Interstitial acceptors - $A_1$**

(a) Methods of detection and study: ESR.[1]

(b) Electronic behavior: In the one case studied (aluminum), interstitial impurity ionizes as a double donor $(Al_I^{++})$.

(c) Stability: $Al_I$ move in the vicinity of 200°C and appear to form complexes with other impurities, notably $Al_I^{++}$-$Al_s^-$.

(d) Other manifestations: None well established.

3. Interstitial-substitutional impurity pairs $(A_I$-$A_s)$.

(a) Methods of detection and study: ESR.[1] (Both $Al_I^{++}$-$Al_s^-$ and $Ga^{++}$-$Ga_s^-$ identified.)

(b) Electronic behavior: Pair acts as single donor in this ionization state which is observed at low (< 20°K) temperature. Other ionization states may exist.

(c) Stability: Produced by annealing to 200°K; upper stability temperature unknown.

(d) Other manifestations: None well established.

C. Other Defects

1. Vavilov and co-workers[6] have demonstrated that irradiation enhanced the concentration of localized states attributable to a certain deep level impurity. The obvious conclusion is that this impurity must be present in the crystal in a form which is electrically inactive and which is dispersed allowing the impurity to enter substitutional sites by the irradiation. Most of these impurities whose state concentration is enhanced are interstitial diffusers: Au, Cu, Fe, and perhaps Ni. The presence of Li was found to profoundly alter the stability of energy levels introduced by irradiation. This indicates that defects form additional complexes with the highly mobile $Li^+$. In addition, Swalin and co-workers[20] have found that irradiation enhances the nucleation rate for Li precipitation in Si, presumably since the O-V complexes are important nucleation sites.

2. Spin resonance investigations at both G. E. and Purdue have yielded other defect resonances which have yet to be identified with defect structures.
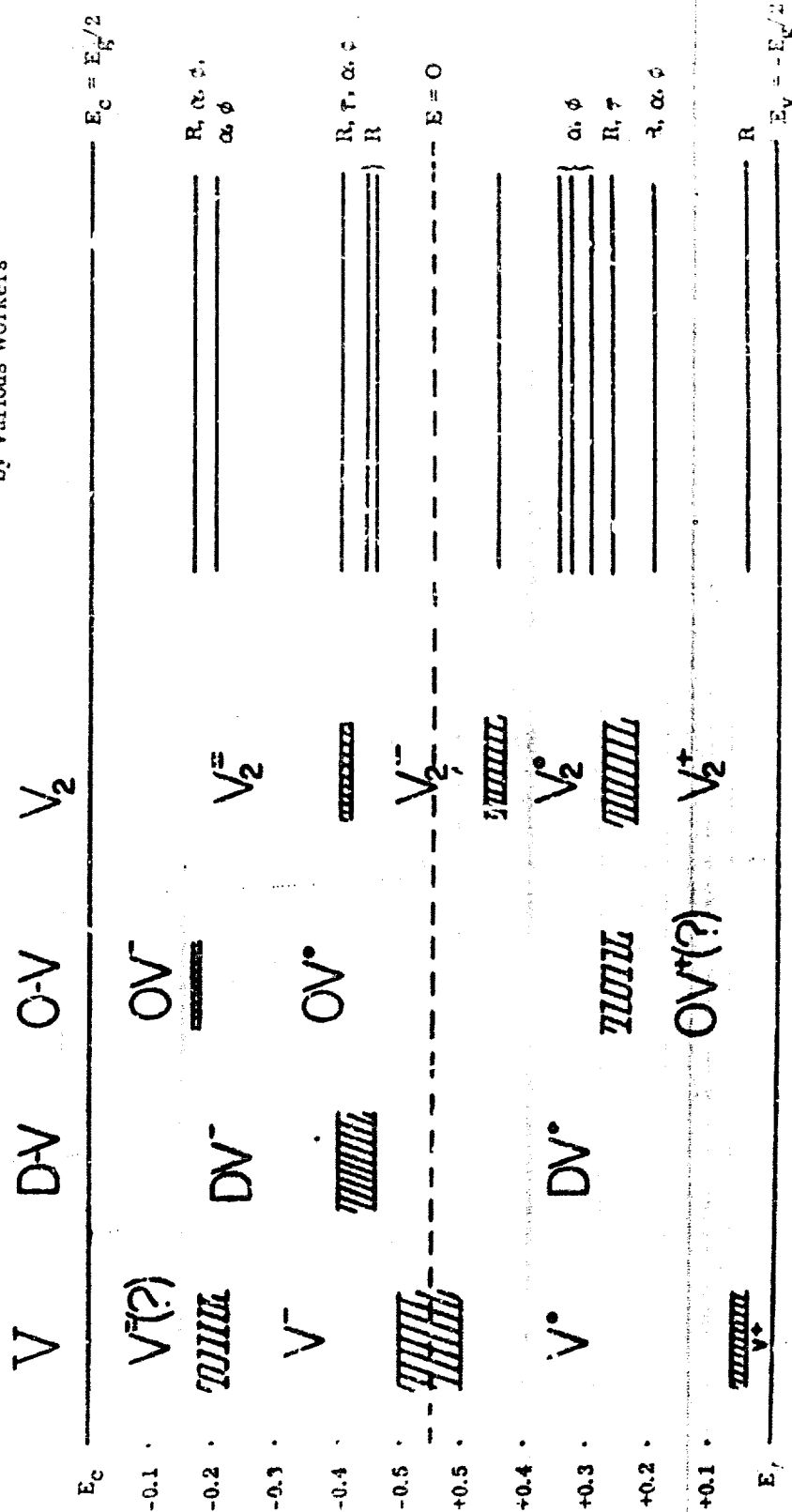
FIGURE 2. Acceptor and Donor states associated with defects in irradiated silicon. The states on the left have been identified and located approximately in the band gap through measurements of ESR (Ref. 1) and the dependence of the resonance signal of interest upon the position of Fermi energy. The charge states of the defects reflect whether acceptor or donor action is observed and the energy range over which it occurs. Vacancies are denoted by V, donor vacancy pairs by D-V, oxygen-vacancy complexes by O-V, and divacancies by $V_2$.

On the right side is a summary of the positions of energy levels determined from a variety of electronic properties. The symbols are defined in the legend.

Means of Locating Level

R = Hall effect.
α = Optical absorption spectrometry.
$\hat{\sigma}$ = Spectral response of photoconductivity.
τ = Minority carrier lifetime.

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## APPENDIX E - CHARACTERIZATION OF POINT DEFECTS IN METALS

### I. General Discussion

We may distinguish two categories pertinent to characterization:

(1) Determining the nature, concentration, and location of the defects.

(2) Obtaining equilibrium and kinetic properties.

In regard to the first category, the inadequacy of most techniques related to direct observation has already been discussed. It is possible, of course, to look at vacancy loops with thin film microscopy, but at the best present resolution one is really looking at dislocations then, although in some laboratories the aggregates may be as small as 30 vacancies. There is hope that field-ion microscopy will prove to be a useful tool. This needs some qualification. For adequate characterization, much more will be needed than getting a few pictures. An intense effort would be required in which all the quantitative tools of this area (such as image intensification) are used. Moreover, there is the need to scan literally hundreds of thousands of pictures so that automated quantitative scanning techniques including tie-in with a computer would be needed. The entire area of direct observation is one requiring improvement.

In regard to the second area, it seems surprising but it is nonetheless true that the only thermostatic values of point defects, obtained directly, which one can accept with reasonable conviction are the energies of vacancy formation in Ag, Au, Cu, and possibly Ni (all face centered cubic noble metals), and sodium in the body centered cubic system. We might add Al to this list but here the value might be for the divacancy rather than the vacancy. It might be stated that in Ag, Au, and Cu it appears reasonably certain that the activation energy for tracer diffusion is the sum of the energy of vacancy formation and the activation energy for vacancy motion;

however, the direct measurement of the latter seems to be exceedingly difficult and the results leave much to be desired. This then summarizes the state of knowledge in one of our prototype materials, copper. The state of knowledge of point defects in our other prototype material iron is easier to characterize: they exist; but the What and Why and When and How and Where and Who simply do not exist other than in wild speculation. We therefore are faced with the situation in which we know something about the single vacancy in a few ultra pure fcc metals and in bcc sodium. If we complicate these systems to include a bit of impurity, 0.1%, so we might get impurity-vacancy complexes or a vacancy supersaturation due to quench ing, we get sizeable divancy concentrations and our knowledge rapidly diminishes. If we continue on to interstitials, our ignorance continues. Now if we think of elemental hcp metals, this knowledge becomes almost vanishingly small. And if we go to more complicated compound metals and intermetallics, it vanishes altogether. Thus our knowledge of lattice defects in metals still remains grossly inadequate, and equally true today is the statement made by Professor Seitz in 1964 as a foreword to the Proceedings of the International Conference on Lattice Defects in Quenched Metals:[1] "It is clear that the field is still in its infancy and that several generations of those concerned with the science of metals will find it a stimulating area in which to work in the future."

It would be of interest to know the effect of pressure on the vacancy concentration and motion, and the electron scattering per defect as well as the effect of electron currents on vacancy motion. Increased studies in which pressure is a variable can also lead to information about the atomic relaxation around vacancies by providing results on volumes of formation. The latter quantities are of fundamental interest in connection with

calculations of energies of vacancy formation. It would be useful to have information on the atomic relaxation in the activated state, which gives the volume of motion. This again can be obtained by the pressure dependence of vacancy motion. Likewise there is a need for further pressure dependence studies of diffusion. Although this section is devoted to metals, it is to be noted that the above general comments on the pressure dependence apply not only to vacancies in metals but to vacancies in other materials and to different point defects in all types of materials.

Information on the average relaxation volume around different disloca-tions can be obtained by measuring density changes upon plastic deformation; however, the possibility of forming pores, voids, fissures, etc., must be eliminated. This can be done by applying hydrostatic pressure in magnitudes about twice the yield strength of the cold-worked material.

The volumes discussed above are of enormous help to the theorist. Imagine the plight of Wigner and Seitz had they been forced to calculate the lattice energy without knowing the unit cell size! The theorist who attempts to calculate the energy of formation of the vacancy in the absence of knowledge of the volume of formation suffers a similar plight. Eventually we may be able to proceed entirely from first principles, but in the mean-while the experimental values are of great importance.

Thus far, we have been concerned only with point defects in the good lattice. There is a great need for understanding defect behavior in the bad parts of crystals; i.e., in or along dislocations and grain boundaries. We shall see in the next section that there are a number of techniques that are available which if properly used and if used in conjunction with other techniques can improve this general situation considerably.

## II. Special Techniques for Vacancy Characterization

### 1. Macroscopic Dilatation and X-ray Measurements

Here one makes extremely precise measurements of the difference between the change in length (relative to some reference length at a referenc temperature) over the base length and the change in lattice parameter over the base parameter. The change in equilibrium vacancy concentration is given by

$$\frac{\Delta n}{n} = 3 \left( \frac{\Delta \ell}{\ell_0} - \frac{\Delta a}{a_0} \right).$$

This represents the only direct measurement of vacancy concentration in metal. It is a tedious, expensive experiment. Extreme care must be taken in all phases of the work to obtain respectable results. Fractional vacancy concentration can be measured to $10^{-5}$. This is a powerful tool for studying vacancies, which has been used by Simmons and Balluffi on a number of fcc metals. It should be exploited in elemental hcp, bcc metals, and also in compound metals. A word of warning: ultrahigh purity materials are needed and extremely careful chemical characterization must be carried out in order to get scientifically significant results. Total impurity levels (including gases) below the fractional vacancy concentration should be used. There is a great need for studies using systematically doped material to find the binding energy of vacancies with impurities.

### 2. Macroscopic Density and Precision Lattice Parameter Determinations

The dilatation measurements discussed above yield values of the equilibrium concentration of vacancies at high temperatures and therefore are of value for obtaining the basic parameters associated with the defect, but do not directly characterize the starting material. More appropriate, therefore, for the latter function are the measurements of macroscopic density together with precision lattice parameters.

Careful measurements of density, using hydrostatic weighing in water, have yielded a precision of approximately one part in a million in the case of silicon.[2] A limitation appeared to be the precision with which the absolute density of water was known. In the case of most materials, a denser liquid would be used, and probably a more universally realistic value for the precision of density determination is to within $10^5$ or a few parts in $10^6$. The precision with which the lattice constant may be determined is perhaps of the same order of magnitude as is the density, although different problems are involved in such determinations.[3] In view of the above considerations it is seen that the determination of defect concentrations of the order of $10^{18} cm^{-3}$ is reasonable, with the possibility of improvement—as is discussed below. It is important to note that the above technique yields the net number of defects only when the defects are of a similar type—mass excess (interstitials) or mass deficiency (vacancies). It will obviously not be successful for antistructure defects or if vacancies and interstitials are both present. The majority of cases involving metals and nonmetals, however, fit into the necessary category.

The value of this method could be considerably enhanced if its precision were improved by at least one order of magnitude; i.e., so that defect concentrations $\lesssim 10^{17} cm^{-3}$ could be determined. Such an improvement is quite difficult to attain for the absolute measurements (for example, the molecular weights are not generally known precisely enough), but far less difficult if one is confined to relative measurements. The latter can be especially useful for comparing a crystal of interest to a reference crystal of the same material. For high precision relative measurements of lattice parameters, a double crystal method can be used, whereby the first crystal is the reference and the second one the unknown. For the relative density measurements, it is no longer necessary to know the absolute density of

the immersion liquid or the thermal coefficient of density. The problem of knowing the temperature to a small fraction of a degree is also elimina in both sets of measurements; it is only required that the difference in te perature between the reference and unknown crystals be kept very small. Both of these types of relative measurements are not already in use and therefore need to be developed; however, the benefits to be derived seem well worth the effort required.

3. Equilibrium Resistivity Versus Temperature and Heat Capacity Versus Temperature

In both of these cases it is assumed that a property such as resistance in the absence of vacancies can be extrapolated correctly into a high temperature region where it is not measured. It is then assumed that the devi. tions of the measured data from the extrapolated values are due to vacan : If we were absolutely sure of the extrapolated values, this would be a val. able tool. However, our meagre knowledge of anharmonic phonon-electron interactions hardly justifies this. In the absence of such knowledge, this tool should be restricted to use in conjuction with a more precise method such as that used by Simmons-Balluffi, namely, the macroscopic dilatation and x-ray measurements.

4. Quenched-in Vacancies

Resistivity measurements on specimens quenched from high temperatur have given interesting results, both for the energy of formation and the energy of motion of vacancies as well as properties of other point defects. If we look back it is likely that the majority of these data are wrong or useless for one reason or another because of lack of proper chemical characterization and proper dislocation characterization. The precise kinetics is often lacking, or is assumed to be first order when it is not.

The number of sinks often changes drastically due to loop or tetrahedra formation, and resistivity studies of quenching should be done in conjunction with thin film microscopy studies of the structural changes.

It should be noted that we have no assurance that the excess vacancies in a quenched specimen are predominately present as vacancies or divacancies. This uncertainty can be resolved by lattice-parameter length-change techniques if the volumes of formations are known and differ sufficiently.

In the proper hands, highly sophisticated and sensitive resistivity techniques (or heat capacity techniques) can be very useful tools, if proper material characterization (chemical and line defects) is made and if they are carried out in conjunction with other techniques, for studying defects both by quenching and by pulse heating.

There are clearly a number of possible advances which can be made in this area such as the use of high speed resistivity equipment for measuring small vacancy lifetimes.

## 5. Diffusion

### A. Tracer diffusion

Tracer diffusion has been a powerful tool for studying defects in solids and will clearly continue to be so. Certainly it was a combination of tracer diffusion, quenching and resistivity measurements and lattice-parameter and length-change studies which elucidated the behavior of the single vacancy in the fcc noble metals Cu, Ag, Au.

These techniques have been put on a fairly firm basis, and developments in measuring extremely small penetration depths are expected and should be encouraged.

Tracer diffusion techniques are now being extended to study tracer diffusion from dislocations, and this will provide valuable information.

B. Nuclear magnetic resonance motion narrowing

This technique has had limited use in metals in studying diffusion. In general it has been limited to diffusion in a few low atomic number cubic metals. The reason for this is the low sensitivity in large metallic specin because of the skin effect. Because of the advent of lock-in techniques 2, ? integration techniques, a number of new possibilities afford themselves. As an example, a possibility is the study of vacancy supersaturations duri deformation, an area in which tracer diffusion does not seem to be of muc'

### III. Divacancies and Other Vacancy Aggregates

Some experimental knowledge of divacancies appears to be emerging for Ag and Au. A number of theoretical calculations of questionable reliability is available. Because many processes take place in metals with large supersaturation present, these defects must play an important role, and a knowledge of them would be most helpful.

### IV. Interstitials

While the vacancy is present in fairly large equilibrium concentrations in face centered cubic metals, the interstitial is not. Consequently, completely reliable measurements on these systems of defects are missing. However, it is known that the interstitial formation energy is larger than the formation energy for the vacancy, while the interstitial motion energy is considerably less. There is much speculation in the literature on the properties of interstitials. Some clarification has resulted from radiation damage studies, as is discussed below.

## V. Radiation Damage Studies in Metals

The bombardment of solids with electrons, neutrons, and ions has been of value in providing a qualitative understanding of some of the characteristics of point defects in metals. While it is true that from a technological viewpoint it might be of interest to study the behavior of solids under bombardment with any or all of the above particles, from the purely scientific viewpoint of elucidating the characteristics of individual defects, such as the vacancy or interstitial, it appears that only certain types of bombardment are really helpful. On this basis, neutron irradiation of metals seems only to add to the confusion, rather than to clarify.

. The defects produced by radiation consist usually of vacancy-interstitial pairs at various distances of separation, although there are interesting exceptions. A general problem is that the concentration of these pairs, either in total or individually (as characterized by the relative geometry of the pair), is not known. Major contributions to the area would be experimental methods which would give the concentrations.

Probably the major contribution of radiation studies in metals has been the achievement of a partial description of the interstitial. While there is still considerable debate among various research groups regarding specific details, we now know that the interstitial and di-interstitial move with a relatively low energy and that there may be more than one type of interstitial. These are difficult problems to solve, in part complicated by the presence of the vacancies. Conceivably, this can be overcome by specific ion bombardment; e.g., gold on gold at orientations which would cause channeling and dynamic crowdion formation, the net result being an interstitial within the crystal. Such experiments are in progress.

Another question of considerable interest is: Where do the point defects go during annealing of an irradiated sample? Detailed investigations of the kinetics, along with transmission electron microscopy studies, have in part answered this question. It seems that electron micro _ope work at considerably higher resolution might supply part of the final answer. Likewise detailed quantitative studies by field ion microscopy of irradiated samples at various stages of annealing could be very helpful. The most comprehensive and useful review of the whole subject of radiation of metals is due to Corbett;[4] the work includes a wider range of radiation types than its title suggests.

## VI. Defects in the Bad Portions of Crystalline Materials

It is important to know equilibrium concentrations of vacancies on dislocations and information concerning how fast they move. The same applies to grain boundaries. How this is to be done is open to question.

## VII. Chemical Factors

Even should there exist an adequate body of experimental knowledge and tools available for studying point defects and their aggregates in a satisfactory fashion in pure elemental metals—which is clearly far from the case—there would still be a great need for studying these defects in alloys. A whole new vast array of problems is introduced in chemical diffusion—problems such as the generation of dislocations and plastic flow by chemical gradients.

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## APPENDIX F - CHARACTERIZATION OF DISLOCATIONS IN METALS

Specific attention is given here to the illustrative materials, copper and iron. The most effective techniques are outlined below.

### I. Etch Pits

1. Copper

Etch pit techniques are available for finding dislocation intersections with {111} planes of relatively pure copper. If the etching is done on a plane within 1-2° of (111) planes the method appears to be nearly 100% reliable, with certain limitations. Densities in the range $1 - 10^7/cm^2$ can be obtained with standard microscopy while in the range up to $10^9/cm^2$ replica techniques of lightly etched specimens can be used. One of the problems is that one doesn't in many cases know if an etch pit is one or two or even several dislocations. Note that an etch pit is about $1\mu$ wide, so that a dislocation dipole several hundred angstroms wide would appear as a single pit. In certain ideal cases it is possible to distinguish between edges and screws and to get the sign of the Burgers vectors. However, we are not currently sure about the reliability of etch pit technique on {110} and {100}.

We want to emphasize in general the tremendous specificity of etch pit technique. This can be affected by the plane on which etching is done, the inclination of the dislocation line to the surface and the inclination of the Burgers vector to the surface. They also may show tremendous sensitivity to impurities. Finally, all etch pits are not necessarily signs of dislocations. As an example we shift from copper to aluminum. Here etch pits which were thought to be at dislocations formed from heating and cooling cycles have been convincingly shown to be present in concentration orders of magnitude higher than the actual dislocation density.

Moreover, the reliability of a given etch pit technique depends upon direct comparison with an absolute technique in which the stress fields of individual dislocations can be viewed directly; e.g., x-ray topography or transmission microscopy.

Also, etch pits in any case do not show any of the fine structure of dislocation lines: they do not distinguish between dipoles and single dislocations, stacking faults cannot be observed, nor can jogs and kinks, etc.

### 2. Iron

There are etch pit techniques available for iron containing on the order of 100 ppm of free carbon (not bound in stable carbides) which are probably reliable. There are a number of etching reagents, however, which clearly underestimate the dislocation density. The available etch pit technique here depends on carbon segregation at the dislocations. The lower limit for the allowed carbon content is not known; it appears that below 30 ppm is not sufficient. The pits have a conical shape. No techniques are available for distinguishing edges and screws or the sign of the Burgers vector. At present there are no etch pit techniques at all for use with pure iron. This is unfortunate because research with pure iron is being carried on in important areas. For example, attempts are under way to establish the role of carbon in the ductile to brittle fracture transition and these would be greatly aided by a reliable etch pit technique for almost pure iron.

## II. X-ray Topography

### 1. Berg-Barrett

This technique gives a direct image of dislocations in the density range of $0-10^4/cm^2$. In back reflection it views a thin region near the surface of a bulk sample. It is not stereoscopic. In transmission the specimen must be thin, not applicable to seeing fine structure of dislocations; resolving

power is only about $10^{-2}$ that of standard etch pit techniques. The technique can be valuable as a calibration on etch pit techniques.

(a) The technique can be used on low dislocation density copper.

(b) The technique can be used on low dislocation density iron.

2. Lang

This gives a stereoscopic image of dislocations in the density range of $0\text{-}10^{4}/cm^{2}$ by transmission through a fairly thin specimen. Because of the low resolving power the fine structure is not observed.

(a) Technique has been used on copper.

(b) Iron???

3. Borrmann

The chemical purity must be sufficiently high so that we can get anomalous transmission. It is a very useful technique applicable to fairly thick specimens (0.5 mm) which should be characteristic of a bulk sample. It gives a stereoscopic 3-d spatial distribution in the dislocation density range $0\text{-}10^{4}$. It is possible to determine the Burgers vectors absolutely.

(a) The technique has been successfully used on copper.

(b) Iron???

### III. Transmission Electron Microscopy

Because thin films ($\sim 1000$ Å) are viewed it is not convenient to work with densities below $10^{6}$. Regions of density as high as $10^{11}$ (and possibly $10^{12}$) can be studied while still denser regions cannot be observed. In the lower density regions ($10^{8}$ or less) it is possible to distinguish between closely spaced dipoles and single dislocations by using tilting and dark field microscopy. It is also possible to do stereoscopic work and to get Burgers vectors. This requires careful diffraction contrast work, densities to $10^{8}$ or less and a great deal of work.

1. A considerable amount of work has been done on copper. Special problems can result from the fact that handling of the thin films often introduces long dislocations. Dislocation rearrangement clearly takes place (image forces) in a thin film. The stress to move an isolated dislocation in pure (1966) copper is nearly zero (2 g/mm), and it is necessary to carry out a pinning treatment (e.g., neutron irradiation) to prevent losses.

This problem of losses is not unique to copper. It can be a severe problem in ultrapure fcc and hcp metals (there are no ultrapure bcc metals in 1966).

The fine structure has been studied. Jog steps of maybe as little as 50 Å can be seen. The stacking fault energy has been measured by the node method; however, this may be disturbed by impurities. Certainly we cannot see individual unit jogs.

Complete characterization of the assembly of dislocations in a specimen in ranges of considerable practical interest (e.g., $10^8$-$10^{12}$) is an over-whelming task experimentally. Even if a complete mapping position, tangent vector and Burgers vector, were correctly made experimentally, the problem of its significance would remain. This is discussed in the next section.

2. A considerable amount of work has been done on iron. The situation here is about the same as with copper. The lower purity of iron and the associated strong pinning of dislocations by carbon means we have less chance of motion and losses. (In iron with no impurities, losses might be severe because of cross-slip.)

### IV. Special Problems

1. Distribution of Dislocations

One of the major problems is characterizing the dislocation distribution.

(a) The crudest characterization is just the total length per unit volume which may be alternately put in terms of the dislocation etch pits per unit area.

(b) It is clearly better to give the dislocation etch pit count in subgra boundaries separately from the count within the grain. Perhaps for work at high temperatures (creep) this is really quite good. (However, a comm experimental procedure in high temperature tests is to remove the stress and then to shut off the furnace. There is little doubt that sizeable rearrangements take place which lead to counts within the subgrain which ar far too low). When instead of well-defined boundaries we have diffuse cell walls or tangles, it is really not quite clear how we characterize the mate rial. (Again it is likely that if thin film techniques are used the count in the nontangled regions may be low because of losses from such regions.)

The problems of characterizing dislocation distributions under such conditions necessitates an understanding of what aspects of the distribution are really important to the specific property under study; our present state of knowledge is very weak in this regard.

2. Fine Structure of Dislocations

(a) The dislocation core in metals is at best poorly understood.

(b) Stacking fault energies are in most cases not accurate.

(c) Jog energies are guesses and no satisfactory way of measuring them appears available.

(d) The climb efficiency of dislocations appears to vary by $10^3$.
A great deal of additional work is needed here. A number of experiments are possible which will cast light directly on this problem.

(e) The rate of tracer diffusion along dislocations is not known, except in nickel and possibly silver.

(f) The rate of motion of point defects along dislocations is not in general known.

(g) Point defect production during deformation is not at all understood in any quantitative manner. There is a considerable need for study of the whole business of dipole formation, point defect production at jogs on moving screw dislocations, etc.

Finally, all of the above problems need detailed theoretical study as well as experimental study.

3. Mobility of Dislocations

Except for experiments which measure the <u>average</u> velocity at given stresses, nothing is known of the actual velocities. Perhaps for high speeds this is not a serious problem. At low speeds it is likely that actual speeds (when moving occurs) are greatly in excess of average speeds.

## V. Indirect Techniques

We want to emphasize the great importance of using several techniques in conjunction with each other to study dislocations. For many studies it is vital to have available several techniques, including those already mentioned as well as those of this section.

1. Stored energy techniques can be used (in conjunction with methods of obtaining direct densities) as one measure of the distribution of dislocation strain fields. For example, sizeable stored energy changes might be obtained upon annealing under situations in which there are sizeable rearrangements but only small changes in number.

2. Nuclear magnetic resonance line broadening occurs as a result of quadrupole coupling with strain fields around dislocations. As with stored energy techniques, it seems that this can be a useful tool when used in conjunction with direct methods.

3. Electrical resistivity is changed by dislocation density and distribution. As with the other techniques in this section, it is the sum of the

effect on a large number of dislocations. Hence its direct interpretation is very complex; e.g., similar to work hardening. In all of these indirect effects one is really involved in studying a macroscopic property.

It should be emphasized that the highly structure-sensitive properties (hardness, etc., ferromagnetic behavior, superconductive behavior) are all in principle useful indirect methods for characterizing dislocations when used in conjunction with direct techniques.

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## APPENDIX G - ORGANIC MATERIALS (ANTHRACENE)

### I. Background Information

The principal sources of our knowledge of defects in anthracene are based on the introduction of defects through radiation damage and plastic deformation. No serious attempts have yet been made to exploit quenching from high temperatures.

The radiation damage work[1-6] has pointed to the existence of effects which may be related to structural defects, but it has provided no convincing evidence that chemical impurities, either present originally or brought about through the radiation process itself, are not involved.

Plastically deformed anthracene has been produced in non-hydrostatic high pressure experiments. In most of these experiments, observations were made of shifts of the fluorescent emission bands with pressure.[7-10] The appearance of an additional band[11,12] in the emission has been observed as well. The latter band has been interpreted as possibly resulting from dimer formation. The possibility of dimer formation is especially interesting since dimers are known to occur in solution when aromatic materials such as anthracene are in an excited state.[13] The high pressure work thus raises interesting questions about the role of vacancies and dislocations in providing favorable sites for the formation of excited dimers or excimers. Only a small amount of work has been done on the effect of pressure on the electrical properties of organic crystals, but dramatic reductions in resistivity which have been observed[14] suggest that more such studies would be profitable.

Annealing studies[15] have been done on crystals which were not intentionally deformed. These showed a reduction in the density of fast-trapping states, which was attributed to reduction in the density of defects, although impurity segregation on the defect site was not ruled out. Recent work[16]

on fluorescence at $4.2^\circ$K has provided evidence that impurities may play only a minor role in determining the behavior of crystals whose fluorescence properties change upon annealing at $130^\circ$C.

## II. Recommendations

The more prominent areas deserving attention are as follows:

### 1. Characterization of Dislocations

Although etch pitting techniques have been used by several investigators,[17,18] the development of decoration methods and x-ray techniques would be very useful. Electron microscopy, which has been used successfully in the study of tiny crystallites of polyethylene, might be applied here.

### 2. Detection of Lattice Vacancies

No satisfactory information exists concerning the concentration, kinetic behavior, electrical, or optical properties of vacancies or vacancy aggregates in anthracene or in any other organic material.

### 3. Defect Interactions

Although nothing seems to be known about the interaction of foreign atoms with lattice imperfections, one may readily expect the presence of lattice vacancies to be of considerable importance in determining the chemical behavior of specific impurities. In silicon, and in the II-VI compounds, for example, it has long been established that interactions between impurities and defects can be highly important. In anthracene and other organic crystals, oxygen is a well-known impurity. Photo-oxidation of the anthracene to anthraquinone or some other intermediate product may very well be facilitated by the presence of nearby lattice defects which can relieve some of the strain resulting from the formation of the relatively rigid covalent bonds during the reaction. Also, the formation of organic free radicals in the presence of chemically reactive impurities would be

most likely if they are located at lattice imperfections which can serve as very deep electron or hole traps. Recent study of the Hall effect in anthracene[19] lends support to the conclusions, based on fluorescence measurements,[16] that there exists a great profusion of such traps in this crystal.

4. Surfaces

The characterization of the surface of anthracene is of the greatest importance because of the known occurrence of direct charge injection[20] phenomena and exciton decomposition charge injection.[21] These effects frequently govern the transport properties of anthracene. More broadly, modification of the surface through physical or chemical changes might be expected to have profound influence upon the transport properties of nearly all organic insulators and photoconductors. Many of these materials are important technologically when used as electrical insulation. It would appear that the obvious importance of this application should command a continuing high level of support for studies of the chemistry and physics of solid polymeric and crystalline organic insulators for some time to come.

A final comment should be made concerning parameters to be studied and measuring techniques to be employed in the characterization of defects in anthracene and other organic crystals. In general, there is no dearth of measurement techniques. Photoconductivity, luminescence, dark conductivity, and the recent success of Hall effect measurements, together with appropriate chemical and physical techniques for characterizing impurities, are all in use at the present time. There does seem to be a general lack of emphasis on spin resonance techniques, and increased use of both ESR and NMR will very likely prove profitable in the future.

The principal strategic recommendation concerning techniques, however, is that more studies be made in which a combination of techniques is applied

to a single specimen which has been carefully prepared. If a variety of different measurements is made on a single example of an organic crystal, it is reasonable to assume that many of the apparently fragmented results which are presently available can be more easily and efficiently fit into an over-all pattern leading to understanding. The practice of exchange of samples among different laboratories is therefore to be encouraged. (This suggestion is not to be construed, however, as supporting the idea that the crystal preparation and measurement functions should be purposely split.)

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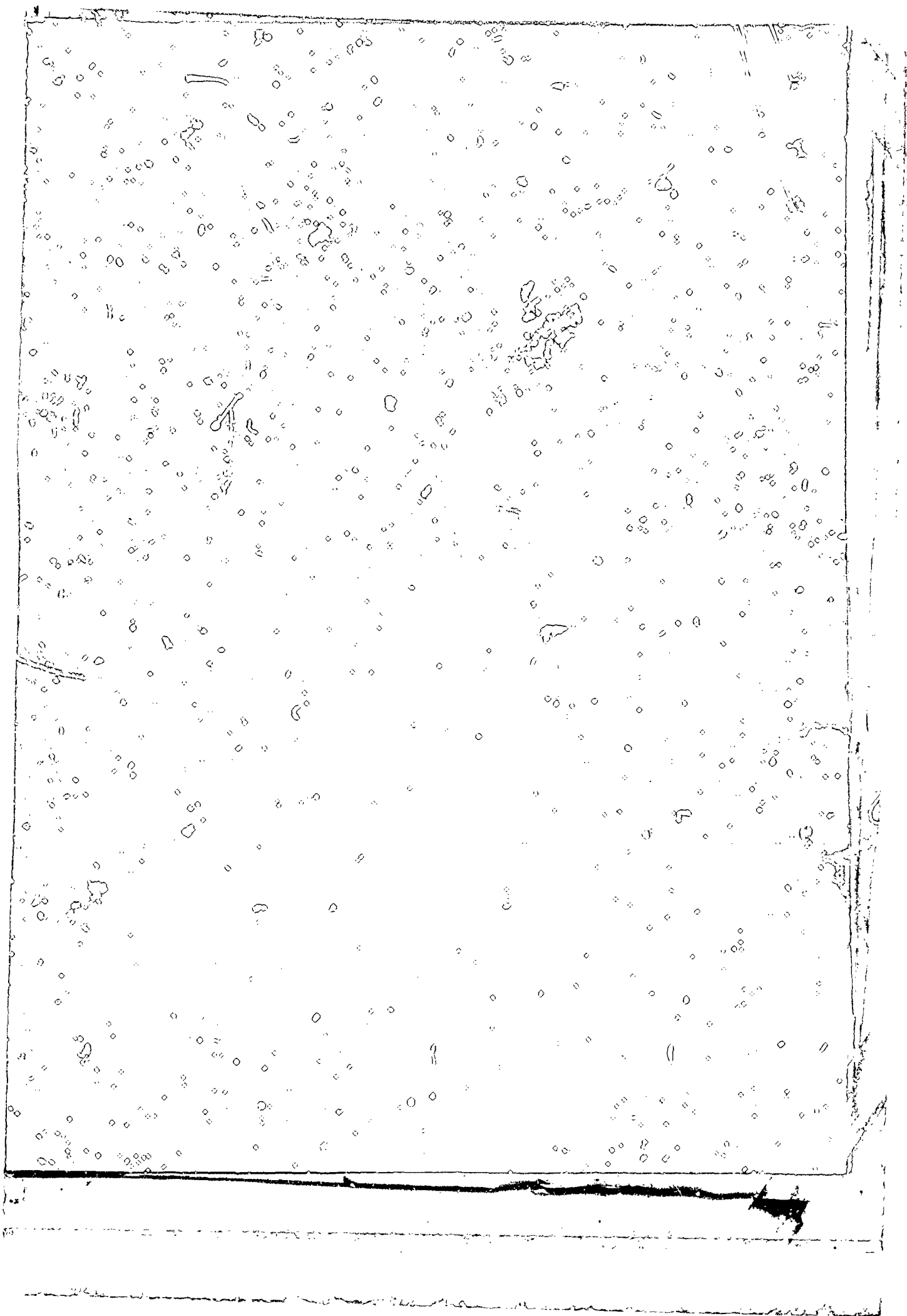
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# CONTENTS

## SECTION V. THE REPORT OF THE PANEL ON POLYCRYSTALS

# THE CHARACTERIZATION OF POLYCRYSTALLINE MATERIALS

## A. INTRODUCTION

The goal of much of materials research is to relate certain aspects of structure and composition either to the reactions which produced them or to the properties they influence. For these purposes a very complete characterization of structure and composition may be desired.

In many of the "real" materials of engineering, however, there is the need for one experimenter to describe for another the material on which he performed his work, in such a way that the material can be reproduced with reasonable assurance. In principle, this can be done by a sufficiently complete statement of structure and composition. In practice, it is usually more efficient to describe certain features of structure and composition coupled with a description of the significant features of the method of fabrication plus a couple of significant properties which may reveal whether almost all important aspects of structure and composition have been reproduced.

The Panel on Characterization of Polycrystals has concerned itself with the useful description of the structure and composition of the polycrystalline and multiphase materials of engineering.

The major objectives of this study were:

1. To list certain descriptive facts about materials which are helpful in permitting one experimenter to reproduce the material of another one.

2. To present a general characterization matrix, listing the major features of structure and composition which should be considered for determination when characterizing a polycrystalline material. A brief discussion of each of these features follows the matrix proper.

3. To survey our current ability to measure the important property controlling features. Most of the comments appear in the narrative discussion of the characterization matrix.

4. To point out those areas where further work, or further improvement in techniques would be advantageous. These opportunities are summarized under recommendations.

5. To call attention to the need, at least in published scientific work, for a sufficiently complete characterization of the material being studied to permit the investigation to be duplicated by another worker.

## B. MATERIAL CATEGORIES

Since this report is concerned with polycrystalline materials in general, it is desirable to develop a method whereby any polycrystalline material may be described. To accomplish this end, it is desirable to first categorize the materials of concern as follows:

1. Elemental Pure Materials
2. Single-phase Multicomponent Metals
3. Nearly Pure Elemental Materials
4. Multiphase Metals (including composites)
5. Single-phase Ceramics Nonmetallic Inorganic Materials
6. Multiphase Ceramics Nonmetallic Inorganic Materials

## C. DESCRIPTIVE MATERIAL FACTS

As will be seen in the characterization matrix to follow, a complete characterization of a material at this point will, in time, at best, be extremely time-consuming and probably very costly. It is, then, an ideal situation which we can strive for over a period of years and, hopefully, eventually complete for materials of interest. In the meantime, the matrix given is primarily to guide us in the direction of the important parameters that should be known about a given material.

In practice, there are limitations in time and cost on how thoroughly we can characterize the composition and structure of a material. If we could define all of those things that might be desired, there are definite limitations in our ability to relate properties to structure. There are also limitations of our abilities to synthesize materials having specific compositions and structures, even though they have been thoroughly described.

The structure and chemical composition are controlled entirely by the specimen history - the nature and composition of the starting material, the degree of purification or extent of contamination accomplished in processing, and the atom and crystallographic arrangements which have resulted from the mechanical and thermal treatments to which it has been subjected.

If all steps of processing are under sufficiently excellent control, a given material can be reproduced by repeating the same processing steps on the same raw material. Indeed, a description of the details of processing is the conventional way of describing many materials.

This approach to the characterization of a material suffers from two major deficiencies: (1) Processes are not under complete control and commonly some supplementary characterization of structure and properties is necessary: a grain size or a carbon content; (2) In the absence of characterization, composition and purity, there is no opportunity to explicitly connect processing to properties through the connecting link of structure and composition.

From a practical viewpoint, it would then seem advisable to include in a characterization, certain descriptive facts that, at least for the time being, will be valuable in the understanding of that material. So then, a second item of characterization would be as follows:

1. Description of Material

    1.1 Nominal composition of the material (e.g., 18-8 stainless steel).

    1.2 The trade name, manufacturer, code number, variety, lot number, etc., if commercially obtained.

    1.3 Similar information about the raw material if made in the laboratory.

    1.4* Significant physical and mechanical properties:

        (1) Resistivity for a semiconductor

        (2) Ductility

        (3) Magnetic permeability

        (4) Yield strength (or presence of a yield point)

        (5) Resistivity ratio at liquid helium temperature for a zone-refined metal

        (6) Thermal expansion

2. Sample History

    2.1 Method of preparation -- cast, extruded, sintered, and times, temperatures, etc., which were used.

    2.2 A description of containers, environment, and other factors which might contribute to contamination.

    2.3 A description of subsequent thermal, mechanical, chemical treatments.

    2.4 A description of the method of final shaping (grinding, cutting, polishing, etc.).

    2.5 Size - shape - original piece or starting material.

    2.6 Sampling technique.

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*These properties are used in addition to other information on a given material, since that information will usually be found lacking in many respects.

3. Structure and Temperature Sensitive Characteristics (sufficient information to indicate whether a structure is stable or metastable with respect to its environment).

   3. 1 Phase stability.

   3. 2 Time dependent distribution.

   3. 3 Temperature dependent distribution.

   3. 4 Environmental dependence of distribution.

## D. CHARACTERIZATION MATRIX

When the category of a material is defined and the descriptive information recorded, we then have the task of characterization. This is primarily concerned with the structure and defects in the structure. It is felt that any polycrystalline inorganic material can be defined by the following matrix, including glasses and amorphous structures.

Only those parts of the matrix will be used that pertain directly to a given material under consideration. Also, it is not implied that a large amount of information need be supplied. The main purposes for using a matrix are to ascertain if (1) enough information is available on a given material to allow research results to be considered valid, (2) to use as a checklist to ascertain the characterization that may be necessary for a given type of experiment, and (3) to document a given research material so that future investigators can benefit from any work on a given material and as work continues over a period of years, a material will be better understood.

It is hoped that some standard method of reporting characterization in publications and reports will evolve so that the maximum use can be made of any characterization effort. It is fully realized that the amount of characterization in various research efforts will vary widely, but that a standard format for reporting the information would be valuable in comparing different sets of data. The accompanying characterizations, although far from complete, will serve to demonstrate the use of the matrix.

The analytical technique used for a given piece of information is important, particularly when more than one method may be used to derive certain information. If nonstandard equipment is used, it should be described thoroughly in a report so that its merits can be evaluated by readers.

## GENERAL CHARACTERIZATION MATRIX

| | | | Analytical Techniques and Equipment | |
|---|---|---|---|---|
| **1.** | **Geometrical Factors** | | | |
| **1.1** | **Grains** | | | |
| | 1.1.1 | Composition, Volume Percent and Structure | | |
| | 1.1.2 | Size & Size Distribution | | |
| | 1.1.3 | Shape & Shape Distribution (including connectivity) | | |
| | 1.1.4 | Relative Orientation | | |
| | 1.1.5 | Special Boundary Configurations | | |
| | 1.1.6 | Internal Strain | | |
| **1.2** | **Second Phases*** | | | |
| | 1.2.1 | Size & Size Distribution | | |
| | 1.2.2 | Composition, Volume Percent and Structure | | |
| | 1.2.3 | Shape & Shape Distribution (Connectivity) | | |
| | 1.2.4 | Relative Orientation | | |
| | 1.2.5 | Special Boundary Configurations | | |
| | 1.2.6 | Internal Strain | | |
| | 1.2.7 | Distribution in Structure | | |
| **1.3** | **Pores**** | | | |
| | 1.3.1 | Size & Size Distribution | | |
| | 1.3.2 | Gas Phase Character | | |
| | 1.3.3 | Shape & Shape Distribution (Connectivity) | | |
| | 1.3.4 | Relative Orientation | | |
| | 1.3.5 | Special Boundary Configurations | | |
| | 1.3.6 | Distribution in Structure | | |
| **1.4** | **Domains (Magnetic, Ferroelectric, Order) (Ferroelastic)** | | | |
| | 1.4.1 | Size & Size Distribution | | |
| | 1.4.2 | Composition, Volume Percent and Structure | | |
| | 1.4.3 | Shape & Shape Distribution (Connectivity) | | |
| | 1.4.4 | Relative Orientation | | |
| | 1.4.5 | Special Boundary Configurations | | |
| | 1.4.6 | Internal Strain | | |

\*   Includes glassy or amorphous "phases"

\*\*  Includes voids, microcracks, cracks

| | Analytical Techniques and Equipment | |
|---|---|---|
| **2. Impurities and Minor Alloying Additions** | | |
| 2.1 Chemical (and structural) Identifications* | | |
| 2.2 Crystallographic Locations | | |
| 2.3 Defect Sites | | |
| 2.4 Clustering / ordering | | |
| 2.5 Distribution within grains | | |
| 2.6 Concentration or denudation at grain or interphase boundaries | | |
| 2.7 Partitioning between phases | | |
| 2.8 Surfaces | | |
| **3. Surface** | | |
| 3.1 Topography (including defect structure of active sites) | | |
| 3.2 Subsurface phenomena | | |
| 3.3 State of strain | | |
| **4. Dislocations** | | |
| 4.1 Substructure | | |
| 4.2 Density | | |
| 4.3 Type | | |
| **5. Solutions** | | |
| 5.1 Crystallographic locations including site occupancy of multivalent atoms | | |
| 5.2 Relative distribution of solutes | | |
| 5.2.1 Defect sites | | |
| 5.2.2 Clustering | | |
| 5.2.3 Ordering | | |
| 5.2.4 Within grains | | |
| 5.2.5 Grain boundaries | | |
| 5.2.6 Surfaces | | |
| 5.2.7 Between phases | | |
| 5.3 Nature of phase interface | | |
| **6. Compounds** | | |
| 6.1 Phase stability | | |
| 6.1.1 Stoichiometry | | |
| 6.1.2 Variation (distribution) of stoichiometry** | | |
| 6.2 Valence state | | |

\* Includes valence state
\*\* Similar factors to 2.5, 2.6, 2.8

Matrix Discussion

It is understood that this matrix is a starting point toward characte-ization and will be extended or modified as the need arises. It certainly may be the case that knowledge of what parameters are important is not really evident at this time.

The following discussion of a few segments of the matrix is aimed at being of assistance in clarifying the use of the matrix. Some of the more difficult ones have been selected.

## 1. Geometrical Factors

The size, shape, arrangement, and orientation of the phases and crystalline grains in polycrystalline multiphase materials is an important aspect of structure. The objective of this section of the characterization matrix is to call attention to the chief geometrical features of this kind which are determinable, at least in principle, and to comment briefly on their importance, the availability of methods for determining these features, and the needs for new techniques, or even new theoretical methods of study.

A grain is a crystallographic domain of single orientation and approximately uniform composition. In an ideal single-phase polycrystal it will be surrounded by other grains of different orientation and identical composition. In a multiphase material there will be grains in each phase, and contacts between grains of different phases.

There are ambiguities in terminology: Commonly, grains are not perfect crystals; their dislocations may be arranged in walls to produce a substructure of "sub-grains." Commonly, very small particles of second phase, dispersed in a coarser grained matrix are called "inclusions." Higher power examination might disclose these inclusions to be single grains, or polycrystalline.

## 1.1 Grains

### 1.1.2 Grain Size and Grain Size Distribution

Consider a single-phase polycrystalline solid divided into a series of

domains which fill space. If the cells are of nearly uniform size, and equiaxed, the average diameter of a cell will specify the grain structure of the material, and this is the parameter almost universally used. It may be determined on a polished surface by a variety of counting and measuring techniques which are satisfactorily described in the literature.

For industrial, and control purposes, it is common to determine grain size by visual comparison with standard figures - either representative photomicrographs or hexagonal arrays, and to express the grain size in arbitrary numbers (e.g., ASTM grain size 4), which are defined by published charts.

The above discussion assumes all grains are the same size and shape. Even if this were true in the three-dimensional array, the grains would appear to be of different sizes in any plane section cut through the specimen. By measuring the size of many individual grains, it is possible to construct an apparent size distribution curve from the two-dimensional appearance of a polished section, and by analytical techniques to deduce approximately from this the distribution of sizes in three dimensions. Two cases may be considered:

a)   The spread in sizes is normal; the maximum grain diameter is not much more than 2X the average grain diameter. Such a structure can usually be well characterized by the statement of an average grain diameter.

b)   Duplex grain sizes exist - the maximum grain diameter is many times the average grain diameter - usually as a consequence of secondary recrystallization or exaggerated grain growth. In these cases it is worthwhile reporting at least the average grain size of each group of grains, and the volume fraction of coarse and fine grains.

Substructure: If veining or dislocation arrays exist in the major grains, it may be possible to also report a grain size for the sub-grain structure.

Photomicrographs: The difficulty of a complete analytical state-
ment of grain size and grain size distribution is sufficiently great that
it is almost always desirable to present a photomicrograph of the structure
in question.

Preparation of Section for Examination: The grain size and grain
size distribution (as well as most of the other geometrical parameters
discussed below) may vary tremendously from point to point in a speci-
men. This is particularly true in castings, and also in ceramics where
the structure on the surface exposed during firing is commonly greatly
different from the surface structure. To obtain definitive information
about grain size and grain size distribution, it is imperative that these
facts be taken into consideration.

In a casting, the distribution of grain size and grain shape over the
whole piece should be determined.

In a ceramic and metal, the section should be taken at a depth of at
least 10-20 grain diameters below the fired surface, unless surface
structures specifically are being investigated.

1.1.3 Grain Boundary Configuration

In an idealized polycrystalline array, the grain boundary configuration
is controlled by surface tension forces, and all grain boundaries will
have approximately equal surface tensions. There is a topological rule
which states that in two dimensions, not more than three grain boundaries
intersect at a point and that the three boundaries will make angles of 120°
with each other if they all have equal surface energies. In three dimen-
sions, two grains will meet along a surface to form a boundary, three
boundaries may meet along a line (the point seen in two dimensions), and
four grains will meet at a point (rarely seen on a plane section). These
are the typical structures of a foam.

Marked deviations from a foam cell structure are indicative of unusual
features of the structure, and should be reported even if they are not
interpretable. If an appreciable number of grain boundaries intersect at

angles strongly deviating from 120°, it is probably indicative of:

a) the presence of boundaries of widely differing energies (e.g., some very low-angle, low-surface tension boundaries present) or

b) the presence of a liquid phase along the grain boundaries at the temperature at which the grains were formed.

Again, the presentation of a well-prepared photomicrograph is most instructive in helping define the structure.

Grain Boundary Shape: Given boundaries in an ideal single-phase substance will be smoothly curved as they pass from intersection to intersection. The presence of cusps on the boundaries are indicative of boundary movement inhibiting inclusions which may, however, not be apparent with the specimen preparation conditions and at the magnification used for examination. Their presence should be noted.

Grain Shape and Shape Distribution: In an idealized grain structure in a polycrystalline array, all the grains are more or less equiaxed. As a result of unusual growth conditions, or because of mechanical deformation, the grain shape may be far from equiaxed. The detection of such structures is commonly made by the preparation of polished sections in three orthogonal directions across the section. From these the approximate shape of the grains can be deduced (disks, filaments, sheets, etc.) and by measurements on the plane surfaces, some estimate of the length to diameter ratio or other important ratios can be made.

At the present time, little attempt is made in the literature to quantitatively relate these aspects of grain shape and shape distribution to properties. Two specific classes of material require special comment:

a) Heavily Cold-Drawn Wires: Heavily cold-drawn wire has a fibrous structure with very high strength being frequently associated with it. Relatively little work has been done to describe the structure of such wires in detail or to relate the structure to properties. There is a great opportunity to improve our ability to describe the structure of cold-worked wires.

b) <u>Cast Structures</u>: Cast structures of both simple and complex shape will have grain structures which vary markedly from point to point in the specimen. In such specimens, it is imperative to present a description of the grain size, shape, and shape distribution over the whole specimen, usually as viewed at a magnification which will permit the structure to be viewed in the context of the shape and probable heat flow paths in the specimen.

### 1.1.4 Relative Orientation of Grains

In the ideal polycrystal the orientation of the grains and the positions of the grain boundaries between them are completely random. For a variety of reasons, there may be a preferred orientation of the grains. Such preferred orientations have been studied in detail in a number of cold-worked and also annealed metals, and quite powerful techniques have been developed for determining and describing the nature of the preferred orientation which exists.

The complete description of the relative orientation of two grains and the position of a planar boundary between them requires five parameters (e.g., the tilt axis, the angle of tilt, the rotation axis, the angle of rotation, and the indices in one crystal of the plane corresponding to the grain boundary).

In general, no such detailed descriptions of orientation are presented. By available and commonly used "x-ray pole-figures" techniques, the intensity or concentration of poles of certain representative planes are presented on a stereographic projection in terms of the ratio of the observed concentration to that which would be observed in a truly random specimen.

Acceptable automatic techniques for such determinations are available.

The only difficulties arise in very coarse grained specimens and the determination is less important in those.

### 1.1.5 Special Boundary Configurations of Grains

A host of special grain boundary configurations may be observed and a

number have been referred to above. The special boundaries associated with mechanical twins and with annealing twins in face-centered cubic metals are extensively discussed in the literature and are primarily of research interest. Special boundaries associated with ferroelectric and ferromagnetic domains are discussed below.

### 1.1.6 Internal Strain

Internal elastic strains exist in many substances for a variety of causes. They are of great importance because the associated residual stress may most markedly influence the strength of the material. In single-phase polycrystalline materials, the most common sources are cooling stresses and anisotropy in the coefficient of expansion of the grains in non-cubic materials. Stresses from this latter source may be computed with reasonable precision. In glass, the magnitude and distribution of residual stresses can be determined quite well by photoelastic measurements in polarized light.

In metals and most ceramics, there is no experimental technique for explicitly determining the magnitude of the stress at a predetermined point in the specimen. The development of such techniques would be of great value.

### 1.2 Second Phases

Most materials have second phases present in large or small amounts and the analytical description of multiphase structures may be very difficult.

### 1.2.1 Size, Size Distribution and Amount of Second Phase

If the second phase is simple in shape, of reasonable size, and uniformly distributed through the matrix; the size of the particles, their size distribution, and the volume fraction present can be determined and described by conventional microscopic techniques.

In many commercial alloys (e.g., high speed steels, and turbine bucket alloys), the microstructure is so complex that a complete description of it is rarely attempted.

### 1.2.2 Composition and Structure of Second Phases

At sizes of several microns and above, current electron beam micro-probe, and selected area electron diffraction techniques permit the identification of the composition and structure of second phases quite satisfactorily. A variety of chemical, microscopic and x-ray techniques can be used in special cases.

Improvement of the resolving power of these tools by an order of magnitude, and extension of the ability to detect the light elements would be of tremendous value in permitting the description of fine structures.

### 1.2.3 Shape and Shape Distribution of Second Phases; Connectivity of Second Phases

Descriptive phrases are commonly used for many precipitates - needle-like; plate-like; lamellar; etc., and certain two-phase aggregates, notably pearlite in steels, have had names assigned to them. In most cases, little quantitative attempt is made to define the shape or shape distribution of second phases.

In filamentary reinforced composites, it is recognized that the length-to-diameter ratio of the individual filament is important and it is commonly reported.

In synthetic dispersions, the size and size distribution of the dispersed phase (e.g., thoria in TD nickel) is difficult to determine, and its stability with time is known to be important. Improved methods of examination should be developed.

The second phase in a material is commonly taken to be the discontinuous one regardless of whether its volume fraction is more or less than 50%. In some systems, there may be two or more interpenetrating continuous phases. There may then be a desire to describe the connectivity of the two phases and there are few straightforward methods of doing this.

Many of the phase-separable glasses, where the phase separation occurs by spinoidal decomposition, show two such interconnected phases. The interconnectivity may be demonstrated by the ability to dissolve one

phase out completely with a given reagent. In these glasses, the scale of the phase separation may be sufficiently small ( < 100 Å) that the revelation of the two phase structure is a problem itself, and the demonstration of connectivity by direct microscopic examination is exceedingly difficult.

Both topological studies to permit simpler description of the connectivity of phases, and improved techniques to display the interconnection are needed.

### 1.2.4 Relative Orientation of Phases

Special orientations may exist between phases in solids because one phase was deposited and grew epitaxially upon the second, or as the result of a topotactical reaction. The most studied of these are the "Widmanstätten" structures which occur in meteorites and in many alloys and ceramics. If the precipitate and matrix structure is coarse, the orientation relationships can be determined straightforwardly by combined microscopy and x-ray orientation techniques. On a smaller scale, etch figures have been used. The determination is rarely a routine one, and the determination of the relative orientation of the two phases may call for great ingenuity on the part of the experimentalist. The need for such determinations is sufficiently small. However, great effort to develop much improved techniques is not warranted.

### 1.2.5 Special Boundary Configurations

Most of the comments under 1.2.4 apply.

### 1.2.6 Internal Strain

The comments on this topic under 1.1.6 apply.

### 1.2.7 Distribution in the Structure

In alloys and probably in ceramics, the distribution of small amounts of second phase in the structure is of very great importance. Commonly, a second phase will be nucleated more readily at the grain boundary and second phases are commonly found at those sites.

If the interphase boundary energy is less than half the grain boundary energy of the major phase, the second phase will tend to be distributed as

a continuous film along the grain boundaries of the major phase. This m...
be good (as cobalt in cemented carbides) or bad (as certain sulfides in
steel, or bismuth in copper). In any case, the phenomenon may usually
be observed directly, and it commonly has a profound impact upon
properties.

The distribution of second phases (inclusions) in the structure, along
with the size and number of the particles, is a commonly carried out
control observation on commercial materials. Under these circumstanc... -
the previously identified inclusions can frequently be identified by their
morphology, color or etching characteristics, with their amount and
character being classified by comparison with standard charts showing
the inclusions. It is common to examine the specimen first in the unetch...
condit'on to see the number and size of the inclusions, particularly if they
have different color or reflectivity than the matrix. Their location in the
structure is then identified by reexamination of the same or similar field,
etched to reveal the matrix grain structure.

## 1.3 Pores, Microcracks, etc.

Strictly speaking, pores and cracks are second phases, and most of
the comments made above with regard to second phases and their de-
scription apply equally well to the examination of pores.

### 1.3.1 Pore Size, Size Distribution and Volume Percent in the Structure

The total volume of pores or microcracks in a specimen can readily be
determined by comparing the apparent density with the true density.

Pore, and crack size, and distribution are, in principle, readily de-
termined by microscopic examination of polished sections. In practice
this is most difficult because of the likelihood of enlarging the pores or
cracks in the polishing operation, or even of creating new pores by pulling
out grains.

In very porous materials (lightly sintered powders), it is substantially
impossible to reveal the pore structure with precision in most materials.

The development of improved impregnation or polishing techniques would be very valuable.

For cracks and large flaws which intersect the surface of specimens, a number of detection techniques have been worked out which depend upon the ability of the crack to take up a liquid by capillarity.

In solid metals, cracks and large voids are routinely detected non-destructively, by radiography, or reflection of sonic impulses.

### 1.3.2 Identity of Gas in Closed Pores

Pores in materials may have a variety of different gases in them. One can conceive of circumstances where part of the pores would have one gas and part of the pores another gas. There are no routine methods for determining the gas in pores. Fracture, or grinding of the specimen in a vacuum, and identification of the gas released in a mass spectrometer are the commonly used techniques.

### 1.3.3 Shape and Shape Distribution of Pores

Total porosity can be readily determined by comparing apparent and theoretical density, and porosity which connects with the surface by determining the amount of a liquid which can be absorbed.

As mentioned in 1.2.3, there are no simple schemes for explicitly describing in detail the over-all connectivity of porosity.

Crack shapes can usually be described qualitatively and shown clearly in a photomicrograph.

### 1.3.5. Special Boundary Configurations

The shape of pores, and whether particular crystallographic faces are exposed in them has been little studied but could be studied by existing techniques. Fractography, where the crack runs through the pore, is probably more useful than conventional polishing techniques because of less distortion of the pore.

### 1.3.6. Distribution in the Structure

The location of cracks and pores, with respect to grain boundaries and inclusions, is of the very greatest importance in diagnosing the mechanism

of fracture or corrosion and in studies of the sintering process. In most cases, conventional metallographic techniques will let the observation be made. In all too many cases, the important observation is not made.

## 1.4 Domains

### 1.4.1 - 1.4.3 - Domain Size, Shape, and Walls

The domains found in polycrystalline materials are essentially the same types as found in the corresponding single crystals; i.e., ferromagnetic domains, ferroelectric domains, and order domains (of which the Jahn-Teller domains are a special case).

Ferromagnetic domains are either of the same size as the crystallographic domain (grain) or they are smaller; in the first case one speaks of single domain grains, in the second case of multidomain grains. However, occasionally domains are found which extend over several grains, probably if the grains in question are nearly parallel. The domain structure is of great importance for the properties of a polycrystalline ferromagnetic material. As compared with the single crystal, the geometry of the domains in polycrystals is affected (and complicated) by the following factors: (1) the presence of grain boundaries which in most cases also represent domain boundaries; (2) pores and microcracks which are common in sintered materials; (3) internal stresses due to thermal expansion anisotropy in non-cubic materials, dislocations, point defects, and magnetostriction; (4) internal magnetic fields due to the interfacial divergence of the magnetization vector (= free magnetic charges) at all boundaries which are not traversed in a symmetrical head and tail fashion; i.e., especially at all grain boundaries. Of greatest interest for the characterization of a material are the domain walls which have to be specified in their physical character (180° wall, 90° wall, etc.) as well as in their area (span) and density.

The methods to determine 1.4.1 through 1.4.3 are: (a) the Bitter method using colloidal magnetite in conjunction with a microscope or electron microscope; (b) magneto-optical methods: Kerr method in

reflection, and Faraday method in transmission; (c) electron beam techniques: Lorentz microscopy, shadow techniques, reflection (mirror) microscope, transmission microscopy; and (d) Hall probe techniques.

In ferroelectric polycrystalline materials, especially $BaTiO_3$, the most useful tools to measure size, shape, and nature of domains are the microscope and the electron microscope in conjunction with a special etching technique: It has been found that the positive end of a c-domain etches much faster than the negative end; this gives invaluable aid in deciphering the otherwise very complex domain structures.

Order domains are measured by x-ray or electron diffraction. Superstructure line techniques are limited by the resolution limits of these techniques (see chart in Section E); Jahn-Teller domains; i.e., areas of common tetragonal axis in otherwise cubic crystals (due to the Jahn-Teller effect of certain ions) can be measured in size by Fourier analysis of x-ray line broadening.

### 1.4.4 Preferred Orientation of Domains

In unpoled ferromagnetic and ferroelectric materials of non-cubic symmetry, preferred orientation of domains can be measured by x-ray methods. The magnetic or ferroelectric hysteresis curve measured along different directions also gives information about preferred domain orientation.

### 1.4.5 Special Domain Configurations

In special cases, the definition of domains as areas of homogeneous magnetization M breaks down. This happens when the crystal anisotropy constant, $K_1$, becomes zero (as function of either temperature or composition) and, simultaneously, the magnetostrictive constant, $\lambda$, is also almost zero. In this case the domain wall becomes very thick and the grains consist practically only of "walls," in which the magnetization vector has a continuously changing direction. In this case the methods to delineate domain structure by making the domain walls visible, have negative results.

5. Solutions

5.1 Crystallographic Locations

Solute atoms may occupy either substitutional or interstitial sites. The size of the solute atom (or ion) relative to the size of the solvent atoms is the major factor determining whether a solution is substitutional or interstitial (unless compound formation occurs).

For an atom to be interstitial, it must be small enough to fit into the "holes" in the lattice. Thus, it is only the smaller atoms, such as hydrogen, boron, carbon, nitrogen, and oxygen, all of which have atom radii less than 1Å, which are likely to form interstitial solutions. The largest "hole" is not necessarily the site of the interstitial atom, however. For example, in body-centered cubic iron, carbon is thought to occupy the 0 0 1/2 positions rather than the larger 1/2 1/4 0 positions.

In solid solutions of the simpler structures, the atomic sites in the lattice are equivalent and solute atoms substitute on any sites, although some deviations from randomness (ordering or clustering) may be observed. When a solute dissolves in a compound, it may substitute on certain sites of one of the atomic species in the compound.

X-ray or neutron diffraction techniques are generally used to study solid solutions. Whether an element is substitutional or interstitial can often be inferred from the known atomic radius and the lattice parameters of the solution. Further indications can be obtained from the change of lattice parameter with solute content since interstitial elements always expand the lattice, whereas substitutional elements may expand or contract the lattice. A comparison of the measured density and the density calculated from the composition and lattice parameter will also distinguish between substitutional and interstitial solutions.

Determination of the location of interstitial atoms is a very difficult procedure. Information may be obtained from the change in shape of various x-ray reflections with composition. Internal friction techniques

may also be useful. With substitutional solutions, the location and especially the intensity of the x-ray reflections serve to locate the position of the atoms. While in theory these may be straightforward procedures, they often present difficult experimental problems. In some cases, the difference in scattering factor between the solvent and solute atoms may not be great enough to give rise to appreciable intensity differences, or the scattering from low atomic number elements may be too weak and neutron diffraction procedures must be substituted for x-ray diffraction.

## 5.2 Relative Distribution of Solute

### 5.2.1 Defect Sites

When either point or line defects are present in a crystal, there will be a strain field associated with the defects which can interact with solute elements. Thus, interstitial atoms and substitutional atoms which expand the lattice reduce the total energy by segregating in the region of the tensile stress field of defects, whereas atoms which contract the lattice may segregate to the regions of compressive stress. Limitations on this are placed by the ability of the atom to diffuse to the defect at the lower temperatures, and by thermal fluctuations which will tear the defect away from the atom at higher temperatures.

Measurement of this segregation is extremely difficult. Often manifestations of segregations can be seen, such as "doping" of silicon by copper to reveal etch pits at dislocations, or strain aging of metals. A measure of the migration of the solute atoms to the defects can be obtained by observing changes in some mechanical or physical property. The best one can do to quantitatively determine the amount of segregation is to assume some model for the effect being measured, and attempt to calculate the amount of segregation that would be required to give rise to an effect of the observed magnitude. This procedure does not definitely locate the solute atom and, of course, is open to many errors.

### 5.2.2 Clustering

Atoms that are distributed on normal lattice sites may or may not be randomly distributed. If atoms of the same kind prefer to occupy sites near each other, clustering is said to occur. Clustering may be found in a solution at high temperatures in cases where precipitation or a spinoidal decomposition will occur at lower temperatures. The reverse of this is termed short range order, where atoms of opposite kinds prefer sites adjacent to each other. Short range order is particularly found at high temperature in alloys where long range ordering occurs at lower temperatures. Both short range ordering and clustering can be defined by short range order coefficients,

$$\alpha_i = 1 - \frac{P_i}{M_A}$$

where $\alpha_i$ = short range order coefficient for the $_{ith}$ shell lying a distance $r_i$ between two lattice points; $P_i$ = probability of finding an A atom at a distance $r_i$ from a B atom; and $M_A$ = atom fraction of A atoms. The values of $\alpha_i$ vary for each shell i, may be either positive or negative, and are zero for a random solution. For the first shell (i.e., nearest neighbors), positive values of $\alpha_i$ denote clustering, and negative values denote short range order.

X-ray diffraction techniques are used to study clustering and short range order. These deviations from randomness in the solid solution are determined by measurement of the intensity of diffuse scattering as a function of the Bragg angle, $\theta$, usually at low angles of $\theta$. Monochromatic radiation must be used, and corrections to the intensity made for temperature diffuse scattering and Compton modified scattering. While clustering can be distinguished from short range ordering by the shape of the intensity versus $\theta$ curve, precise determination of the short range order coefficient requires a solution of a three-dimensional Fourier series by Lipson-Beever strips or a computer. Single crystal and powder

specimens of cubic metals have been studied. Because of the complexity of the technique, it can hardly be considered a standard research procedure.

Reference:   B. F. Warren and B. L. Averbach, "The Diffuse Scattering of X-rays," Modern Research Techniques in Physical Metallurgy ASM, 1953, p. 95-130.

### 5.2.3 Ordering

Short range order has been described in 5.2.2 above. Superlattice formation or long range order is another type deviation from randomness which occurs at simple ratios of the atomic constituents. In this case, specific lattice sites are occupied by one of the atom types over relatively long distances and the other sites are occupied by the other atom type.

Long range order generally occurs below some specific critical temperature, and the degree of order increases the lower the temperature. Above the critical temperature, thermal fluctuations destroy the long range order, but short range order will persist. In short range order, the emphasis is on the nearest neighbors to an atom, whereas, in long range order the important feature is that certain sites in each unit cell are occupied by the same atom.

As an example, in the alloy $AuCu_3$ in the disordered state, the gold and copper atoms occupy more or less random sites on a face-centered cubic lattice. In the ordered state, the gold atoms are at cube corners and the copper at face centers.

In an ordered structure, the regularity of spacing of the ordered atoms will give rise to new x-ray reflections ("superlattice lines") at the appropriate Bragg angles. The intensity of these superlattice lines is governed by the degree of order in the alloy, as well as the difference in scattering factors of the elements comprising the structure. For this reason, long range order is difficult to detect by x ray in such alloys as CuZn, since the scattering factors of Cu and Zn are similar and neutron diffraction may be advantageous. Long range order can also be detected

by an anomalous increase in specific heat at the critical temperature, by a decrease in the electrical resistivity.

References: C. S. Barret, "Structure of Metals" 2nd Ed, Chapter VII, McGraw-Hill, New York, 1952.

A. Taylor, "X-ray Metallography" Chapter 11, John Wiley & Sons, New York, 1961.

### 5.2.4 Within Grains

### 5.2.5 Grain Boundaries

Various types of nonuniform distribution of solute elements within grains have been described in 5.2.1, 5.2.2, and 5.2.3, above. In addition, there may arise a difference in composition between grain boundaries. Evidence of such segregation to grain boundaries can be found in intergranular failures of metals, often accompanied by precipitation of a second phase, but sometimes in the absence of any such precipitate. Hotshortness, or the lowered melting point of the grain boundary region, and preferential corrosion of grain boundaries have also been attributed to grain boundary segregation.

The reasons for segregation to grain boundaries are the same as for segregation to defects, primarily to relieve strain misfit caused by a difference in size of the atoms. This would be expected since low angle boundaries consist of a row of dislocations, and even high angle boundaries can be considered as a complex array of dislocations. Segregation to grain boundaries generally increases the greater the size difference between the solute and solvent atoms, and decreases the higher the annealing temperature.

Quantitative determination of grain boundary segregation is difficult. One reason for this is a lack of precise characterization of grain boundaries themselves; i. e. , what are the locations of the solvent atoms in the grain boundary, and what "width" should be associated with a grain boundary. Indirect methods such as determining the amount of the solute to cause intergranular failure or internal oxidation can be used.

Autoradiography has also been used to show grain boundary segregation but with limited success. Electron probe microanalyses would appear to be the most direct method to obtain quantitative information. The major limitation is the size of the beam which is large compared to the width of the grain boundary.

Reference: R. W. Cahn, "Grain Boundaries, Substructures and Impurities," Impurities and Imperfections, American Society for Metals, Cleveland, 1955, p. 40-83.

### 5.2.6 Surfaces

Surfaces of materials often have a composition different from the bulk material. These composition differences may arise by the selective depletion of a solute into the atmosphere, or addition of atoms to the surface region or at the very surface.

Examples of depletion of a solute can be seen in the dezincification of brass or the decarburization of steel. These may be rather gross effects, and can often be seen visually. Optical microscopy may suffice to determine the size of the depleted zone. Electron probe microanalysis can be used to study the concentration at the surface where the depleted element has a sufficiently high atomic number.

When the surface of a material is oxidized or otherwise alloyed by the environment, standard metallographic techniques may, in some cases, suffice to determine the extent of surface penetration. Electron diffraction techniques can be used to determine the structures of surface layers such as oxides at thicknesses of less than 100Å. Even thinner layers can be studied by specialized x-ray diffraction methods. For determining the amount of light elements such as carbon and oxygen present at the surface of materials, activation analysis is now being used.

### 5.2.7 Between Phases

Impurity elements will distribute themselves between two phases in a structure according to an equilibrium distribution ratio given by the phase diagram. If the appropriate phase diagram is not known, this information

can often be obtained directly. For many systems, electron probe micro
analysis will provide the necessary information. Limitations exist for
the lower atomic number elements which cannot be detected, and for
structures where the dispersion of the phases is so fine that individual
particles of each phase are finer than the beam.

Another technique that has been used quite successfully to determine
the structure and composition of second phases, such as carbides or non-
metallic inclusions, is x-ray and chemical analysis of electrolytically
extracted particles. One difficulty is finding an electrolyte and co. "tion..
which will dissolve the matrix and not decompose the particles. For very
fine particles, the structure can be determined from extraction replicas
by electron diffraction.

## 5.3 Nature of Phase Interface

The interface between two phases in a structure may be considered as
a grain boundary, with the exception that the structure and composition is
different on either side of the boundary. In many cases, this boundary is
incoherent with a random orientation difference between the two phases.
In other cases, when one phase has precipitated within the other, there
may be an orientation relationship between the phases, and the boundary
may even be coherent. This coherency will occur in the early stages of
precipitation, before the actual formation of well-defined second phase,
and where there is a matching of atom spacings across the interface.
The strain arising from this forced registry of the atom planes across
the interface may give use to etching effects in optical microscopy, and
can be seen by contrast effects around the precipitates in transmission
electron microscopy.

## E. SURVEY OF ABILITY TO CHARACTERIZE

The purpose of this report is not to go into any detail in analytical techniques, but it would seem worthwhile to point out deficiencies in analytical methods and consequently define the needs for development in this area.

There are certainly advances needed in the field of analytical methods. However, there are probably both a wider variety and more powerful characterization methods available than are commonly utilized by many investigators and, in many cases, a great deal of information can be obtained by using several techniques on a given problem.

Material characterization is a field in its own right; it has its own experimental and theoretical tools which are most efficiently used by trained and experienced specialists. This has some important consequences. There might be some people who are specialists in several fields and who might be competent in material preparation, material characterization, material properties, and special material uses (devices). However, such people are exceptions; the rule is that one is a specialist in one field and a more or less well-educated layman in several others. It follows that of all people dealing with materials-developing, producing, testing, analyzing, measuring, designing, and using, those who specialize in material characterization will give the best characterization and do it most efficiently, with some reservation. A certain skill in the selection of the important parameters to be determined is required, and this skill must be exercised by the person investigating the process or a set of properties. It is therefore imperative that either an experimentalist do the characterization himself, or that he closely collaborate with an expert in characterization in studying the material being used in a given experiment. The real answer to this problem is to involve the characterization expert in the research problem as much as possible, so that he has a feel for the analytical requirements of the research.

We are saying then - with the proper people and attitude toward characterization that a much better job of characterization could be done than is normally the case. Realizing that even though proper preparation and characterization of a material for research is very time-consuming, it is nevertheless an essent.al operation in the first important step. This is not meant to imply that no group of scientists does a good job of characterization, but is rather an effort to induce everyone to improve the situation.

It would appear then that much more of the matrix can be filled out in a given case than would at first appear to be the case. This does not, however, negate the fact that serious deficiencies do exist which are of very real significance for research, as well as practical problems. One of the most perplexing areas is in improved selected area methods, particularly for the light elements. The deficiencies in our capabilities will be covered under Recommendations (Part F).

The following chart defines the various structural parameters that we are seeking knowledge about, and the analytical methods and their limitations that are presently used in studying them.

STRUCTURAL FEATURE

LIMIT OF
RESOLUTION

GRAIN SIZE

SINGLE PHASE MATERIAL

WIRE
REINFORCEMENTS

PRECIPITATES

WHISKER
REINFORCEMENTS

POROSITY

DISLOCATION CELL
STRUCTURES

SURFACE FINISH

MICROCRACKS

DISPERSED
PARTICLES

GP ZONES

VACANCY
CLUSTERS

0.1 cm

0.01 in.

0.01 cm

1 mil — 0.001 in.

$10\mu = 0.001$ cm

0.1 mil — $10^{-4}$ in.

$10^{-6}$ m $= 10^4$ Å — $1\mu = 10^{-4}$ cm

WAVELENGTH OF
VISIBLE LIGHT

1000 Å — $0.1\mu = 10^{-5}$ cm

$10^{-6}$ in.

100 Å — $0.01\mu = 10^{-6}$ cm

10 Å — $0.001\mu = 10^{-7}$ cm

1 Å — $10^{-4}\mu = 10^{-8}$ cm

CURRENT LIMITED
SELECTED AREA
MASS OR EMISSION
SPECTROSCOPY

LIMIT OF
SELECTED AREA
X-RAY METHODS

CURRENT RESOLUTION
LIMIT OF
MICROHARDNESS
MEASUREMENTS

RESOLUTION
LIMIT OF
MICROBEAM
PROBE
(COMPOSITION)

SMALLEST SPOT SIZE FOR
PARTICLE KOSSEL LINE
VISIBLE IN TECHNIQUES
NORMAL AND SELECTED
OPTICAL AREA
MICROSCOPE ELECTRON
DIFFRACTION

RESOLVING LIMIT
OF REPLICA
ELECTRON
MICROSCOPY

SMALLEST PARTICLE
VISIBLE IN
ULTRA-MICROSCOPE

RESOLUTION LIMIT
FOR "CELL SIZE" OR
"PARTICLES" IN
TRANSMISSION
ELECTRON MICROSCOPY

# F. RECOMMENDATIONS

### General

An effort needs to be made to foster characterization.   Publicity on the facts and needs of characterization will certainly help.   Meetings with this topic as a main theme are being held and will no doubt continue. Another more concrete suggestion is some type of Characterization Information Center.   Functions of this organization might be:

1. Maintain a supply of well-characterized material for investigators. These would be opportunistic materials at any given time and over a number of years.

2. Maintain information on these materials as it is generated.   The use of the material would obligate the user to supply any information generated.

3. To advise users on the techniques of characterization and where assistance might be obtained.   Hence, they would be familiar with the characterization competence of the scientific community.

4. Make recommendations as to areas of characterization that need bolstering and promising new areas as they arise.   Of course, this organization, if it had an experimental capability would be able to take a role of leadership in characterization work.

It would seem that this sort of effort falls naturally into the program now in effect at the National Bureau of Standards.   It would at least be handled in a similar manner.   An organization of this type is probably necessary to force characterizations and make inroads into the problem. The scope of NBS should be strongly expanded so it will be a source of pedigree materials and can provide a materials information function. This, no doubt is the most logical way to approach this problem

### Specific Areas of Characterization Where Improvement is Needed

1. Develop improved equipment to permit x-ray and electron diffraction studies of small selected areas ($<10\mu$ diameter).

2. Develop techniques to permit the nondestructive measurement of internal strain in materials, both on the scale of a few microns and on a scale of a few centimeters.

3. Develop improved techniques for the automatic collection of microstructural data such as grain size and the volume fraction of various phases.

4. Develop improved techniques for surface characterization.

5. Develop better understanding of the structure of heavily cold-worked metals. Improve our ability to describe this structure. At the present time the only feasible way to describe these materials is in terms of prior mechanical and thermal treatment.

6. Develop improved techniques for thinning nonmetallic (ceramic) specimens for examination by transmission electron microscopy.

7. Develop improved techniques (a millimicroprobe) for determining compositions of volumes of matter having dimensions of 100 Å or less.

8. Develop techniques for improved description of the size, shape, and degree of aggregation of powder particles. This is of great importance to sintering. (This area was not studied in detail by the Panel - we nevertheless feel it to be important.)

9. In situ measurements at high temperatures.

# APPENDIX

## 1. Important Factors in the Characterization of Specific Materials

The purpose here is to indicate those parameters of importance in characterizing a special material. It must be borne in mind that the primary function of any characterization is for research materials that have definite experiments in mind and will vary from one investigator to another. The next section will give a comparison with specific characterizations on materials that have been used in experimental programs. There will, of course, be little information on some and much more on others.

## BERYLLIUM OXIDE

### Sample History

Raw Powder — manufacturer, methods of preparation, purity, particle size distribution, etc.

Methods and Conditions of Preparation (pressure, temperature, time, atmosphere, container, etc.)

1. Calcining, pressing, extrusion, sintering, etc.
2. Hot-pressing, high pressure techniques
3. Others

Subsequent thermal, mechanical (including shaping), and chemical treatments

Storage conditions

### Significant Physical and Mechanical Properties

Elastic properties — Young's and shear moduli, Poisson's ratio, dependence on temperature

Creep properties — dependence on temperature, stress, strain rate, environment of testing; recrystallization, and grain growth under creep conditions; etc.

Fracture properties — dependence on temperature, stress rate, and environment

Thermal properties

Electric properties — d. c. and a. c. conductivity, dielectric loss, temperature, and frequency dependence

Optical properties — depending on usage of material

### General Characterization

Grain size and distribution, preferred orientation and texture

Pore size and distribution

Second phases, nature and distribution, both internal and along grain boundaries

Impurities and defects, nature and distribution, internal and near surfaces or grain boundaries. These problems are up to now little explored.

Surface characteristics, topology, grain boundary grooving, etc.

Stresses, internal and subsurface. This is also an unexplored area.

Stability, time and environment dependence of above.

## MANGANESE FERRITE

### Sample History

Raw Powder — manufacturer, methods of preparation, purity, partic
size distribution, etc.

Methods of Mixing, Calcining, Sinterin particularly the following:

1. Time and condition of ball milling

2. Time, temperature, and atmosphere of calcination

3. Pressing and sintering conditions — soaking time, temperature ar
atmosphere, heating and cooling rates

Subsequent thermal, mechanical, and chemical treatments

Storage conditions

### Significant Physical and Mechanical Properties

Elastic properties

Thermal properties

Electrical properties — d. c. and a. c. conductivity, dielectric loss,
temperature, and frequency dependence

Magnetic properties

1. Saturation magnetization, permeability, hysteresis, etc.

2. Curie temperature and inversion

3. Magnetostriction and crystalline anisotropy of grains

4. Microwave Faraday rotation

5. Ferromagnetic resonance damping, line width, temperature and
frequency dependence

6. Susceptibility dispersion

### General Characterization

Grain size and distribution, preferred orientation and/or texture

Pore size and distribution, connectivity

Second phases, nature and distribution

Site, valency and distribution of Mn, Fe, and O io· · — this encloses a
broad range of solid state physics activities

Stoichiometry — distribution of Mn, Fe, and O vacancies

Grain boundary characteristics — impurities, defects, second phases, etc

Impurities (magnetic and nonmagnetic) — valency and distribution

Stresses — internal and subsurface

Magnetic domains within grains, nature, and distribution

Dislocation structures within grains — nature and identification

Stability of above — time and environment dependence

## GLASS

Inorganic glasses present a fundamentally different problem of characterization than do crystalline materials. There is an ideal reference state of a pure stoichiometric crystal for which ideal atom positions can be described, and most real characterization can be defined in terms of deviation from this ideal. The ideal structure can be readily determined by a variety of diffraction techniques.

No such condition exists for glasses. Both chemical composition and atomic arrangement can vary over wide limits, and there is no straightforward method of determining the atomic arrangement. Because the essence of the glassy state is a lack of long range order, it is unlikely that any such explicit techniques of structure determination will be developed.

Many of the properties of a glass are defined by giving it nominal chemical composition and the manufacturer's code number. If made in the laboratory, additional information on starting materials, melting crucible, source of heat, melting atmosphere, melt size and firing time, and thermal cycle are desirable.

For special shapes, such as filaments, further information about drawing speed, orifice size, melt temperature, drawing atmosphere, and final surface protective treatment are desired. Similar information should be given for plate, rod, or other shapes.

These data on technique of preparation will define reasonably well the nature of the glass being studied, and its response to heat treatment. Once it is cooled to room temperature (or below the glass temperature $T_G$), it becomes more difficult to explicitly define the state of the glass.

It is common in glass science to speak of the "Fictive Temperature," which is really a measure of the glass density. A rapidly cooled glass will be less dense than a slowly cooled one, and in most cases will have a lower density. The temperature at which this lower density would be stable for long times is the fictive temperature. The term is generally used

qualitatively, and the concept is probably not a useful one for quantitative characterization.

In the liquid state, viscosity of glass is readily measured and is an important property. A plot of viscosity versus temperature will define with considerable precision many of the properties of a glass, including the softening point ($10^{11}$ - $10^{12}$ poises) (generally taken as $10^{7.6}$ poises for a glass of density 2.5 gms/cc), the annealing point and the strain point, and finally $T_G$, the glass transformation temperature. Methods for the determination of these properties seem well established (Morey, "Properties of Glass," Reinhold Publishing Co., 1954, p. 165).

Another important property is coefficient of expansion, and its dependence upon temperature and time. Again, acceptable methods for its determination are available. Index of refraction and birefringence give excellent indications of the density and homogeneity of glasses. Excellent methods of study are available.

All of these properties are bulk properties and are of importance in the selection of a proper glass or in its heat treatment to obtain desired properties. It would, of course, be desirable to be able to define atomic arrangement in glasses with the precision available in crystalline solids. This cannot be done. The diffraction techniques developed by Warren provide some information, but these are more properly to be considered as research techniques than as methods to be frequently used for the characterization of specific glasses. The situation is similar with respect to Mössbauer effect studies, NMR and ESR studies on certain glasses.

Chemical composition can be determined for the major elements with sufficient precision by conventional chemical techniques. Stoichiometry (oxygen to silicon ratio, for example) is of increasing interest in controlling properties - it is easily determined with satisfactory precision by gravimetric techniques.

Perhaps the problem of greatest importance is the surface structure c glasses since it controls strength. Direct microscopic observation has not been particularly useful. One of the most useful techniques in charac terizing surface structure is to measure the fracture strength at lic uid nitrogen temperature where atmospheric corrosion effects do not operate

## Phase Separation

Glasses are commonly thought to be homogeneous. There is now a great body of evidence which indicates that many glasses may contain twc or more phases, on a scale less than 100 angstroms. There is a need i? better techniques to reveal these structures. Electron microscopy replic techniques are useful down to about 50 angstroms, if suitable etching can be done. Low angle x-ray diffraction gives reasonable indication of structure. It would be most helpful to have a device like an electron-bea microprobe which would permit the determination of variations in compo- sition among light elements in dimensions of 100 angstroms or less.

## Summary

The characterization of a glass is fundamentally a different problem from the characterization of a crystalline material. For most purposes, the currently used techniques are acceptable. The development of tech- niques to reveal atom positions would be most helpful to glass research but it is not clear that they can be developed. A major possible contri- bution would be the improvement of techniques for revealing structure on the scale of 10-100 angstroms. There is a need for techniques to be able to study phase compositions and inhomogeneity of composition on the scale of 10-100 angstroms.

## 2. Sample Characterizations

In this section are shown some characterizations of specific materials on which research has been carried out. In no case is a major part of the matrix filled out, but serves to illustrate the state of the art at present.

## CHARACTERIZATION OF $Al_2O_3$
### (Polyphase Nonmetallic Inorganic Materials)

**Description of Material**

99.5% $Al_2O_3$

Al 995 Wesgo - Lot No. A449 Specimen A

467 Specimen C

**Chemical Analyses**

A semiquantitative spectrographic analysis of the test materials was made by the American Spectrographic Laboratories in San Francisco, a: the following figures represent oxides of the elements indicated.

|     | <u>A</u> | <u>C</u> |
|-----|----------|----------|
| **Al Principal Constituent** | | |
| B   | 0.04%    | 0.05%    |
| Si  | 1.75     | 2.0      |
| Fe  | 0.12     | 0.12     |
| Mg  | 0.8      | 1.0      |
| Mu  | 0.001    | 0.001    |
| Ga  | 0.04     | 0.05     |
| Ti  | 0.015    | 0.01     |
| Cu  | 0.007    | 0.005    |
| Ca  | 0.06     | 0.06     |
| Cr  | 0.001    | 0.001    |
| Ba  | 0.003    | 0.002    |

The total of impurities amounts to 2.837% and 3.299% in batch A-499 a batch 467, respectively. Since Wesgo Al 995 is nominally a 99.5% alumina body, and has been found by other investigators to contain less than one p cent of impurities, the analyses were repeated with emphasis on the silic. and magnesia content, but identical results were obtained.

**Sample History**

Isostatically pressed in rods 4" x 4" x 24" gas fired in air at 1750°C, 3 hours.

Thermal history only inferred from known characteristics of the two kilns used.

A special kiln — has a setting area of 12-18 inches — firing cycle of 24-28 hours.

C specimen kiln — large furnace setting area of 30 x 90 inches — firing cycle of 30-32 hours.

The wall thickness of the "as-fired" specimens was between 0.102 inch and 0.107 inch. No significant out-of-roundness was found. All specimens tested had smooth edges and a few specimens with chipped edges were discarded.

The grinding operation was carried out as follows. Approximately ten specimens were stacked and centerlessly ground to the final outside diameter dimension. Then each specimen was individually mounted in a special collet, faced and ground on the inside. The pebble tumbling treatment sometimes used for "deburring" of ground surfaces was not employed. The surface finish was measured with a Brush Instruments Model MS-1000 Surfindicator. The ground specimens had a finish ranging from 20 to 35 microinches. The average density of the final specimens was A = 96.75% and C = 96.90%.

## Mechanical Properties

At any given load rate specimens (C) have a fracture strength to 1400-2200 psi higher than (A).

TENSILE STRENGTH OF 99.5% ALUMINA -
INFLUENCE OF SELECTED PROCESS VARIATIONS

| Group | Tensile Strength (psi) | | |
|-------|---------------|----------------|-------------------|
|       | At 70 psi/sec | At $10^3$ psi/sec | At $3 \times 10^3$ psi/sec |
| A | 24,210± 497 (2.05%) | 26,530± 1300 (4.90%) | 29,570± 1110 (3.75%) |
| C | 26,050± 1220 (4.67%) | 28,920± 758 (2.62%) | 30,920± 1175 (3.80%) |

## GENERAL CHARACTERIZATION

### Aluminum Oxide

| 1. Geometrical Factors | | A | C | Analytical Techniques and Equipmer |
|---|---|---|---|---|
| 1.1 Grains | | | | |
| | 1.1.1 Size & Size Distribution | $26\mu$ | $23\mu$ | PM, LI |
| | 1.1.2 Composition, Volume Percent and Structure | $\alpha$ Al$_2$O$_3$ | $\alpha$ Al$_2$O$_3$ | X-ray lattice constant |
| | 1.1.3 Shape & Shape Distribution (Connectivity) | Equiax | Equiax | PM |
| | 1.1.4 Relative Orientation | Random | Random | CN |
| | 1.1.5 Special Boundary Configurations | Crystallo-graphic | Crystallo-graphic | CN |
| | 1.1.6 Internal Strain | None detected | None detected | CN |
| 1.2 Second Phases* | | | | |
| | 1.2.1 Size & Size Distribution | $1-5\mu$ | $1-5\mu$ | |
| | 1.2.3 Shape & Shape Distribution (Connectivity) | Isolated at boundaries | | |
| 1.3 Pores** | | | | |
| | 1.3.2 Composition, Volume Percent and Structure | 3.25% | 3.1% | Pycnometer |
| | 1.3.3 Shape & Shape Distribution (Connectivity) | Spheres not connected | Spheres not connected | PM thin sections |
| | 1.3.4 Relative Orientation | None | None | PM |
| 3. Surface | | | | |
| | 3.1 Topography (including defect structure of active sites) | $20-35\mu$ in. | $20-35\mu$ in. | Surfindicator |

\* Includes glassy or amorphous "phase"

\*\* Includes voids, microcracks, cracks

PM – photomicrographs
EM – electron micrograph
LI – line intercept
CN – crossed Nicols (thin section)

Transmitted Light
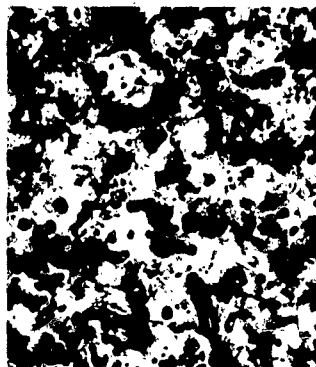
Transmitted Light
Crossed Nicol Prisms

Polished Section
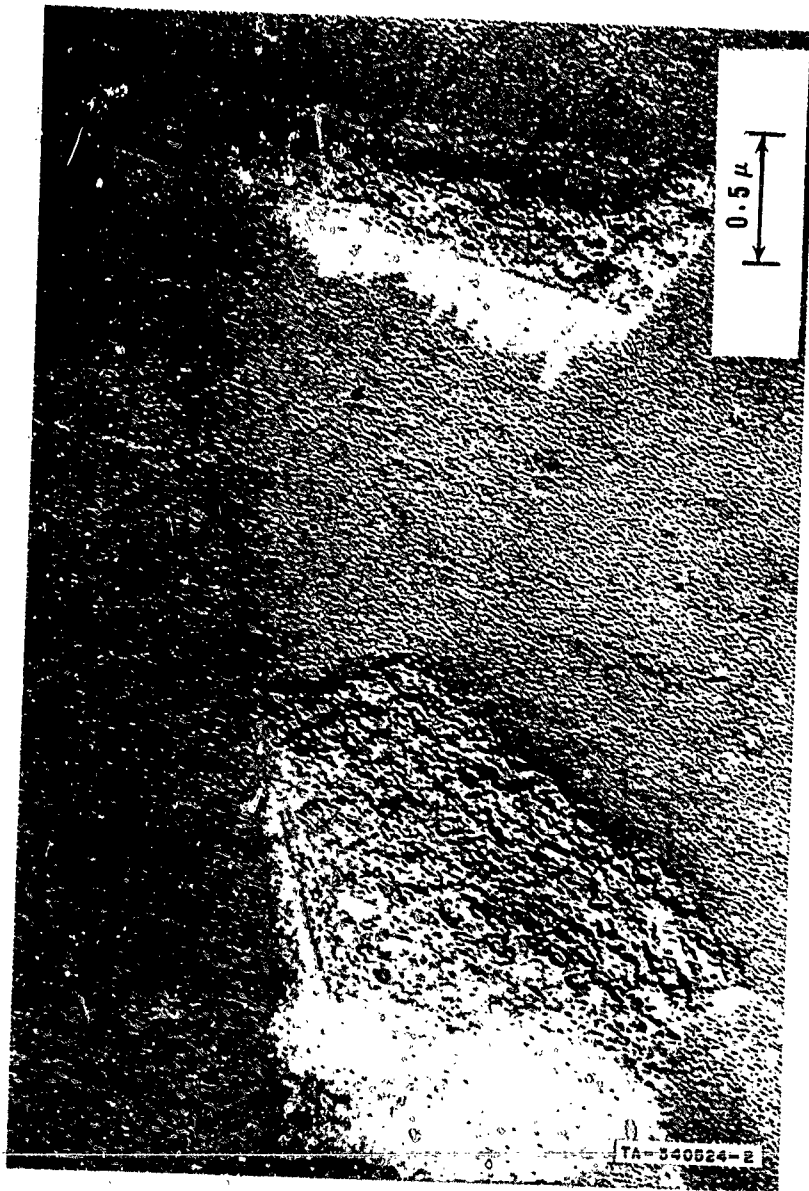
Group A

Group C

TA-340524-8

STRUCTURE OF A 99.5% ALUMINA BODY

0.5 $\mu$

TA-340524-2

$Al_2O_3$ — AD995
40,000X Replica

## CHARACTERIZATION OF A MANGANESE-ZINC-FERRITE
### (Single-Phase Nonmetallic Inorganic Material)

### Description of Material

Nominal composition: $(Mn^{++}_{0.5955} \ Zn^{++}_{0.2986} \ Fe^{++}_{0.1058}) \ Fe^{+++}_{2} \ O^{--}_{4}$

Chemical composition of prereacted raw material:

| | | |
|---|---|---|
| MnO | 17.52% b.w. |
| ZnO | 10.47 |
| $Fe_2O_3$ | 69.84 |
| $SiO_2$ | 0.12 |
| $TiO_2$ | 0.01 |
| MgO | 0.03 |
| $Na_2O$ | 0.11 |
| $K_2O$ | 0.02 |

$Al_2O_3$, CaO below 0.01% b.w.

Excess: 1.85 b.w.

### Abbreviations:

$\mu_i$       = initial permeability

$\mu_{max}$       = maximum permeability

$H_c$       = coercive force

$B_R$       = remanence

$B_M$       = maximum induction

$\mu_i 1Kcps$       = initial permeability at 1Kcps

$\dfrac{W}{V}$       = D.C. hysteresis loss

$\bar{S}_v$       = average grain boundary area

$\bar{S}_{v_{xs}}$       = average grain boundary area of cross section

$\bar{S}_{v_L}$       = average grain boundary area of transverse section

$\bar{d}$       = average intercept grain size

$d_{xs}$       = average intercept grain size of cross section

$d_L$       = average intercept grain size of transverse section

Tabulation of Some Experimental Results, Air Atmosphere, 1400°C Firing Temperature Measurements at Room Temperature

| Sample | 1. Sample 1-AH30-86 | 3-AH30-85 | 9-AH30-80 | 2. Sample 1-AH30-86T | 3-AH30-85T | 9-AH30-80T |
|---|---|---|---|---|---|---|
| $\mu_1$ | 2522 | 3080 | 2829(2) | 2464 | 3318 | 2739 |
| $\mu_{max}$ | 5043 | 6362 | 6022(2) | 4925 | 6777 | 5958 |
| $H_c$(oer) | 0.192 | | 0.144 | | 0.127 | |
| $B_R$(gauss) | 1723 | | 1354 | | 1513 | |
| $B_M$(gauss) | 4672 | | 4724 | | 4927 | |
| $\frac{W}{V}$ (ergs/cm$^3$) | 268 | | 108 | | 113 | |
| $\mu_1$1Kcps | 1956 | | 2054 | | 2387 | |
| $\bar{S}_v$(mm$^2$/mm$^3$) | 90.6±1.5(2) | | 50.4±15.6(4) | | 69.1±8.2(6) | |
| $\bar{S}_{v_{xs}}$ | 89.9 | | 53.4(2) | | 77.3(3) | |
| $\bar{S}_{v_L}$ | 91.4 | | 47.4(2) | | 60.9(3) | |
| $\bar{d}$ (microns) | 22.0±0.3(2) | | 41.8±11.9(4) | | 29.5±3.8(6) | |
| $d_{xs}$ | 22.2 | | 41.1(2) | | 25.9(3) | |
| $d_L$ | 21.9 | | 42.6(2) | | 33.1(3) | |

## Sample History

Dry-pressed.

Fired on $Al_2O_3$ plate, suspended on Pt wire in Mullite MW 30 tube.

Fired in air 1 hr. at 1400°C, cooled 30°C/min. at constant weight atmosphere.

Toroid 1-11/16" O.D., 1-1/8" I.D.

All toroids fired under these conditions tested for grain size, 1/2 of the toroids tested for permeability.

Related samples: These samples were manufactured under one of 57 different firing conditions of the same composition; altogether 114 samples.

Magnetic permeability: Initial permeability of one toroid was 2522, of the other toroid 2464; more properties in the Appendix.

Composition is stable at firing conditions (1400° in air) but becomes unstable during cooling at about 1040°C. If cooled fast enough (in this case, e.g., at 30°C/min), the metastable phase is maintained through room temperature.

# GENERAL CHARACTERIZATION

## Manganese-Zinc-Ferrite

**1. Geometrical Factors**

**1.1 Grains**

| | | |
|---|---|---|
| 1.1.1 | Composition, Volume Percent and Structure | 96.79% b. v. spinel phase lattice constant; 8.4864 A. U., line width of (751) reflection 0.52° 2θ against 0.28° theoretical, x-ray density 5.0593 gm/cm³ |
| 1.1.2 | Size & Size Distribution | 1-AH30-86 22.0 ± 0.3μ |
| 1.1.3 | Shape & Shape Distribution (including connectivity) | Average number of edges – 6 |
| 1.1.4 | Relative Orientation | No orientation texture |

**1.3 Pores**

| | | |
|---|---|---|
| 1.3.1 | Size & Size Distribution | About 2-3μ, wide spread |
| 1.3.2 | Gas Phase Character | Total volume of closed pores 3.22% b. v. |
| 1.3.3 | Shape & Shape Distribution (connectivity) | Spherical, not interconnected. Most pores are in the interior of the grains. |

**1.4 Domains (Magnetic, Ferroelectric, Order) (Ferroelastic)**

| | | |
|---|---|---|
| 1.4.1 | Size & Size Distribution | Due to the disappearing crystal anisotropy energy in this material, the domain walls are very thick and practically the whole domain (and grain) consists of domain walls. |

**2. Impurities and Minor Alloying Additions**

| | | |
|---|---|---|
| 2.3 | Defect Sites | The defects are cation vacancies, produced simultaneously with the oxidation of some of the Fe$^{++}$ to Fe$^{3+}$ and Mn$^{++}$ to Mn$^{3+}$, these vacancies are on the octahedral sites. |
| 2.4 | Clustering/ordering | If is suspected (but cannot be proven for this sample because of low concentration) that the Mn$^{3+}$ ions on the octahedral sites produce tetragonal Jahn-Teller distortions which might order into Jahn-Teller domains. |
| 2.6 | Concentration or denudation at grain or interphase boundaries | Impurities dissolved. All impurities listed under C13, perhaps with exception of the SiO$_2$ which might preferably go to the grain boundaries. |

**3. Surface**

| | | |
|---|---|---|
| 3.2 | Subsurface phenomena | Small Zn-loss during firing at the external surface of the sample (about 10 mil thick). |
| 3.3 | State of strain | Internal strain suspected due to Zn-loss at surface due to difference in lattice constant and thermal expansion coefficient. |

*Includes voids, microcracks, cracks

## CHARACTERIZATION OF ZONE REFINED IRON
### (Polycrystalline Metallic Material)

Description of Material

Made at Franklin Institute Laboratories from vacuum and arc melted iron.

Sample History

High purity iron was zone purified using the floating zone method.

1. Swaged to 0.0625 in diameter and annealed in a dynamic vacuum at 900°C.

2. Drawn to 0.031 inch diameter, cut into specimens with a 3/4 inch gage length, and hand-polished to a four zero paper finish.

3. Recrystallized in the region of 600°C for various times.

Significant Physical and Mechanical Properties

Room Temperature Flow Stress

Ratio of Ultimate Stress to Yield Stress

| Testing Temperature °K | Vacuum Melted Iron After Zone Purification |
|---|---|
| 4.2 | 1.20 |
| 77 | 1.07 |
| 199 | 1.11 |
| 298 | 1.74 |

## Analysis of High Purity Iron

| Elements | Zone Purified Iron, Calculated, ppm |
|---|---|
| Oxygen | — |
| Nitrogen | — |
| Hydrogen | 0. 05 |
| Carbon | 0. X (low) |
| Aluminum | X |
| Antimony | < 0. 1 |
| Arsenic | < .5 |
| Barium | < 1 |
| Beryllium | — |
| Bismuth | — |
| Boron | 0. 05 |
| Cadmium | — |
| Calcium | — |
| Chromium | < 1 |
| Cobalt | < 1 |
| Columbium | < 1 |
| Copper | X (low) |
| Gallium | — |
| Germanium | < 1 |
| Gold | < 1 |
| Lead | — |
| Magnesium | — |
| Manganese | 0. X (low) |
| Molybdenum | X |
| Nickel | < 0. 5 |
| Phosphorus | 0. 07 |
| Silicon | X |
| Silver | — |
| Sodium | — |
| Strontium | — |
| Tantalum | — |
| Tellurium | — |
| Tin | .1 |
| Titanium | < 1 |
| Tungsten | — |
| Vanadium | 0. X |
| Zinc | < 1 |
| Zirconium | < 1 |

< means element not detected; figures shown indicate limit of detection
X = 1 to 9

# GENERAL CHARACTERIZATION

## Zone Refined Iron

1. Geometrical Factors
    1.1 Grains

| | | |
|---|---|---|
| 1.1.1 | Size & Size Distribution | ASTM 5-6 |
| 1.1.4 | Relative Orientation | Equiax |
| 1.1.5 | Special Boundary Configurations | Random |

2. Impurities and Minor Alloying Additions

| | |
|---|---|
| 2.2 Crystallographic Locations | Interstitial elements (C and N) occupy octahedral positions $(0, -0, -1/2)$ at the midpoint of the cell edge. The exact location of H and O is not known. |

## CHARACTERIZATION OF TITANIUM - 3 w/o COPPER
### (Multiphase Metal)

The object of the experimentation was to characterize
the microstructure before and after working, so both
types of samples will be specified in the characterization.

### Description of Material

Raw Material Source: Leytess Corporation, New York, N.Y.

Purity: Titanium  99.8%

    Copper  99.999%

### Chemical Analysis:

### Spectrographic (A. F. Materials Laboratory)

| Element | ppm |
|---------|-----|
| Cr | 15 |
| Mg | < 15 |
| Mn | < 15 |
| Sn | < 15 |
| Al | < 15 |
| Pb | < 15 |

Oxygen 250 ppm — Determined by Standard ASTM method.

Copper 2.85 wt. % by wet chemical analysis.

### Volume Fraction $Ti_2Cu$:

.0714 — Calculated from phase diagram.

### Sample History

#### Alloy Preparation

Three (3) buttons weighing approximately 33 grams each were arc
melted in an argon atmosphere after it had been gettered by melting a
pool of unalloyed iodide titanium.  The buttons were melted twice on each
side to minimize alloy segregation.  These buttons were subsequently
placed in a cigar-shaped copper crucible, and an ingot weighing approx-
imately 100 grams was produced.  This ingot was melted three times

prior to giving it a final homogenization anneal at 800°C. The ingot was sealed in a quartz capsule under a partial pressure of dry argon and annealed for 72 hours at 800°C.

The homogenized ingot was cold swaged at room temperature to approximately .250 inch without any intermediate anneals, and no cracks due to swaging were observed. The chemical analysis reported in Section II (p. V-43) was made on this material. The .250 inch rod was given a recrystallization anneal at 800°C for one (1) hour in a vacuum of $5 \times 10^{-7}$ torr. The annealed rod was subsequently cold rolled to a controlled final thickness, so that final deformation, after another recrystallization anneal, resulted in strips of alloy 10 mil thick. A reduction of approximately 10% per pass was used, and the rolling direction was changed 180° after each pass. The samples described in this report were given 70% reduction of area in the final deformation.

## Discussion of Experimental Results

### Annealed Structure

When beta (bcc) titanium transforms below the eutectoid temperature, the reaction product consists of a mixture of alpha (hcp) titanium and $Ti_2Cu$. As shown in Fig. 1, the eutectoid structure consists of alternate plates of $Ti_2Cu$ and alpha, with alpha being the continuous phase. The structure is analogous to pearlite formed in steel during isothermal or furnace cooling. Fig. 1 shows how the eutectoid structure is grossly distributed. Decomposition of beta occurred by heterogeneous nucleation and growth, occurring primarily at the grain boundaries and to a lesser extent in the center of the grains. Nucleation within the grain provides indirect evidence that concentration gradients are present in the material or some of the $Ti_2Cu$ was not dissolved completely by the last 800°C anneal. An electron micrograph of the sample resolves the lamellae, as shown in Fig. 2, and areas of alpha plus fine particulate $Ti_2Cu$. The lamellae of alpha and $Ti_2Cu$ have respective widths of about 1 to 1. A volume fraction

**FIG. 1 PHOTOMICROGRAPHS OF STRIP SPECIMEN, 0.030 INCH THICK, AFTER ANNEALING FOR 1 HOUR AT 800°C** 200X (4 × 5 in.) enlarged to 5 × 7 in. Etchant 25 ml HNO₃, 25 ml H₂O, 1 ml HF.

FIG. 2  5,000X — COLONIES OF EUTECTOID STRUCTURE
ADJACENT TO ALPHA TITANIUM HAVING A RANDOM
DISTRIBUTION OF $Ti_2Cu$

analysis by point counting resulted in a volume fraction of fine particulat $Ti_2Cu$ of 0.16, which is more than twice that calculated from the phase diagram. Considerable error in the size of the particles can result fron both etching and replicating. For a given colony of eutectoid constituent, the $Ti_2Cu$ plates have a common orientation in space.

Cold-Worked Structure

The structure of the material after 70% reduction of area had the sam general appearance as it did in the annealed condition as shown in Fig. 3. The lamellae of $Ti_2Cu$ appeared to be elongated, and their width was cor spondingly reduced. Transmission electron microscopy performed on th material showed a 1 to 1 correspondence between it and replica micros (Fig. 4). It is obvious that cold-working has changed the relative width o $Ti_2Cu$ to alpha from a ratio of about 1 to 1 to a ratio of about 1 to 2 respe tively. A cell structure can be seen in the area that is free from the pearlite-like structure, which is similar to other cold-worked dispersion hardened alloys. It should be noted that the cell structure is poorly defin in comparison to pure materials.

Another type of deformation structure is shown in Fig. . This is a banded structure that evolves because of twinning. Electron diffraction patterns reveal that a rotation about the zone axis [ 0001 ], and tilting abo the [ 10$\bar{1}$0 ] direction in the plane of foil occur. Relative rotations about the zone axis were measured on a full circle goniometer. Starting at posi tion 1, the relative rotations were 21° between 1 and 2; -2° between 2 and 3; 56.4° between 3 and 4, and a total of 75.4° between positions 1 and 4. Selected area electron diffraction patterns were taken of cell structure as shown in Fig. 4. The rotations were no more than 3 or 4 degrees. Since the cell structure that forms can be associated with both rotation about the zone axis and tilting about a direction in the plane of the material, the

FIG. 3 LIGHT MICROGRAPH OF 70% COLD ROLLED Ti-3 wt %
Cu TITANIUM 200X (4 × 5 in. enlarged to 5 × 7 in.).
Etchant 25 ml HNO₃, 25 ml H₂O, 1 ml HF.

FIG. 4 TRANSMISSION ELECTRON MICROGRAPH, 25,000X
Pearlite-like eutectoid structure becomes elongated and width
reduced. $\alpha$:Ti$_2$Cu width ratio is about 2:1. Cell structure
forming in area free of lamellar structure. Cell size ~ 0.4$\mu$.

FIG. 5  25,000X  —  BANDED AREA SEPARATING AREAS
OF HIGH DISORIENTATION

boundaries must consist of dislocations of more than one family. The
boundaries are therefore low angle unsymmetrical boundaries, which are
immobile. Tilting in the plane of the foil eliminates the possibility of
simple twist or tilt boundaries.

## GENERAL CHARACTERIZATION

### WORKED MATERIAL

Titanium — 3 w/o Copper

1. Geometrical Factors
   1.1 Grains

| | |
|---|---|
| 1.1.1 Composition, Volume Percent and Structure | $\alpha$ (hcp) Ti |

   1.2 Second Phases*

| | |
|---|---|
| 1.2.7 Distribution in Structure | Ratio of the width of alpha titanium to that of $Ti_2Cu$ for the pearlite-like structure after 70% reduction of area: <br><br> $\alpha : Ti_2Cu \simeq 2:1$ |

4. Dislocations

| | |
|---|---|
| 4.1 Substructure | Deformation cell size: $.4$ micron x $.6$ micron $\leq a \times b \leq .8$ micron x $1.2$ micron. Most cells were rectangular having dimensions a and b. Angle of orientation variation across boundaries ranged from $1° \leq \theta \leq 4°$. Types of deformation twins observed by transmission electron microscopy: $(1)-(10\bar{1}1)$; $(2)-\{10\bar{1}0\}$. This deformation twin is not expected, because the $(10\bar{1}0)$ plane is a plane of symmetry for the hcp lattice. |
| 4.3 Type | Cells were formed by a rotation about the zone axis plus tilting about a direction in the plane of the sample. Cell boundaries are classified as low angle unsymmetrical boundaries which are immobile. Simple twist and tilt boundaries are ruled out because boundaries consist of dislocations from more than one family. |

*Includes glassy or amorphous "phases"

## GENERAL CHARACTERIZATION

ANNEALED MATERIAL

Titanium — 3 w/o Copper

1. **Geometrical Factors**
   1.1 **Grains**

| | | |
|---|---|---|
| 1.1.1 | Composition, Volume Percent and Structure | $\alpha$ (hcp) Ti |
| 1.2.3 | Shape & Shape Distribution (Connectivity) | Appeared as a lamellar structure of alternate plates of $\alpha$ (hcp) titanium and $Ti_2Cu$. Nucleated primarily at the grain boundary during furnace cooling. Some nucleation occurred within grain, suggesting that a concentration gradient existed or some $Ti_2Cu$ was not dissolved during recrystallization for 1 hour at 800°C. |
| 1.2.7 | Distribution in Structure | In the lamellae, the ratio of the widths alpha to $Ti_2Cu$ was about 1 to 1 respectively. Volume fraction of fine particulate $Ti_2Cu$ by point count method was .16. This can be in considerable error due to over-etching and replication process. Some islands of alpha plus fine particulate $Ti_2Cu$ were observed in areas between colonies of eutectoid constituent. Mean free distance between fine particles of $Ti_2Cu$ $$MFD = \frac{1 - f_v}{P_L} = 0.168\mu = 1680°$$ where $P_L$ is the number of particles intersected per unit length. Mean spacing between fine $Ti_2Cu$ particles, $S_p$ $$S_p = \frac{1}{P_L} = \frac{1}{5}\mu = 2,000 \text{ Å}$$ $$S_p \simeq MFD$$ |

# SECTION VI

## THE REPORT OF THE PANEL ON POLYMERS

NATIONAL ACADEMY OF SCIENCES
NATIONAL ACADEMY OF ENGINEERING
DIVISION OF ENGINEERING - NATIONAL RESEARCH COUNCIL
MATERIALS ADVISORY BOARD
AD HOC COMMITTEE ON CHARACTERIZATION OF MATERIALS

## PANEL ON POLYMERS

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Staff Engineer

## FOREWORD

The purposes of the Panel on Polymers were to:

1. Select a set of characterization parameters relating to polymers either as isolated molecules or assemblies of molecules in solution or bulk, which set of parameters would serve two ends: .

   a. Permit an accurate description of any given polymer in quantitative terms intelligible to and acceptable to polymer scientists.

   b. Hopefully, permit the calculation of polymer properties that affect the practical utilization of plastics, fibers, rubber, foams, etc.

2. Ascertain the state of art concerning our ability to determine these parameters.

3. Ascertain the extent to which present abilities are being used by polymer scientists.

4. Make specific recommendations relative to how our ability to characterize polymers can be both extended in use and improved in quality. These recommendations should be of such clarity and form as to be valuable to governmental, academic, institutional, and industrial groups concerned with:

   a. Conducting research on polymers

   b. Funding research on polymers

   c. Reporting and/or publishing research results on polymers

   d. Using polymers

5. Prepare all this in the form of a finished report to the MAB Ad Hoc Committee on Characterization of Materials.

Names of panel members have already been listed. This roster was selected to cover the following types of institutions:

- Academic
- Governmental

- Institutional
- Polymer Producer
- Producer-User
- Polymer User,

all of whom had experience in characterizing polymers. Eight to ten members were originally planned, but with the design of a questionnaire at our first meeting, it was decided that the intended additional coverage could be obtained via circulation of a questionnaire.

Several different methods were used in filling out this questionnaire. Each panel member, and Dr. Hannay, contacted colleagues in their respective organizations. Dr. Starkweather had questionnaires filled out by 14 duPont experts in the fields of plastics, fibers, and elastomers. He then submitted a single questionnaire but weighted the answers according to who was most expert in a given field.

Dr. Reding explained the questionnaire to a group of 10 polymer experts at the Union Carbide Research Laboratory in South Charleston before having individuals fill out their replies. Dr. Shultz held two group meetings at the General Electric Research and Development Laboratory in Schenectady - one with physical chemists and one with organic chemists. He received 5 replies. Dr. Hoffman had 9 questionnaires filled out by polymer experts in the Polymer Division at the National Bureau of Standards. Professor Billmeyer divided his initial group of 10 questionnaires among his own colleagues at Rensselaer and outside academic plus industrial contacts. Dr. Boyer selected a six-man Dow team which met four times for a total of eleven hours. Boyer submitted a single questionnaire with weighted answers.

The final tabulation reflects the views of at least 70 of the country's top polymer experts although each expert who worked on the questionnaire did not attempt to answer all questions.

Dr. Starkweather compared the averages as calculated by Professor Billmeyer with the specific weighted replies from the duPont group. He found remarkably good agreement. In his opinon, this signified two things:

1. The questions were generally being interpreted in the same manner by all groups, and

2. There was reasonably uniform opinion as to problem areas.

Most people who worked with the questionnaires considered this a worthwhile exercise that benefited the individual.

The Panel hereby thanks the many polymer experts who gave of their time to aid this project. It also deeply appreciates the assistance of Donald Groves and Bruce Hannay. The latter called repeatedly on his colleagues at The Bell Telephone Laboratories for technical assistance on specific questions which arose, as well as offering advice and criticism in the preparation of this report.

Finally, special thanks go to Miss Bea Prankienas, Plastics Department, The Dow Chemical Company, who assisted in the typing and editing of the draft report of this panel.

## CONTENTS

### SECTION VI. THE REPORT OF THE PANEL ON POLYMERS

## I. INTRODUCTION

Polymer molecules are uniquely different from other structural materials and this complicates the problem of characterization. Section II will elaborate this statement. A condensed synopsis of the problems follows.

Polymer molecules are long chain, thread-like, high molecular weight materials containing a distribution of molecular weights clustering about an average. Neither this average molecular weight nor the distribution of molecular weights about the average are unique for a given polymer such as polystyrene: instead, they depend on the kinetics of the chemical reaction by which the polymer is formed.

The long chain nature of polymer molecules introduces a number of complications of which the following are typical:

1. Poor packing is common in the glassy state with density - and hence free volume - dependent on prior thermal history.

2. Detailed structural features along the polymer chain are exceedingly difficult to characterize.

3. Orientation in amorphous and crystalline polymers during fabrication is facilitated and this introduces anisotropy in physical properties relative to the direction of orientation.

4. Crystallization is difficult for those polymers which can crystallize, so that complete crystallization is obtained only in special cases and all crystals usually contain many defects. The number, size, and type of crystals are dependent on previous thermal history. Polymer molecules, called "tie molecules," can go from one crystal to another. The properties of a crystalline polymer are determined by the amount of crystallinity, the morphology of the crystalline material, the nature of the tie molecules, and by the nature of the unit cell.

Having in mind the complexities mentioned above, the Panel attempted to do two things:

1. List those characterization parameters which seemed of significance for defining a given polymer sample, and for calculating some of its properti

2. Recognize that in the present early state of polymer science it would also be necessary to resort to physical measurements of properties such as:

- thermodynamic properties,
- dynamic mechanical loss,
- creep,

etc., simply because such quantities could not be calculated from the basic characterization parameters.

However, for purposes of this report, our panel wishes to emphasize that the set of characterization parameters which we have selected are used primarily to define a given polymer sample and differentiate it from all other samples in as quantitative a manner as is possible today.

This does not preclude the use of other physical measurem ..ts such as:

- thermodynamic properties,
- optical properties,
- dynamic mechanical loss,
- dielectric loss,

etc., from being used also. We are suggesting a minimum set of character-ization parameters, a necessary and sufficient set for characterization but not an all inclusive set. In fact, the more measurements there are on any sample, the more completely can it be described as well-characterized. This general problem will be discussed again in Section II G.

## II. THE NATURE OF POLYMERS

### A. INTRODUCTION

Polymer Science is a relatively new field (three Nobel Laureates to date; i.e., Staudinger, Natta, and Ziegler) - but old enough to recognize that polymers present a bewildering, complex array of types and structural anomalies. Both the newness and complexity of the subject matter make difficult the characterization of polymers. The following essay is intended to set the stage for discussing problems in characterization of polymers.

The word "Polymer" is a generic term which covers the following classes of materials:

1. Plastics
    a. Thermoplastics
    b. Thermosets
    c. Resins
    d. Latexes
2. Textiles
    a. Natural (Cotton, Wool, Silk, Linen, etc.)
    b. Synthetic (Rayon, Nylon, Dacron, Acrylics, etc.)
3. Rubbers
    a. Natural (Hevea, Gutta Percha)
    b. Synthetic (GR-S, Neoprene, Nitrile, Thiokol, Ethylene-Propylene, etc.)
4. Natural Polymers
    a. Cellulose (Wood, Cotton, etc.)
    b. Starch
    c. Amber
    d. Various Resins Used in Varnishes

5. Biological Polymers

    a. RNA, DNA

    b. Polypeptides (Proteins)

    c. Chitin, etc.

6. Polyblends (Blends of two or more polymers)

7. Foams

8. Composites

    a. Filled Polymers, i.e., Rubber-Carbon Black

    b. Reinforced Polymers, i.e., with Fiberglass

    c. Sandwich Panels

This report is not concerned with foams, composites, nor with any detailed aspects of biological polymers.

B. GENERAL ARCHITECTURE OF POLYMERS
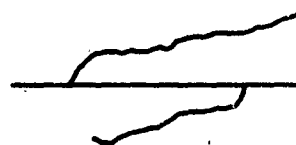
Polymer molecules are high molecular weight chain molecules. The chains have several general forms:
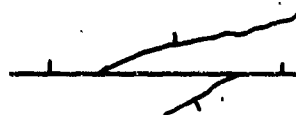
Figure 1

Linear (Polystyrene)

Short Chain Branches
(High Density Polyethylene)

Long Chain Branches
(GR-S Rubber)

Short-Plus-Long Chain
Branches (Low Density PE)

Cross-Linked or Three-
Dimensional or Vulcanized
Chains (Vulcanized rubber)
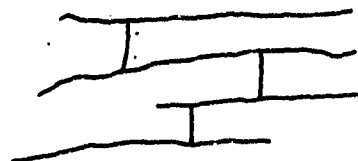
## Molecular Weight

A given polymer does not have a single molecular weight but a distribution of molecular weights. Hence it is necessary to speak of an average molecular weight. Shown below is a typical molecular weight distribution curve for polystyrene (prepared thermally at 140°C.), and the location of four different types of average molecular weights in common use; namely, the number average $\overline{M}n$, the viscosity average $\overline{M}\eta$, the weight average $\overline{M}w$, and the Z average $\overline{M}_z$. The molecular weight scale is divided into three general regions—A, B, and C—for ease of subsequent discussion.

### Figure 2



MOLECULAR WEIGHT
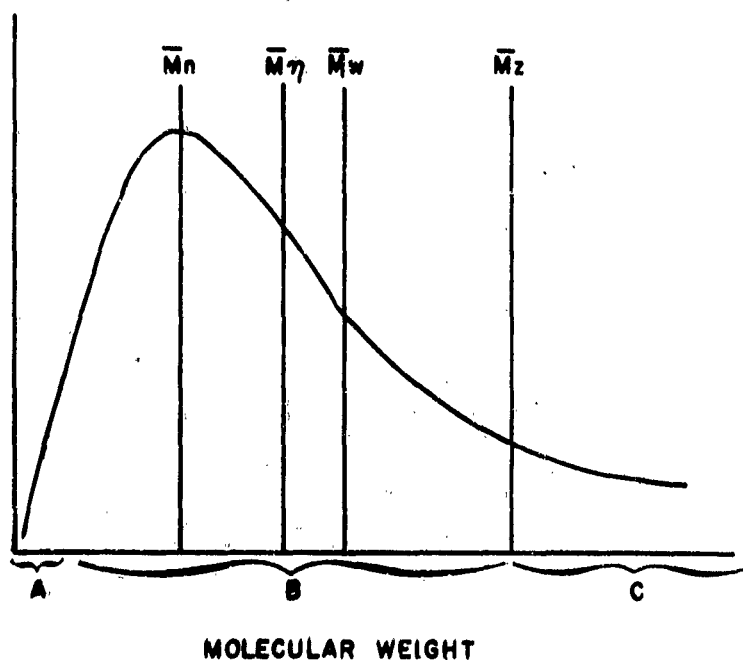
For this particular polystyrene

$\overline{M}n = 136,000$

$\overline{M}w = 257,000$

$\overline{M}z = 396,000$

or to a first approximation

$\overline{M}z:\overline{M}w:\overline{M}n = 3:2:1$

Physical properties depend on these averages as follows:

$\overline{M}n$

Tensile strength and other destructive physical properties increase with $\overline{M}n$ as shown schematically.

### Figure 3
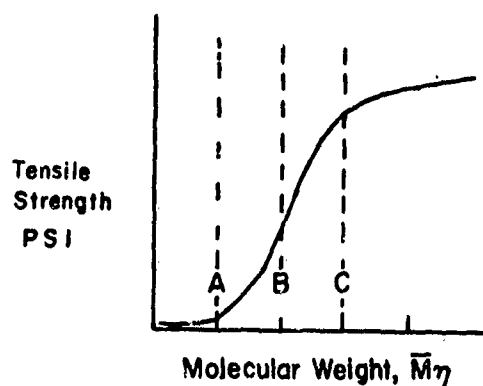


Molecular Weight, $\overline{M}\eta$

The three characteristic regions—A, B, and C—in Fig. 3 depend on the structure of the polymer: They occur at lower molecular weights for a highly polar polymer, such as nylon, and at very high molecular weights for a non-polar polymer, such as polyethylene.

$\overline{M}\eta$

The intrinsic viscosity, $[\eta]$*, is directly proportional to $\overline{M}\eta$. If $x = 1$, $\overline{M}\eta = \overline{M}w$; if $x < 1$ $\overline{M}\eta < \overline{M}w$; if $x > 1$, which ' ~lds true for very stiff chains, $\overline{M}\eta > \overline{M}w$. x is defined at the top of the next page.

$$* [\eta] = \left( \frac{\eta - \eta_0}{\eta_0 \quad c} \right) \quad c \to 0$$

where $\eta_0$ is the viscosity of the solvent and $\eta$ is the viscosity of the solution when the concentration of dissolved polymer is c.

$\overline{M}w$

The intrinsic viscosity, $[\eta]$, determined from dilute solution measurements, varies as $(\overline{M}w)^{x}$ where x can be from 0.5 to 2.0 depending on solvent and polymer type. For many polymers, x is around 0.8.

Melt viscosity (viscosity of the molten polymer at elevated temperatures in the fabrication range) varies as

$$\overline{M}w^{1.0}$$

for molecular weights below about 30,000 and as

$$\overline{M}w^{3.4}$$

for molecular weights above about 30,000.
The molecular weight at which this change in $\overline{M}w$ dependency occurs is affected by the nature of the specific polymer.

$\overline{M}z$

The tendency of a polymer to orient during extrusion or spinning increases as $\overline{M}_z$ increases. $\overline{M}_z$ increases as the amount of material in region C of Figure 2 increases.

The Three Regions of Figure 2

While the bulk of a polymer sample lies in region B of Figure 2, relatively small amounts of material lying in regions A and C can have profound influence on many physical properties. Area C, as already mentioned, affects the tendency of polymer chains to orient during extrusion. Small amounts of very high molecular weight polymer may be added to commercial polymers to increase the total material in region C without appreciably increasing $\overline{M}n$ or $\overline{M}w$.

Region A, generally with molecular weights below 1000, consists of a variety of materials; i.e.,

Impurities in the original monomer

Unpolymerized monomer

Dimers, trimers, tetramers, etc.

Oxidation products

Catalyst fragments

Etc.

Among the influences of such materials are:

Increased tendency of polymers to discolor in sunlight

Increased tendency to creep

Increased tendency to craze (develop hairline cracks)

Lowering of the heat distortion temperature

Deleterious effect on physical properties

Increased ease of flow during fabrication

In addition to these naturally occurring low molecular weight materials, it is common practice to add low molecular weight organic materials such as plasticizers, stabilizers, slip agents, and dyestuffs as well as inorganic substances such as pigments, fillers, and carbon black.

IT IS THUS OBVIOUS THAT COMPLETE CHARACTERIZATION OF THE MOLECULAR WEIGHT OF A POLYMER REQUIRES KNOWLEDGE OF:

1. THE ENTIRE DISTRIBUTION CURVE
SHOWN IN FIGURE 2;

2. THE DETAILED COMPOSITION OF REGION A
SHOWN IN FIGURE 2; AND

3. SOLID ADDITIVES.

The values of $\overline{M}w$ from light scattering and $\overline{M}n$ from osmotic pressure are frequently used to characterize a distribution curve but are of necessity convenient rather than precise. Osmotic pressure and light scattering provide absolute methods of determining $\overline{M}n$ and $\overline{M}w$. $\overline{M}\eta$ requires calibration by an absolute method. $\overline{M}_z$ is obtained from sedimentation equilibrium ultracentrifuge measurements.

The entire distribution curve, except for region A of Figure 2, can be determined by three methods:

a) The ultracentrifuge

b) Gel permeation chromatography

c) Resolution of the sample into a number (preferably greater than 10) of narrow fractions by fractional solubility methods and determination of $\overline{M}n$ or $\overline{M}w$ or both for each fraction.

One obvious problem in characterizing region A is that such materials must first be clearly and completely separated from the overwhelming bulk of high molecular weight polymer. Once this separation is achieved, the low molecular weight components can be analyzed by conventional means.

There is no such thing as a characteristic molecular weight distribution curve or set of molecular weight averages for a specific polymer. For example, polystyrene can be prepared with $\overline{M}n$ values ranging from several hundred to several million and with distribution curves varying from extremely narrow to extremely broad.

THE AVERAGE MOLECULAR WEIGHTS AND THE MOLECULAR WEIGHT DISTRIBUTION ARE DETERMINED BY THE KINETICS OF THE POLYMERIZATION REACTION WHICH DEPEND ON FIVE MAIN FACTORS:*

1. CHEMICAL STRUCTURE OF THE MONOMER

2. CATALYST

3. SOLVENT AND/OR CHAIN TRANSFER AGENT

4. TEMPERATURE OF POLYMERIZATION

5. EXTENT OF CONVERSION OF MONOMER TO POLYMER.

* Moreover, once a polymer is made, heat, ultrasonics, mechanical shearing, etc., can rupture polymer chains, thereby shifting the distribution curve to the left. Ultraviolet light, ionizing radiation, oxygen, ozone, etc., will degrade some polymers and cause others to cross-link, but in either case, altering the distribution curve.

In **Figure 4**, we show three different distribution curves all having the same $\overline{M}n$ for polystyrene prepared by three different methods.

## Figure 4

A. Thermal polymerization at 140°C. to 37% conversion (same as Fig. 3
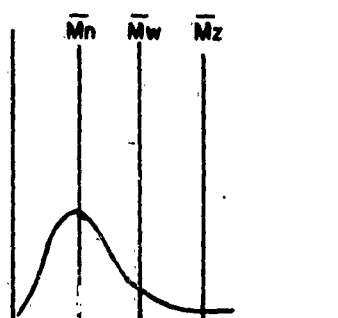
$$\overline{M}_z : \overline{M}w : \overline{M}n = 3:2:1$$

B. Thermal polymerization at several consecutive temperatures from 60°C. to 200°C. and 100% conversion (schematic only)
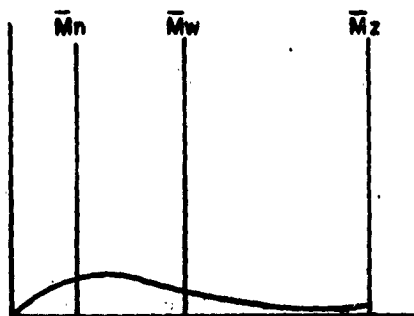
$$\overline{M}_z : \overline{M}w : \overline{M}n = 6:3:1$$

C. Anionic catalysis by the method of Szwarc or Morton
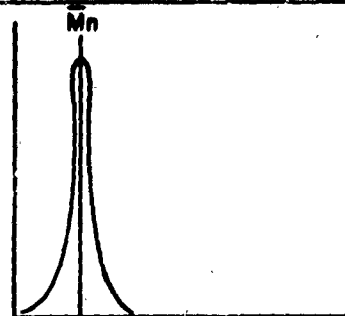
$$\overline{M}_z : \overline{M}w : \overline{M}n = 1.12:1.07:1$$

## C. BASIC POLYMER CHEMISTRY

Polymers are formed and/or modified by a variety of reactions of which the principal ones are:

1. Addition Polymerization (No by-product, no elimination)

    a. Homopolymerization

    b. Copolymerization *

        (1) Random Copolymerization

        (2) Block Copolymerization

        (3) Graft Copolymerization

2. Condensation Polymerization (something eliminated; i.e., water)

    a. Thermosets

    b. Thermoplastics

    (These two terms can also apply to Addition Polymers)

3. Hybrids

4. Vulcanizates

5. Chemical Modification of an Existing Polymer

6. Polyblends (Blends of two or more polymers)

* Copolymerization can occur by either the addition or the condensation mechanisms.

## 1. Addition Polymerization

Addition polymerization which, in its simplest form, consists of n mol cules of a monomeric starting material such as styrene coupling consecu tively to build up a long polymer chain, i.e., a homopolymer:
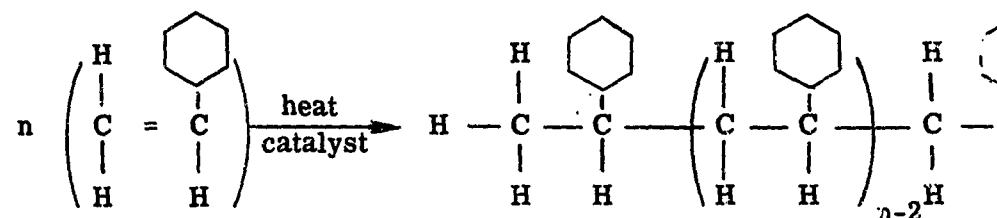


(hydrogen atoms to cap each chain end were added for convenience).
The above represents a single chain. In a real polymer system there will be a distribution of n values corresponding to the final molecular weight distribution.

### a. Homopolymerization

There are several different types of homopolymer addition polymerizati

(1) **All Carbon Backbone Chain,** which is generically

$$-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - \underset{\underset{R_2}{|}}{\overset{\overset{R_1}{|}}{C}} -$$
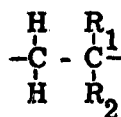
| $R_1$ | $R_2$ | Polymer |
|-------|-------|---------|
| H | H | Polyethylene |
| H | $CH_3$ | Polypropylene |
| H | Cl | Polyvinylchloride (PVC) |
| H | phenyl | Polystyrene |
| H | F | Polyvinyl fluoride (Tedlar) |
| Cl | Cl | Polyvinylidene Chloride (Saran) |
| $CH_3$ | $CH_3$ | Polyisobutylene |

and also special cases; i.e.,

$$-\overset{\overset{\displaystyle F}{|}}{\underset{\underset{\displaystyle F}{|}}{C}}-\overset{\overset{\displaystyle F}{|}}{\underset{\underset{\displaystyle F}{|}}{C}}- \ \text{Teflon}$$

$$-\overset{\overset{\displaystyle F}{|}}{\underset{\underset{\displaystyle F}{|}}{C}}-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle F}{|}}{C}}- \ \text{Kel F}$$
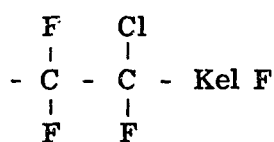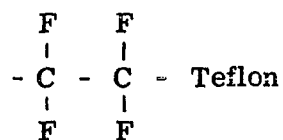
(2) Heteroatom Backbone Chain, as, for instance, in polyformalde-hyde (Delrin, Celcon)

$$-\overset{\overset{\displaystyle H}{}}{\underset{\underset{\displaystyle H}{}}{C}}-O-\overset{\overset{\displaystyle H}{}}{\underset{\underset{\displaystyle H}{}}{C}}-O-\overset{\overset{\displaystyle H}{}}{\underset{\underset{\displaystyle H}{}}{C}}-O-$$
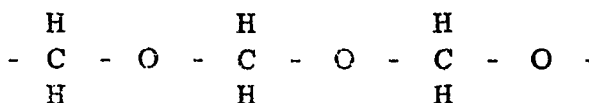
(3) Ring Opening Compounds. A compound like tetrahydrofuran:
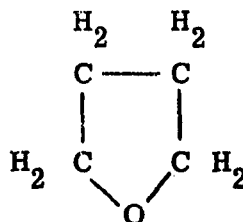


can be caused to polymerize and form a linear heteroatom chain; i.e.,

$$-CH_2-CH_2-CH_2-CH_2-O-CH_2-CH_2-CH_2-CH_2-O-$$
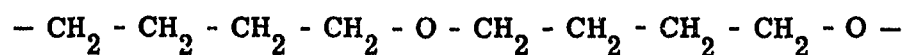
(4) Inorganic Backbone Polymers.

Polymers with no carbon atoms in the chain are said to have an inorganic backbone. The silicones are a familiar example in which the chain is alternating silicon and oxygen atoms; i.e.,

$$
\begin{array}{ccccccccc}
& CH_3 & & & CH_3 & & & CH_3 & & & CH_3 \\
& | & & & | & & & | & & & | \\
-\ Si & - & O & - & Si & - & O & - & Si & - & O & - & Si & - & O - \\
& | & & & | & & & | & & & | \\
& CH_3 & & & CH_3 & & & CH_3 & & & CH_3 \\
\end{array}
$$
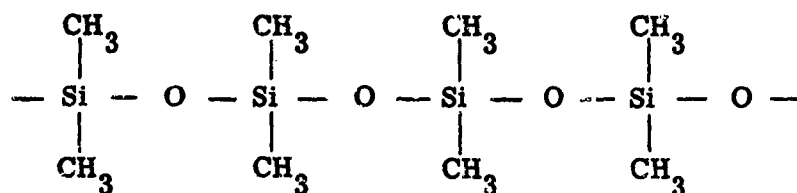
In this case the methyl side groups on the silicon atoms are organic in nature and hence this particular polymer, polydimethyl siloxane, is a mixed organic-inorganic polymer, with an inorganic chain.

WARNING: THE REPEAT UNIT IN THE POLYMER CHAIN MAY BE DIFFERENT FROM THAT EXPECTED OF THE MONOMER UNIT. FOR EXAMPLE, THE MONOMER, TRICHLOROPROPENE

$$
\begin{array}{cc}
 & Cl \\
 & | \\
H & Cl- C - Cl \\
C = & C \\
H & H \\
\end{array}
$$
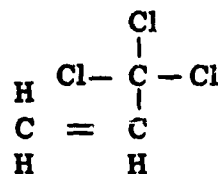
GIVES A REPEAT UNIT IN THE POLYMER AS

$$
\begin{array}{ccc}
H & Cl & Cl \\
- C - & C - & C - \\
H & H & Cl \\
\end{array}
$$
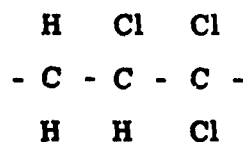
RATHER THAN THE EXPECTED

$$
\begin{array}{cc}
 & Cl \\
 & | \\
H & Cl - C - Cl \\
- C - & C - \\
H & H \\
\end{array}
$$
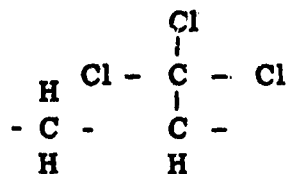
Butadiene affords a more complex case. The monomer

$$
\begin{array}{cccc}
H & H & H & H \\
C = C & - & C = C \\
H & & & H \\
\end{array}
$$
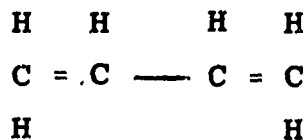
can appear in the polymer chain as

$$\begin{array}{cccc} H & H & H & H \\ -C & - C & = C & - C - \\ H & & & H \end{array}$$
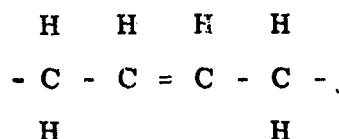
(in either the cis or trans form to be explained later)

and

$$\begin{array}{cc} H & H \\ -C & - C \\ H & | \\ & CH \\ & \| \\ & HCH \end{array}$$

as well as combinations of the above; i.e.,

$$\begin{array}{cccccc} H & H & H & H & H & H \\ -C & - C & = C & - C & - C & - C \\ H & & & H & H & | \\ & & & & & C \\ & & & & & \| \\ & & & & & C \end{array}$$
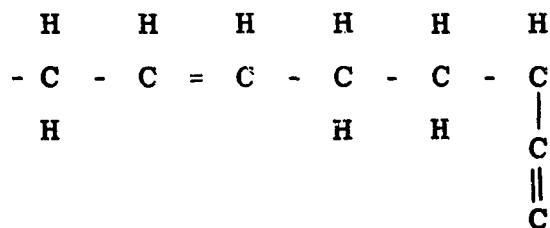
all depending on catalyst, solvent and temperature of polymerization.

The repeat unit, or units, must be identified, usually by infrared, as part of polymer characterization.

b. Copolymerization

This is the case where two or more monomers are used to build up a polymer chain.

(1) Random Copolymerization

Monomers A and B are mixed together and caused to polymerize with heat and/or catalyst. The two monomers enter the chain apparently at random but actually according to well understood principles concerning the electrical charge and the chemical reactivity at the growing end of the polymer chain.

With equimolar amounts of monomers A and B, we might get sequence
like

-----------------A A B    A    B B B A A-------------------

but no two chains are likely to be identical either in distribution of sequence
or in average composition.

Only rarely will a pair of monomers tend to alternate and give the
sequence

-------------------- A B A B A B A B --------------------------

THUS, IN GENERAL, COPOLYMERS OF THE ADDITION TYPE WILL
REQUIRE FOR CHARACTERIZATION FOUR THINGS:

- THE AVERAGE COMPOSITION (not necessarily the same as the
starting composition of monomers)

- DISTRIBUTION OF MOLECULAR WEIGHTS

- DISTRIBUTION OF AVERAGE COMPOSITION PER POLYMER
CHAIN

- DISTRIBUTION OF SEQUENCE LENGTHS ALONG EACH CHAIN.

Hence, copolymers possess all of the problems inherent in the character-
ization of homopolymers but to an even greater degree. This is true even
with a binary copolymer of known origin (known monomer pair) but the
problem is greatly compounded for copolymers of unknown origin and/or
of more than two components.

Copolymers pose several classes of new problems not inherent in homo-
polymers:

(a) Proportion of monomers

(b) Distribution of proportions which arises both from the statistical nature
of the copolymerization reaction and from the drift in average composition
with conversion.

(c) Sequence lengths

(d) The double distribution of both molecular weight and proportions.

In general, the characterization of each copolymer system is a research problem in itself, varying in effort between that of an MS and a PhD thesis. The variation is from relatively simple systems like styrene-methylmethacrylate where the monomers are vastly different to an extremely complex case such as vinylchloride-vinylidene chloride. These characterization problems can be solved with varying degrees of success if an incentive exists for solving them and if sufficient effort is applied. Analysis of complex polypeptides and DNA show what can be accomplished when incentive exists to expend the needed effort.

Synthesis of model compounds to duplicate representative short sequences of co-monomers along the chain can be very helpful. Because copolymer theory is in such excellent shape, precision kinetic studies can provide powerful clues as to probable sequence distributions and composition distributions.

### (2) Block Copolymerization

Under certain polymerization conditions, addition copolymers can be made in the form of blocks

----------- A A A A A A A — B B B B B B B --------------

or of sandwiches

--------- A A A A B B B A A A A B B B A A A A-----------

Distribution of molecular weights and of sequence lengths needs to be determined.

### (3) Graft Copolymerization

Methods are available for grafting polymer chains of one composition onto backbone chains of a different composition.

```
                                        B
                                        B
                                        B
- - - - - - - - - - - - - - - A A A A A A A A A A - - - - - - - - - - - - - - -
                        B          ↑
                        B          └backbone chain
                        B
                        B
                        B ←
                        B        grafted chain
                        B
                        B
```
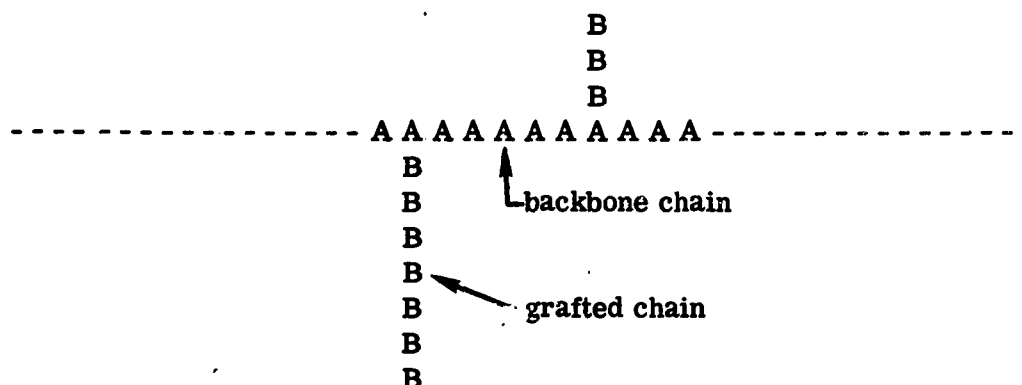
Here for characterization it is necessary to know —

- Average composition

- Distribution of molecular weights

- Distribution of graft lengths

- Distribution in number of graft chains per backbone chain

- Distribution of distances along the backbone between graft points

IT IS OBVIOUS THAT COPOLYMERS OF ANY TYPE; — i.e.,

- RANDOM

- BLOCK

- GRAFT

PRESENT SOME CHALLENGING PROBLEMS FOR CHARACTERIZATION.

2. Condensation Polymerization in which two ingredients X and Y co-react to build up a polymer. There are two generic types:

   a. Thermosets, or three-dimensional polymers, such as are made by condensing phenol plus formaldehyde or urea and formaldehyde.

   b. Thermoplastics, or linear polymers, such as the reaction product of a dibasic acid like adipic acid with a diamine such as hexamethylene diamine to produce the Nylon 6, 6 polymer chain.

```
      H   H   H   H   H   H H   O       H   H   H   H       O
                                ||                          ||
   --C - C - C - C - C - C N - C - C - C - C - C - C—
      H   H   H   H   H   H           H   H   H   H
```
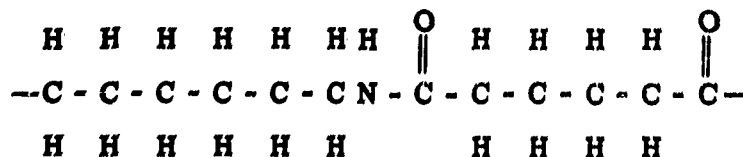
THERMOSET CONDENSATION POLYMERS ARE EXTREMELY DIFFI-
CULT TO CHARACTERIZE BECAUSE THEY ARE INSOLUBLE AND INFU-
SIBLE AND HAVE ESSENTIALLY INFINITE MOLECULAR WEIGHT.

THERMOPLASTIC CONDENSATION POLYMERS CAN BE CHARACTER-
IZED IN MUCH THE SAME FASHION AS HOMOPOLYMERS MADE BY
ADDITION.

3. Hybrids

Styrene-polyester systems represent a hybrid. An essentially linear
condensation polymer is made by condensing three ingredients, for instance

Ethylene Glycol $\quad\quad\quad$ HO - $CH_2$ - $CH_2$ - OH

Phthalic Anhydride
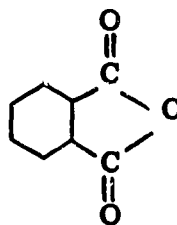
Maleic Anhydride
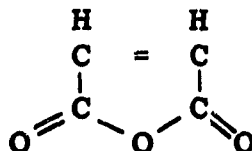
to give a linear polyester chain containing unsaturated double bonds from
the maleic anhydride. This linear condensation polymer is dissolved in
liquid styrene monomer. Addition of catalyst causes the styrene to poly-
merize with itself in an addition type reaction and to copolymerize with
the double bonds in the polyester molecules to give a three dimensional or
cross-linked hybrid copolymer.

Hence, even though the starting polyester can be characterized, and even
though linear chains of polystyrene can be characterized, a hybrid thermo-
set such as a styrene-polyester resin is virtually impossible to characterize
with presently known techniques.

## 4. Vulcanizates

In many cases, an essentially linear polymer or copolymer is fabricated into a useful form and then converted to a three-dimension or thermoset polymer. The best-known instance of this is the sulfur vulcanization of rubber in which short chains of sulfur atoms link together (cross-link) the long rubber molecules. Polyethylene can be cross-linked with peroxides or ionizing radiation such as electrons from an accelerator or gamma rays from Cobalt 60.

Physical properties of the vulcanized (or cured or cross-linked) polymer are very sensitive to the degree of cross-linking. For moderate amounts of cross-linking, a property such as tensile strength might vary as indicated below:

### Figure 5
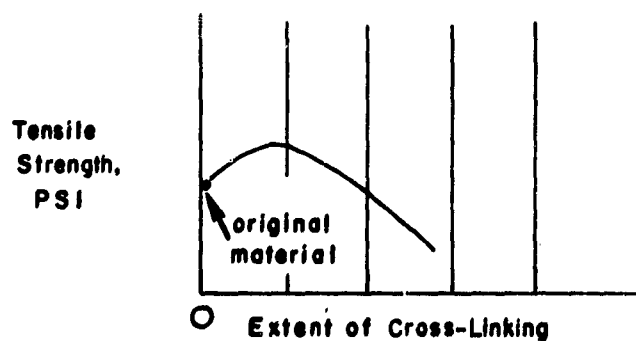


Thus some cross-linking is beneficial but too much cross-linking can be detrimental. Other properties such as solvent and heat resistance increase continuously with increasing cross-linking.

While the starting polymer may be well characterized, the vulcanized three-dimensional polymer virtually defies complete characterization because it is both insoluble and infusible.

There are two characterization parameters:

(1) The average molecular weight between cross-links, $\overline{M}c$, which can be determined from equilibrium swelling measurements in solvents.

(2) The detailed topology of the network structure which could include the distribution of molecular weights between cross-links, chain entanglements, length of cross-links, etc. Network topology currently defies analysis.

## 5. Chemical Modification of an Existing Polymer

In many instances, a natural or synthetic polymer is treated with a chemical reagent to achieve some desired set of properties. A current example is the chlorination of linear polyethylene to give chlorinated polyethylene of any chlorine content in the range from zero up to about 80% by weight. Such chlorinated products can be compared with two well known addition homopolymers, PVC and Saran A or polyvinylidene chloride.

PVC (polyvinylchloride) contains 57% chlorine and has the chemical structure:

```
      H     Cl    H     Cl.   H     Cl
  —   C  -  C  -  C  -  C  -  C  -  C   —
      H     H     H     H     H     H
```
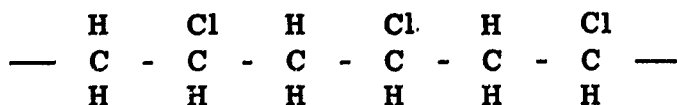
whereas Saran A, with 72% chlorine, is

```
      H     Cl    H     Cl    H     Cl
  —   C  -  C  -  C  -  C  -  C  -  C   —
      H     Cl    H     Cl    H     Cl
```
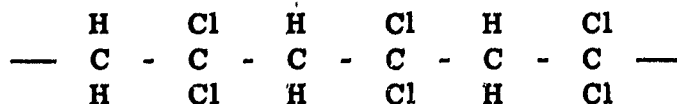
Linear polyethylene is

```
      H     H     H     H     H     H
  —   C  -  C  -  C  -  C  -  C  -  C   —
      H     H     H     H     H     H
```
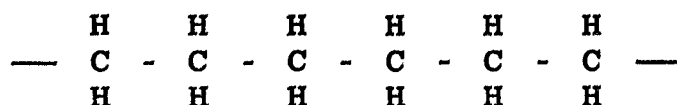
A chlorinated polyethylene with the same chlorine content as PVC will have properties different from those of PVC. A product with the chlorine content of Saran will have properties different from those of Saran.

Hence, we can have two polymers, PVC and chlorinated linear polyethy, both with 57% chlorine, both with the same average molecular weight, bot with the same molecular weight distribution, and yet with markedly differ ent physical properties.

This arises because of detailed differences as to the disposition of chlo: along the chain. Chlorine atoms tend to lie somewhat randomly along the chain in the chlorinated product; i.e.,

$$
\begin{array}{ccccccccc}
 & H & Cl & Cl & H & H & H & Cl & Cl \\
\text{---} & C & - & C & - & C & - & C & - & C & - & C & - & C & - & C & \text{---} \\
 & H & H & H & H & H & H & H & Cl
\end{array}
$$
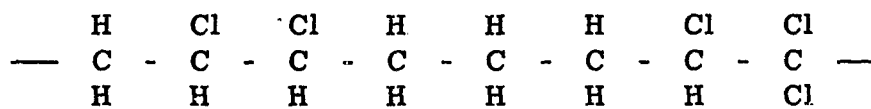
and hence the differences in physical properties.

## 6. Polyblends

It is common practice to blend two or more polymers in order to achiev some desired combination of physical properties. For example, non-burnin polyvinylchloride may be mechanically blended with a chemical, heat, and impact resistant ABS polymer (acrylonitrile-butadiene-styrene polymer) to combine self-extinguishing, impact, heat, and chemical resistance in a single molding compound.

Another important example consists in modifying normally brittle polym such as polystyrene or polymethylmethacrylate with 3 up to 30% of a rubber to improve impact strength. Such a polyblend can be achieved in three different ways:

(1) Mechanical milling of polymer and rubber

(2) Mixing latexes obtained separately or in situ of the polymer and the rubber followed by coagulation of the mixed latex system

(3) Dissolving the polymeric rubber in the monomer of the brittle polymer and polymerizing.

It is generally true that two polymers are not compatible—hence not mutually soluble. Therefore polyblends are usually two-phase systems in which the dominant polymer tends to be the continuous phase and the minor polymer is present as dispersed particles. Some polyblends may consist of two interpenetrating continuous phases. In some polyblends, the continuous phase can change, depending on thermal history. In blends of a rigid polymer and a rubber, the sample will be rigid if the former is the continuous phase, but semi-flexible if the latter is the continuous phase.

Figure 6* shows a phase contrast photomicrograph of a typical section in the two-phase system which results from dissolving a rubber such as polybutadiene in styrene monomer and polymerizing to give rubber modified or impact polystyrene. The dark continuous phase is polystyrene while the white dispersed phase consists of rubber particles, each of which appears to contain small discrete particles of polystyrene. There may be graft copolymer at the interface between the polystyrene phase and rubber particles.

Figure 7** is an electron micrograph at much higher magnification showing the detailed structure of several of the essentially circular dispersed rubber particles in a polystyrene matrix. The polystyrene particles within each rubber particle are now much more apparent. See Reference 22 for details. Figures 6 and 7 are cross-sectional views.

Characterization of such a two-phase polymer system would require knowledge of the following:

* p. VI-24
** p. VI-25
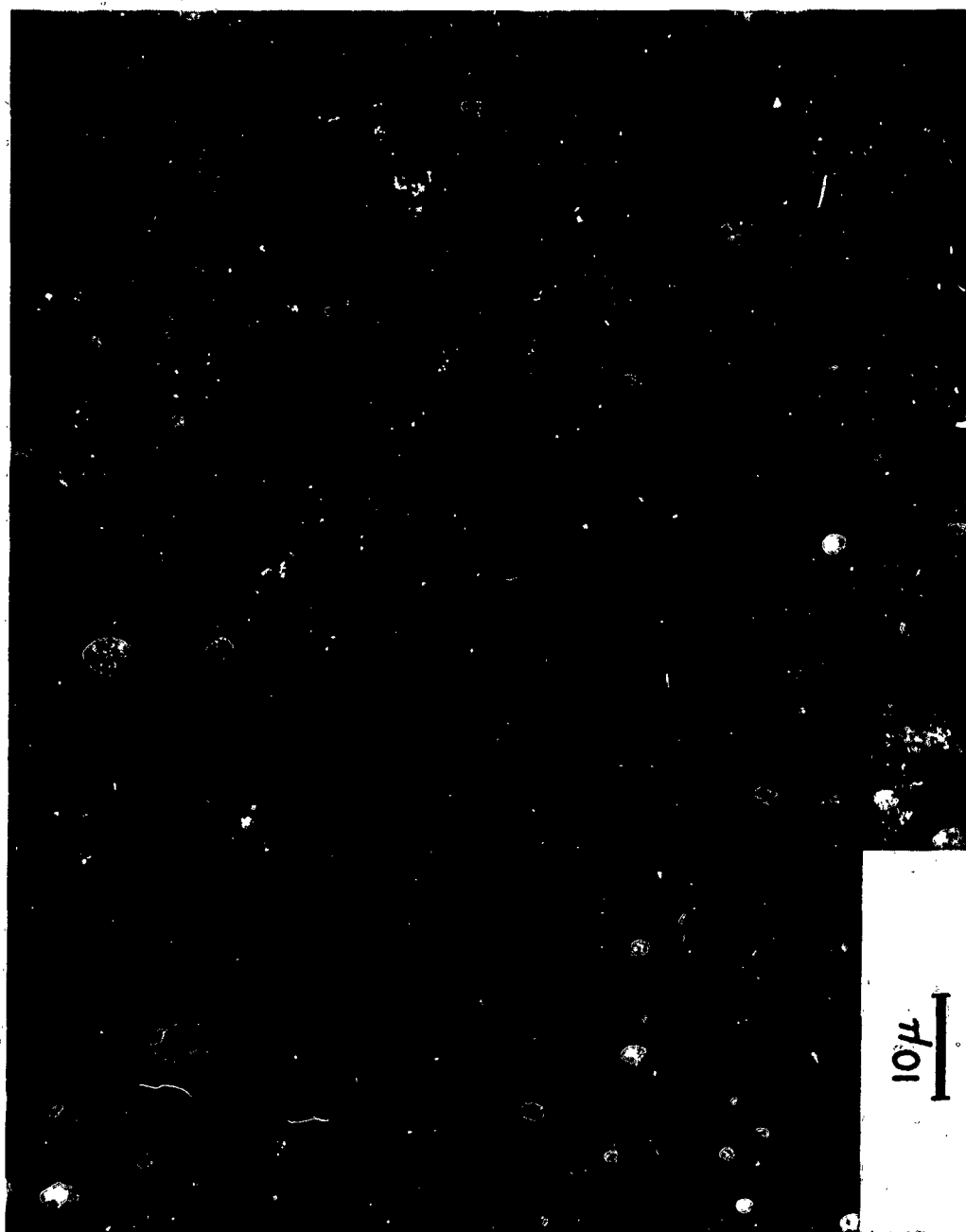
Fig. 6. Phase contrast photomicrograph X1900 showing polyblend of rubber polymerized in styrene. Dark areas are polystrene, light areas are rubber.
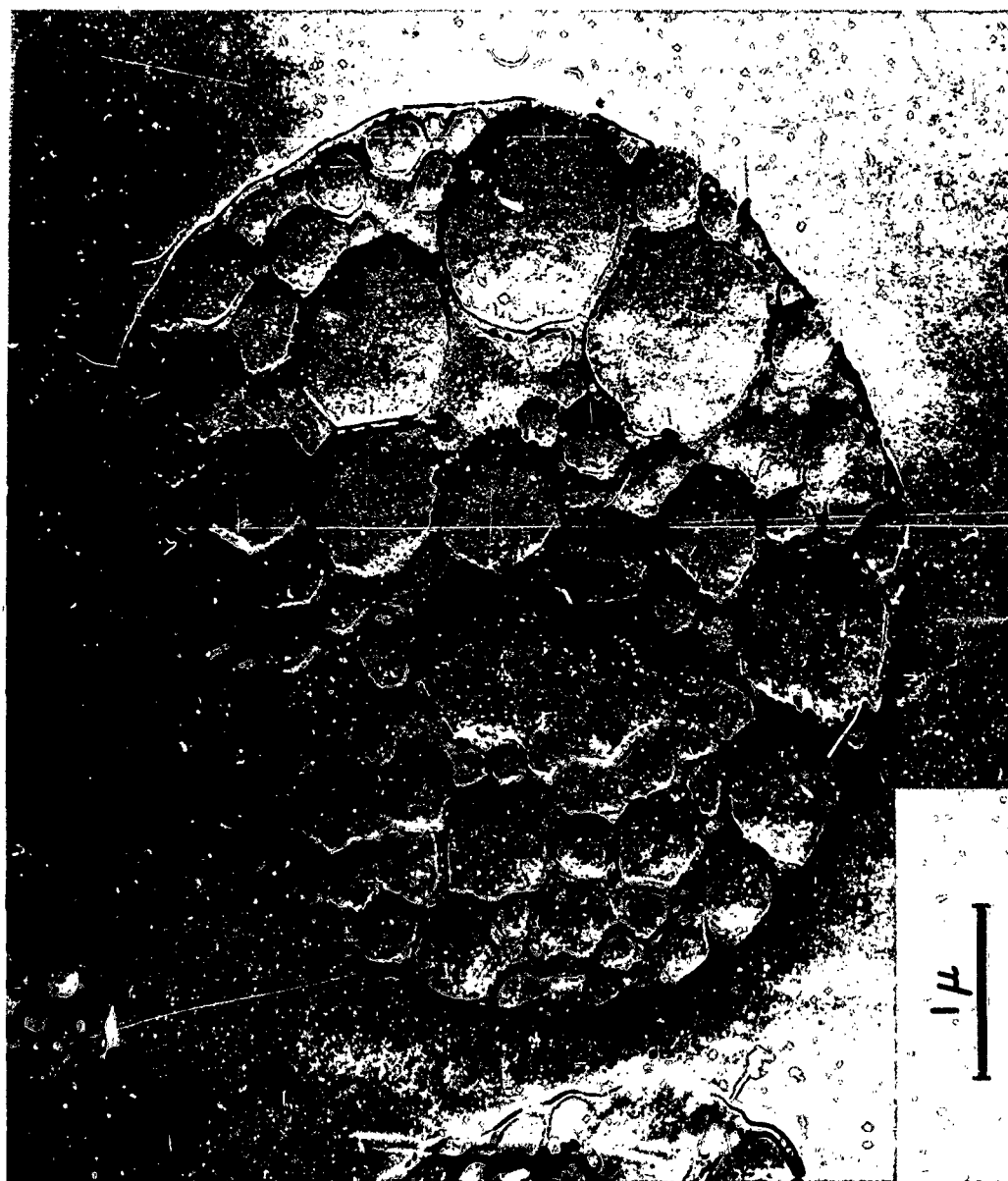
Fig. 7. Electron micrograph X31,000 of a single rubber particle from Fig. 6, showing islands of polystrene inside the rubber particle, and general complexity of such two-phase systems. Rubber and polystyrene are not mutually soluble. Graft copolymer formed by reaction of styrene with rubber molecules may reside at the interface between rubber and polystyrene and act as a polymeric soap.

a. Characterization of the continuous polystrene phase.

b. Characterization of the starting rubber.

c. Chemical fate of the rubber during polymerization; i.e.,

    (1) grafting of styrene to rubber,

    (2) cross-linking of rubber,

    (3) etc.

d. Physical fate of the rubber,

    (1) number, size and shape of dispersed rubber particles,

    (2) number, size and shape of polystyrene particles inside each rubber particle,

    (3) location of graft copolymer (which may act as a solubilizing agent) with respect to rubber particles and continuous polystyrene phase (Fig. 6 and 7 courtesy Pascal A. Traylor, The Dow Chemical Company)

## D. THE DETAILED PHYSICS AND CHEMISTRY OF POLYMER CHAINS

Given the gross chemical composition, the nature of the repeating unit along the chain, the molecular weight distribution, the various average molecular weights, and the low molecular weight components, there are still many subtle factors of both a physical and a chemical nature about the polymer chains that are not readily apparent but which profoundly affect physical behavior. These polymer parameters will now be discusse

### 1. Physical Parameters

Representation of the chemical formula of polyvinylchloride on a flat piece of paper; i.e.,

$$
\begin{array}{ccccccccccc}
 & H & & Cl & & H & & Cl & & H & & Cl & & H & & Cl & & H & & Cl \\
- & C & - & C & - & C & - & C & - & C & - & C & - & C & - & C & - & C & - & C & - \\
 & H & & H & & H & & H & & H & & H & & H & & H & & H & & H \\
\end{array}
$$
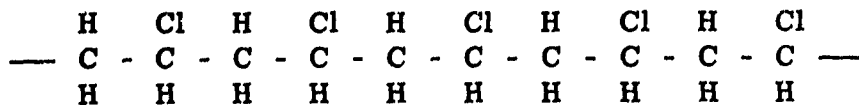
tells one nothing about its appearance in three dimensions as it must exist in a bulk polymer. There are three aspects:

(1) The shape of the hydrocarbon backbone

(2) The disposition of the substituent atoms with respect to each other

(3) Bond energetics.

a. The Backbone Chain

The backbone chain may exist as a planar zigzag



or a helix



or other forms.

In the case of polymers containing double bonds along the chain, such as natural rubber and polybutadiene, there can be

cis isomers:
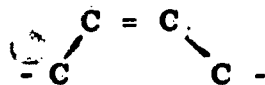


trans isomers:
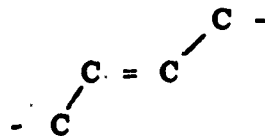


or mixtures.

Chemically, natural (Hevea) rubber and gutta percha are both polyisoprene, whose repeat unit is:

$$- \underset{\underset{H}{\overset{H}{|}}}{C} - \underset{\overset{CH_3}{|}}{C} = \underset{\underset{H}{\overset{H}{|}}}{C} - \underset{\underset{H}{\overset{H}{|}}}{C} -$$
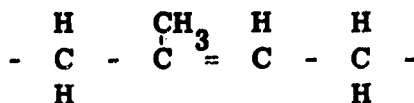
The good rubbery properties of Hevea arise because its chains all hav
the cis conformation. Conversely, gutta percha, with an all trans confor-
mation, is like a plastic rather than a rubber. Cis-trans isomer ratios
can be determined by infrared.

b. <u>Disposition of Chain Substituents; i.e., Tacticity or Touch</u>

If all of the chlorine atoms in the formula for polyvinyl chloride shown
above are on the same side of the chain, the polymer is said to be isotact
(i.e., having the same touch all along the chain).

If the chlorine atoms alternate on opposite sides

```
        H     Cl     H     H     H      Cl     H     H
  —     C  -  C  -  C  -  C  -  C  -  C  -  C  -  C  —
        H     H     H     Cl     H     H     H     Cl
```
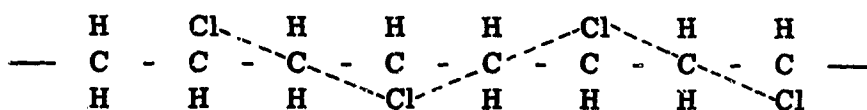
the polymer is called syndiotactic.

A random disposition, such as

```
        H     Cl---H----Cl     H     H     H      Cl---H---Cl
  —     C  -  C  -  C  -  C  -  C  -  C  -  C  -  C  -  C  —
        H     H     H     H     H     Cl     H     H     H
```
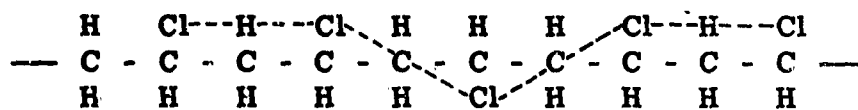
is said to be atactic.

Isotactic and syndiotactic polymers can crystallize whereas atactic
polymers are usually completely amorphous. Some polymers may have
short sequences of isotactic or syndiotactic placements which can lead to
slight crystallinity.

Polypropylene made by Ziegler-Natta catalysis is isotactic; crystalline
PVC made at low temperature is syndiotactic; polystyrene prepared ther-
mally is atactic. Polymethylmethacrylate (PMMA) can be syndiotactic or
isotactic, depending on the catalyst used.

Syndiotactic PMMA has a glass temperature of 110°C.; isotactic PMMA has a glass temperature of 60°C. In each case the chemical formula and the molecular weight distribution can be identical.

IT IS THUS OBVIOUS THAT A PRECISE KNOWLEDGE OF CHAIN CON-FIGURATION --- TACTICITY --- IS ESSENTIAL TO CHARACTERIZE A POLYMER. NUCLEAR MAGNETIC RESONANCE IS CURRENTLY THE MOST POWERFUL TOOL FOR THIS.

It frequently happens that an essentially isotactic or syndiotactic polymer will have short sequences of atactic placements. These latter will serve to reduce the maximum extent of crystallization but can be difficult to detect.

Copolymerization usually destroys crystallinity regardless of the tactic-ity situation.

c. Chain Energetics

There are four characteristic features of the polymer chain which affect its physical behavior under a variety of conditions such as in

- dilute solution
- rubbery state
- polymer melt
- solid state

These parameters are:

(1) bond distances between atoms along the chain

(2) bond angles

(3) chain stiffness or chain flex energy

(4) energy barriers to rotation about bonds

(5) interaction with solvent.

The first three affect the size of the randomly coiled polymer chain in dilute solution, in rubbers, and in melts. Chain stiffness, which affects the

equilibrium configuration of polymer solutions, can be determined from temperature variation of intrinsic viscosity or of rubber elasticity. "(e)" plays a key role in dilute solution properties. Energy barriers affect the speed with which a polymer chain can change from one configuration to another - and hence affects dynamic properties such as the bounce of a rubber ball. The excellent performance of Hevea rubber is ascribed to the ease of rotation about single bonds adjacent to the double bond in the cis-polyisoprene chain. Rotational barriers are frequently measured in the gaseous state on model compounds. The results may not apply exactly to bulk polymers, especially in the glassy state.

Polymer molecules can diffuse in the melt and in dilute solution. However, in three common states,

- vulcanized rubber,
- crystalline,
- glassy,

the entire chain cannot translate. Instead, Brownian motion of chain segments and chain ends takes place. Chain stiffness, energy barriers to rotation, and intermolecular forces, as well as packing of molecules, all play an important role in this motion.

### 2. Chemical Parameters

There are usually some chemical anomalies along the polymer chains such as:

    (a)  double bonds in or attached to the chain

    (b)  carbonyl groups resulting from oxidation

    (c)  end groups resulting from catalyst

    (d) peroxide links in the chain

    (e)  branches

    (f)  head-to-head and tail-to-tail links.

This latter item requires a brief explanation. A monomer adding to a growing chain usually does so in such a way as to preserve the normal head-to-tail addition.

```
                        head        tail    head
                          \           \     /
             H           Cl           H    Cl
    ———       C   ———     C   ———  +   C =  C
             H           H            H    H

                        head        tail    head
                          \           \     /
             H           Cl           H    Cl
    ———       C   ———     C   ———      C —— C   ———
             H           H            H    H
```
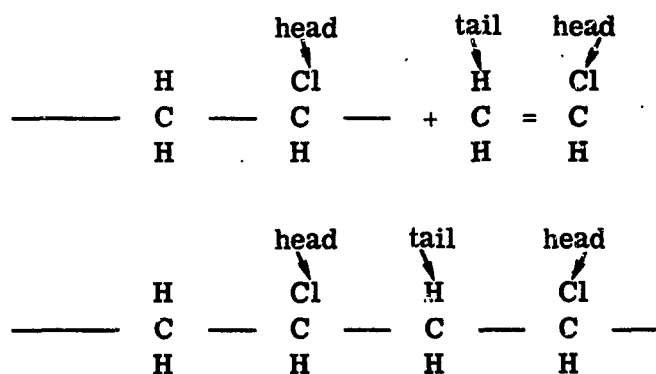
Occasionally there can be a head-to-head addition

```
           tail        head    head        tail
             \           \      /           /
             H           Cl    Cl           H
    ———       C   ———     C ——— C   ———      C   ———
             H           H     H            H
```
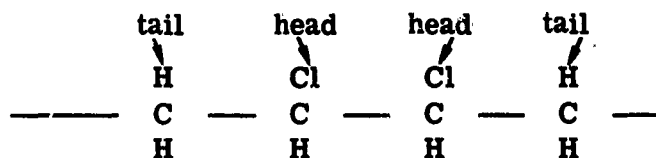
This can be a point of chemical weakness in the chain.

All of these six anomalies are usually present in very small amounts so that their detection is quite difficult.

Since these groups can affect oxidative stability, thermal stability, dielectric properties, etc., it is essential that they be studied as part of polymer characterization.

E. SOLID STATE ORGANIZATION IN POLYMERS

The long chain nature of polymer molecules leads to a very high viscosity even in the molten state. This has three major consequences:

(1) The amount and type of crystallinity as well as the number of defects

in crystal regions are very sensitive to thermal history. Complete crystal-linity is probably never achieved.

(2) There is relatively poor packing in the amorphous areas (the free volume can be 12 to 18%, depending on the definition used).

(3) In addition, the long chain molecules are readily oriented, with prop-erties strongly dependent on the amount of orientation. This orientation can be of several types:

(a) Deliberately produced, as in the making of synthetic fibers and certain polymer films.

(b) Occurring as a result of the flow processes used in fabrication.

(c) Reversible, as when a rubber band is stretched and released.

Hence it is obvious that physical properties of the solid polymer will be very dependent on previous thermal and mechanical history. Therefore, a detailed knowledge of the solid state organization of polymers is an essential part of their characterization. This will be discussed under four headings:

(A) States of Order

(B) Orientation

(C) Crystallization

(D) Free Volume

(A) <u>States of Order</u>

Table I is a list of states of order of polymers arranged in a hierarchy from complete chaos to complete order. This is not a linear hierarchy but a multidimensional one involving both orientation and crystallinity.

Various combinations of the above are possible. For example, normal amorphous noncrystalline vulcanized Hevea rubber becomes crystalline on stretching to 500% elongation, at which point the chains are oriented in

the stretch direction. On release of the stretching force, the chains revert to a nonoriented, noncrystalline state.

(B) Orientation

Many physical properties of amorphous polymers are sensitive to the amount and the direction of orientation of the polymer chains. This is shown schematically in Figure 8 below.

Figure 8



Tensile
Strength

Uniaxial orientation, properties measured II to orientation

Equal biaxial orientation, properties measured in the plane of orientation

Uniaxial orientation, properties measured ⊥ to orientation

Extent of Orientation
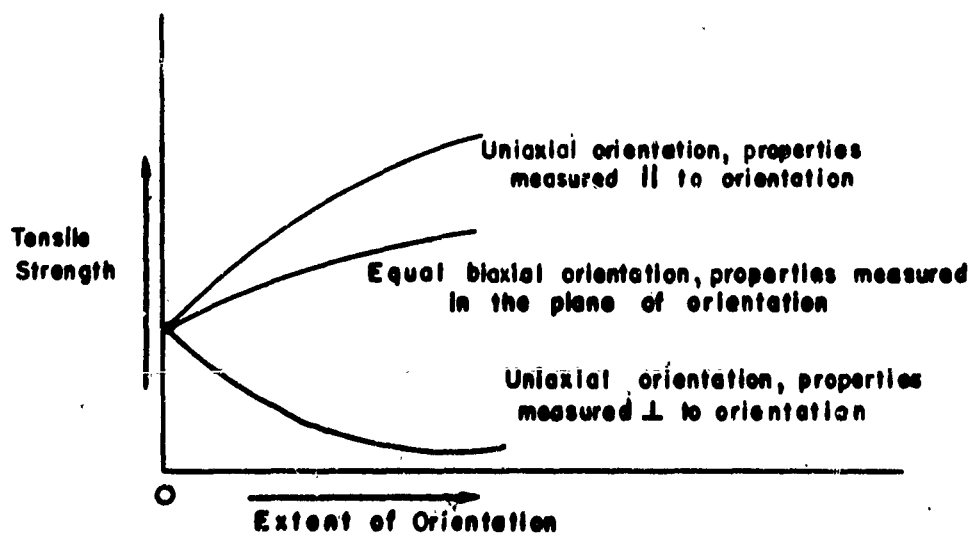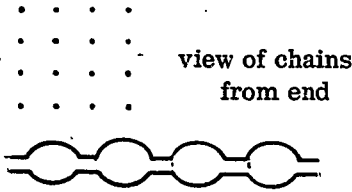
## TABLE I

### STATES OF ORDER FOR POLYMERS

| State of Order | Examples |
|---|---|
| 1. Unoriented, amorphous ≈ no correlation between direction of segments in same or adjacent chains | a) Vulcanized natural and synthetic rubbers <br> b) Glassy polymers such as polystyrene |
| 2. <br>    a. Biaxial orientation <br>    b. Uniaxial orientation ≈ adjacent chains parallel over appreciable molecular lengths, but no crystallinity | Biaxially oriented film of polystyrene <br> Uniaxially oriented fibers of polystyrene |
| 3. Two-dimensional order without orientation <br>    a. Lateral order but no lengthwise order <br>    b. Lengthwise order but no lateral order | view of chains from end <br><br> view of chains from side |
| 4. Crystallinity or three-dimensional order without orientation ≈ axes of crystallites oriented at random | Crystalline polymers such as polyethylene and polypropylene |
| 5. <br>    a. Crystallization plus biaxial orientation <br>    b. Crystallization plus uniaxial orientation | Biaxially oriented polyester film such as Mylar <br><br> Textile fibers such as cotton, nylon, Dacron |
| 6. Topotaxic Crystals | Single crystals of trioxane polymerized in the solid state by radiation to give bundles of parallel fibers with high crystallinity |

Orientation usually introduces a marked anisotropy in physical properties. Orientation may be a concomitant of the shear forces present during fabrication acting on the long chain molecules—as in extrusion, bottle blowing, etc.—or it may be done deliberately to optimize physical properties as in the preparation of films and textile fibers.

It frequently happens that a fabricated object will be isotropic over-all and yet have local regions that are highly oriented. The actual performance of the fabricated part can be controlled by these local areas which signify regions of high stress concentration.

In the case of crystalline polymers, several additional factors relating to orientation must be considered:

(1) Orientation can facilitate crystallization both by speeding up the process of crystallization and by increasing the total amount of crystallinity.

(2) The crystallographic axis may or may not coincide with the orientation axis, depending on the amount of orientation and the combined orientation-thermal history of the sample.

(C) Crystallization

The subject of crystallinity in polymers offers some novel concepts and some challenging problems of characterization. Several general levels of crystallinity should be distinguished:

(1) Low crystallinity, < 10%, as with polyvinylchloride. This is generally a result of a high atactic content in homopolymers, or to chain irregularity as in copolymers.

(2) Medium crystallinity, < 50%. This can result from a variety of causes, some of which are listed below:

| EXAMPLE | CAUSE |
|---|---|
| Low density polyethylene | Short chain branches interfere with crystallization. |
| Polypropylene | Atactic content; Insufficient nuclei; Incomplete crystallization. |
| Saran (vinylidene chloride-vinyl chloride copolymer) | Insufficient nuclei; Sluggish, and hence incomplete, crystallization; Interference from co-monomer. |

It is necessary to distinguish between the terms, crystallizability and crystallinity.

A sample of polypropylene might be 95% isotactic, hence almost completely crystallizable, and yet show only 50% crystallinity because the long chain nature of the polymer chains has interfered with the process of crystallization. There are also stereoregular polymers (especially those with long repeat units) which cannot crystallize at all because of an inability to pack into a lattice.

(3) High crystallinity, > 50%.

This is characteristic of very regular polymers such as polyethylene,

$$\left(\begin{array}{cc} H & H \\ C - C \\ H & H \end{array}\right)_n \qquad \text{and polytetrafluoroethylene,} \qquad \left(\begin{array}{cc} F & F \\ C - C \\ F & F \end{array}\right)_n$$
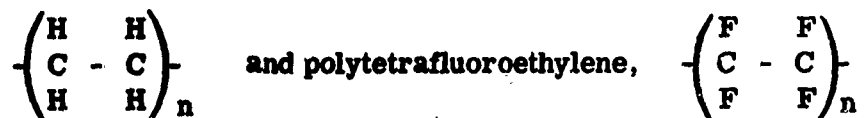
which can be in the range of 50-90% crystallinity. Single crystals can exceed 90% crystallinity, although the crystals may have many defects.

Three basic types of crystals appear in semicrystalline polymers:

(a) fringed-micelle crystals, (b) extended-chain crystals, and (c) folded chain crystals. These are illustrated schematically in Figure 9.* The fold length, h, of a folded-chain crystal increases with temperature of crystallization and/or annealing. It is usually in the 50-150 Å range.

*p. VI-37

## TYPES OF POLYMER CRYSTALS
### (SCHEMATIC)

FRINGED-MICELLE

EXTENDED-CHAIN

LOOP
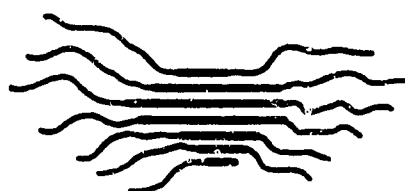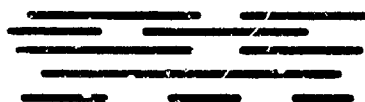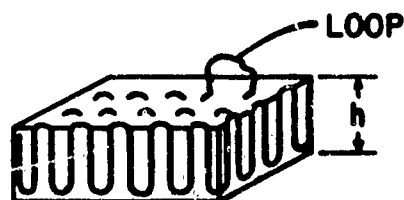
FOLDED-CHAIN

h INCREASES WITH T

## HIGHLY CRYSTALLINE BULK POLYMER
### (SCHEMATIC)

CILIA

FOLDED-CHAIN
LAMELLAE

INTERLAMELLAR LINK OR
TIE MOLECULE
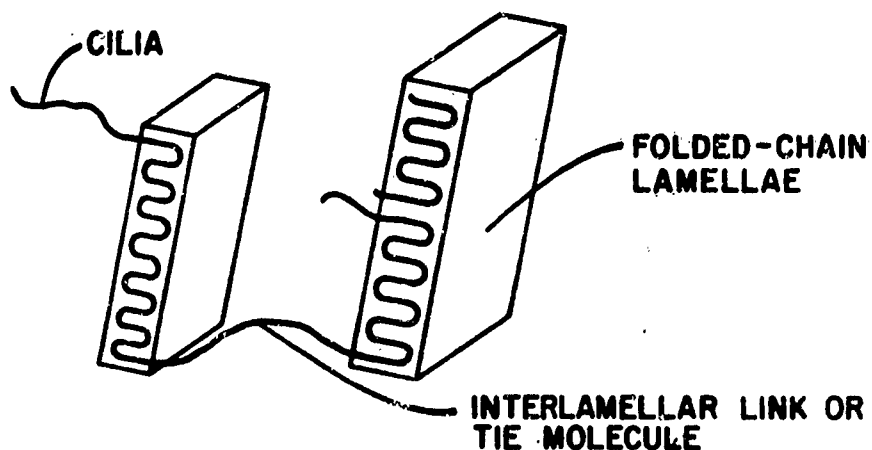
Single crystals are more or less regularly folded. Here the characterization problems involve such factors as the determination of the number of crystal defects, number of cilia, length of fold, h, and roughness of chain-folded surface. Lively disputes presently exist on these crystals, even with regard to such simple properties as the density.

Highly crystalline bulk polymers, such as polyethylene, have a basically chain-folded structure, but with many modifications. The chain-folded lamellae are often arranged in spherulites. A spherulite is a large crystallite visible in an optical microscope (dimensions in the micron range) and having circular symmetry if grown in a plane or spherical symmetry if grown in bulk. Spherulites are composed of a number of lamellae whose planes may twist as they progress from the center to the edge of the spherulite. A spherulite grows out from a single nucleus (dimensions in the Angstrom range) but gradually loses the orientation of the three crystallographic axes of the nucleus and acquires radial and tangential orientation. The ultimate radial growth of a spherulite is stopped because of impingement of other spherulites. The final polyhedral form resulting from many growing spherulites is shown in Figure 10.

Characterization problems center around such factors as the number of interlamellae links, number and type of crystal defects, number of cilia, surface roughness, and number of loops (nonadjacent re-entry). Furthermore, characterization problems occur with respect to the noncrystalline component in the semicrystalline polymer. At the present time, we know too little about how to measure the amount of the amorphous component, and we know even less about how to fully characterize this "quasi amorphous" component. The shortchain component of a semicrystalline polymer is apt to crystallize in the extended-chain form, so that a semicrystalline polymer with a broad molecular weight distribution consists of chain-folded
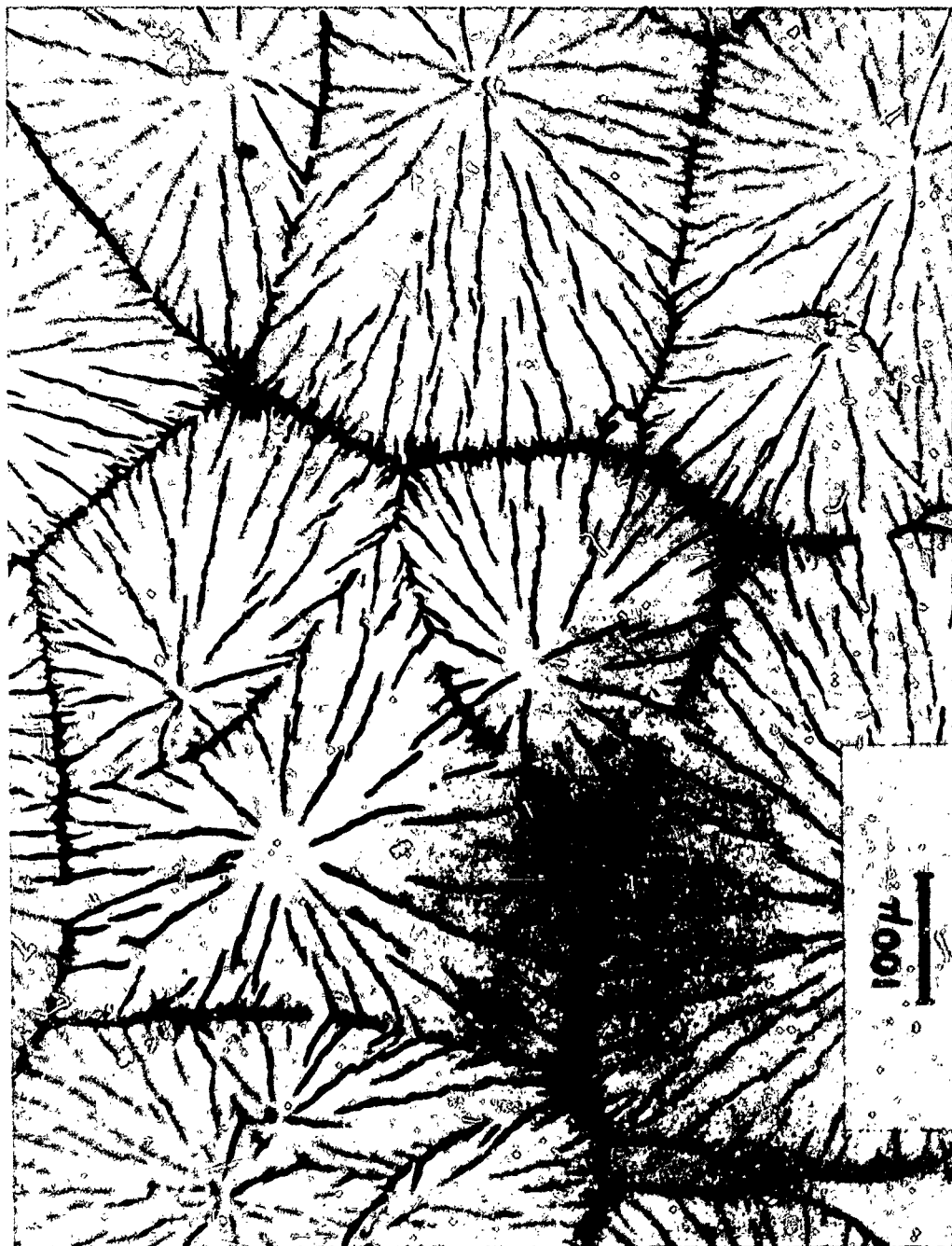
Fig. 10. Photomicrograph X340 of spherulitic structure in isotactic poly-propylene. These spherulites are usually large because of slow crystal-lization. This sample is extremely brittle because of the large spherulites as well as the voids present inside spherulites and at the boundaries between spherulites.

Fig. 11. Intercrystalline links in linear polyethylene crystallized from the melt. These links are up to 15,000 Å in length and 30-300 Å in thickness. Molecular chains are oriented parallel to the links. These links seem to nucleate on tie molecules formed by the simultaneous crystallization of different parts of the same molecule on the surfaces of two different crystals. For details, see Keith, Padden and Vadimsky, J. Poly. Sci., A-2, Vol. 4, p. 267, 1966.

lamellae + extended-chain crystals + amorphous component. Characterization of the extended-chain phase, including measurement of the fraction of it that is present, raises further serious problems. Figure 11 shows intercrystalline links (really bundles of polymer chains) between crystallites.

Rather similar problems occur in the case of the "medium crystallinity" polymers, and no major distinction is necessary, except to note that the problems with characterization of the amorphous component are relatively more important.

Low crystallinity polymers in general raise a new set of questions. The low crystallinity is usually associated with a moderate to high degree of atacticity. As has been already noted, this is itself difficult to characterize. Very little is known about how to characterize the crystals in weakly crystalline polymers. It is not known for certain which type they are—fringed-micelle, extended-chain, or folded, or some admixture thereof. It is difficult enough just to measure the amount that is crystalline.

Fibers fall into another category where basic scientific characterization parameters of the basic crystalline element are lacking. The basic crystal structure can be determined, and rough estimates of the crystallite size may be obtained, but detailed characterization parameters that link molecular and crystal behavior with performance characteristics do not exist to a sufficient extent.

In all crystalline polymers, the degree of crystallinity, texture, and indeed the performance characteristics, depends strongly on the thermal and mechanical history of the specimen in question. The basic reason is that, owing to the high viscosity of polymer melts, and the fact that crystallization is nucleation-controlled, the crystals are formed relatively slowly compared to, say, a metallic system, and thereafter change only slowly.

Therefore, states somewhat removed from equilibrium (such as a chain-folded crystal) persist for enormous periods of time in semicrystalline polymers.

As hinted earlier, the physical properties of a fabricated item will depend strongly on the crystal morphology. Figure 10 shows a photomicro-graph of a sample of polypropylene crystallized for several hours at 135°C in a thin film. (The melting point of isotactic polypropylene is 184°C.) This sample has very poor mechanical properties and can be crumbled between the fingers. Cracks or voids in the dark areas between the spheru-lites and between the fibrils presumably lead to poor strength. This same polymer crystallized rapidly at 110°C shows the normal strength of poly-propylene. A photomicrograph of this sample at the same magnification shows no detail—because the crystallites are so small— and hence is not included. While the existence of tie molecules was only recently demon-strated, it seems obvious that their presence or absence can have pro-found effects on the physical properties of a polymer. (Figure 10 is by courtesy of Padden and Keith while Figure 11 is by Keith, Padden, and Vadimski, all of the Bell Telephone Laboratories.)

## Effect of Crystal Structure on Physical Properties

Recent work by E. H. Andrews and P. E. Reed of Queen Mary's College, London, England, is so pertinent to this report that it is being quoted with their permission prior to publication:

Thin films of natural Hevea rubber were stretched to different extents and allowed to crystallize in the stretched state. The type of crystals which formed differed greatly, depending on the amount of stretch. Normal spher-ulites formed in the unstretched sample and possibly oriented folded-plate crystals in the stretched samples. The term "α crystals" signifies crystals

whose "c" axis is parallel to the orientation but which grow at right angles to the orientation along the "a" axis.

The "$\gamma$ crystals" are essentially chains of nuclei with "c" axis parallel to the orientation but with growth in the "a" direction inhibited.

The crystalline samples were cooled to -120°C so as to be in a glassy state and were measured for tensile strength.

The results are shown schematically below. The dramatic and startling effect of crystal texture or morphology on physical properties emphasizes why crystal structure aspects are considered as key characterization parameters.

Figure 12
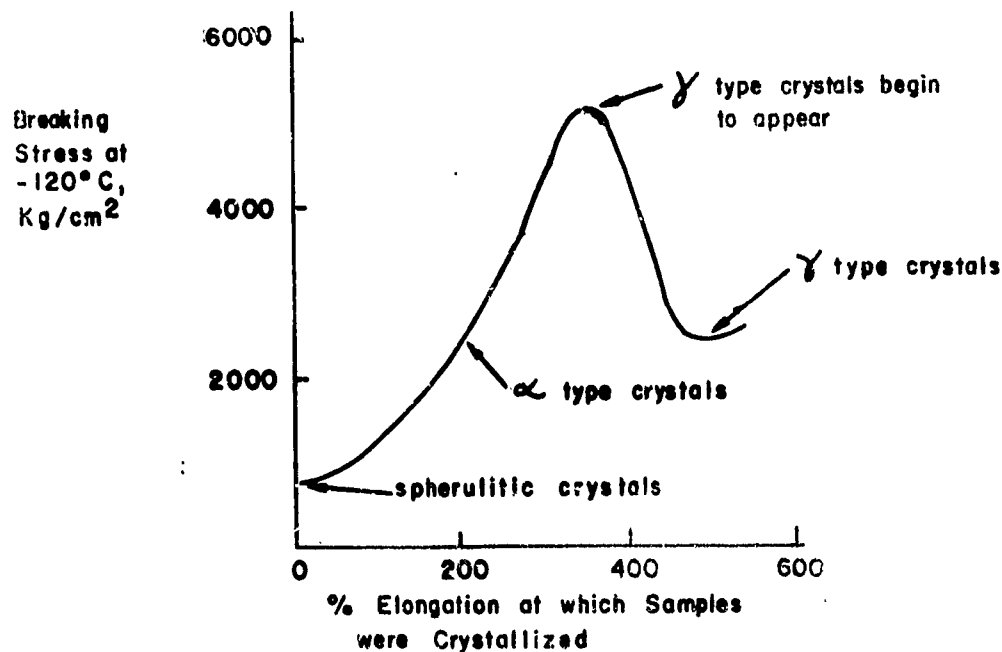


(D) Free Volume

Polymers tend to have more molecular free volume in the solid state than do other structural materials. Physical properties are quite sensitive to the actual amount of free volume present. For example, rapidly cooled

polymethylmethacrylate has 100 times faster creep rate at 20°C than does a slowly cooled sample of the same material.

The subject of free volume is a controversial one regarding concepts, definitions, and experimental data. Figure 13 is an attempt to portray one self-consistent definition of free volume for purposes of illustration. The following points are to be emphasized:

(1) An ideal crystalline polymer, completely crystallized and free from defects would expand with temperature according to the lowest straight line. It would be devoid of free volume by definition. (We avoid the melting region to simplify the drawing.)

(2) Any real polymer will follow the heavy black line for slow heating and cooling, and will possess about 12.5% of free volume in the glassy state. This amount can be reduced slightly by an annealing process just below the glass temperature; it can be increased by rapid quenching from above the glass temperature, both of which cases are indicated.

IT IS THUS OBVIOUS THAT MANY KEY PROPERTIES OF A POLYMER CAN DEPEND ON THREE SOLID STATE PARAMETERS:

- ORIENTATION
- CRYSTAL MORPHOLOGY
- FREE VOLUME OR PACKING

THESE ARE INFLUENCED BY THE PREVIOUS THERMAL AND ME-CHANICAL HISTORY OF THE SAMPLE. THE ABOVE THREE PARAMETERS CAN BE STUDIED RESPECTIVELY BY:

- POLARIZED LIGHT
- X RAY, ELECTRON MICROSCOPE, OPTICAL MICROSCOPE
- DENSITY, THERMAL EXPANSION

VI-45   FIG. 13

SCHEMATIC REPRESENTATION
OF FREE VOLUME IN A POLYMER
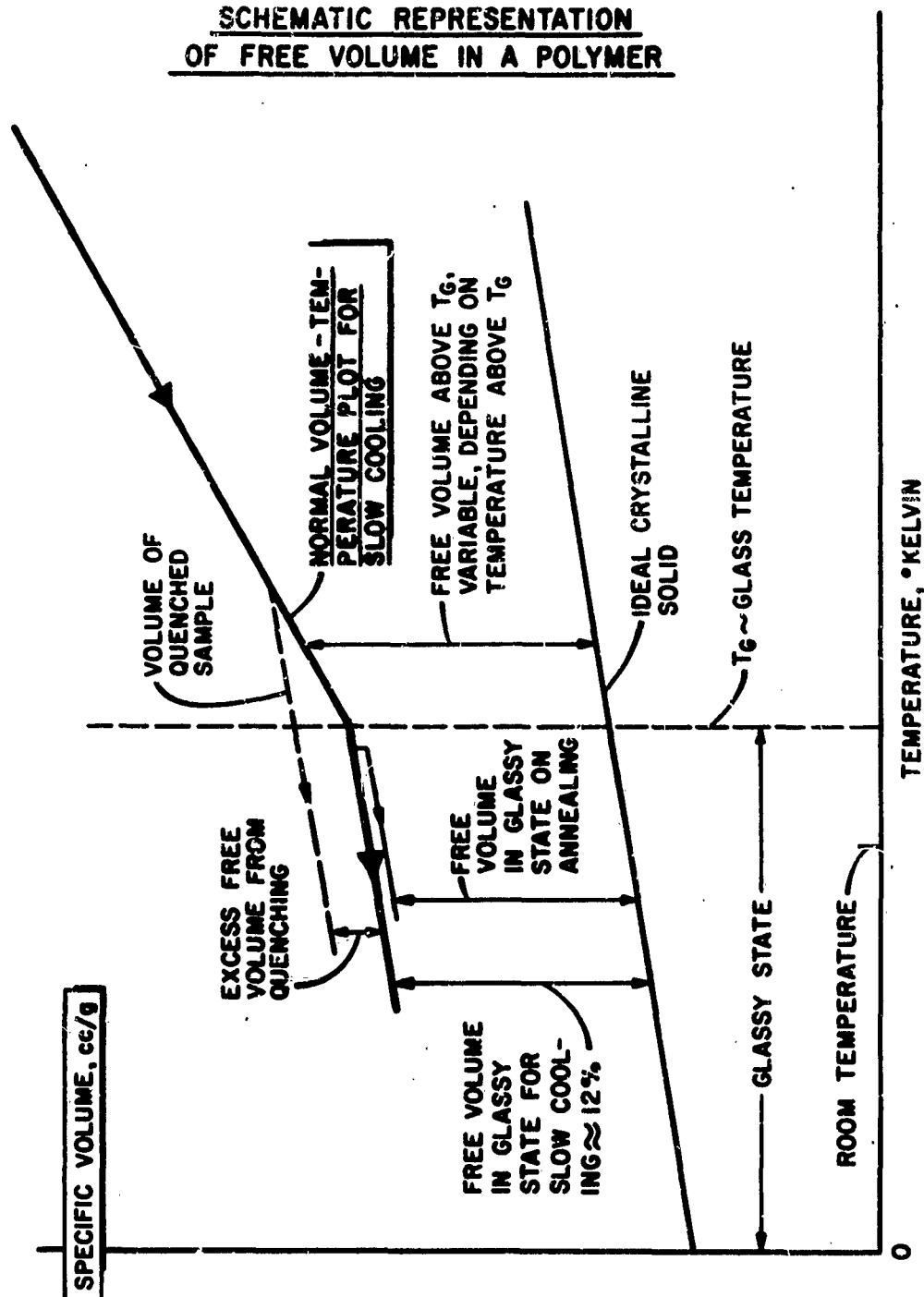
Hence, for characterization purposes, it is not sufficient to know the chemistry, molecular weight distribution, low molecular weight component. and detailed chain structure of a polymer; in addition, one must know the detailed solid state organization of the constituent molecules.

## F. SUMMARY OF CHARACTERIZATION PARAMETERS FOR POLYMERS AND COMMON TOOLS OF MEASUREMENT

| PARAMETER | COMMON TOOLS |
|---|---|
| Elemental Analysis | C, H, O, S, N Analyses |
| Repeat Unit in Chain | Infrared*, Chemical Analysis |
| Molecular Weight Distribution | Ultracentrifuge; |
| | Gel Permeation Chromatography; |
| | Fractionation |
| | |
| Average Molecular Weights | |
| Number Average, $\bar{M}n$ | Osmotic Pressure** |
| Weight Average, $\bar{M}w$ | Light Scattering, Ultracentrifuge; |
| Viscosity Average, $\bar{M}\eta$ | Dilute Solution Viscosity but |
| Z-Average $\bar{M}_z$ | Requires Calibration; |
| | Ultracentrifuge |
| | |
| Composition Distribution in Copolymers | Fractionation and Elemental Analysis |
| | Nuclear Magnetic Resonance* |
| | |
| Details of Low Molecular Weight End of M.W. Distribution Curve | Separation, Chromatography, Analysis |
| | |
| Details of Chain Physics | |
| Bond Lengths and Angles | X Rays, Electron Diffraction |
| Bond Energetics | Light Scattering, Rubber Elasticity |
| Tacticity | N M R* |
| Cis and Trans Double Bonds | Infrared* |

* Usually model compounds must be synthesized.
** There is a new technique called Elasto-osmometry described in Ref. 17, page 667 ff. For molecular weights less than 25,000 there are the three classical techniques: ebulliometry, cryoscopy, and vapor pressure lowering.

| PARAMETER | COMMON TOOLS |
|---|---|
| Details of Chain Chemistry | |
|   Double Bonds | Infrared*, Chemical Analysis |
|   Oxidation Products | Infrared*, Chemical Analysis |
|   Head-to-Head Addition | Infrared*, Chemical Analysis |
| Structure of the Solid State | |
|   % Crystallinity | X Rays, Infrared, Density |
|   Orientation | Polarized Light, X Rays, Polarized Infrared, Thermal-Mechanical Tests |
|   Packing, Free Volume | Density, Thermal Expansion |
|   Crystal Morphology | Light Microscope |
| | Electron Microscope |
| | X Rays |

## G. CHARACTERIZATION PARAMETERS VS. PHYSICAL PROPERTIES

In view of the complex problems in molecular weights, polymer chain chemistry, polymer chain physics, and solid state organization, just recited in preceding sections, it should be readily appreciated that a young science like polymers is not yet ready to bridge the gap between basic characterization parameters and ultimate performance. There are, however, a number of physical properties which do correlate rather well with ultimate performance such as:

- Tensile strength
- Modulus
- Impact strength
- Creep
- Heat distortion temperature
- Fatigue
- Etc.

* Usually model compounds must be synthesized.

Since it is not within its charter, it is not the intent of the Polymers
Panel to discuss these engineering properties. However, we must recogn
in closing this review, that there is a class of basic physical measureme\
which partake of some of the features both of characterization parameter\
and of physical properties—and which, therefore, bridge the gap between
basic molecular parameters and ultimate properties.

For example, if a semicrystalline polymer such as a high molecular
weight isotactic polypropylene with crystallinity in the range of 40-50% is
examined with an instrument which measures energy loss per electrical
or mechanical cycle at constant frequency over a wide range of temperat\
the resulting energy loss spectrum resembles that shown schematically i\
Figure 14. The assignment of the various energy loss peaks is still pro-
visional but probably correct for this relatively simple polymer.

WHILE ONE MAY PREDICT FROM MOLECULAR STRUCTURE THE
PROBABLE EXISTENCE OF SUCH LOSS PEAKS, IT IS NOT POSSIBLE,
EVEN FOR SIMPLE POLYMERS, TO PREDICT THE HEIGHT AND
BREADTH OF SUCH LOSS PEAKS NOR THE EXACT LOCATION OF
EACH PEAK ALONG THE TEMPERATURE SCALE, MUCH LESS THEIR
VARIATION WITH CRYSTALLINITY AND ORIENTATION. AND YET THE
DETAILED PHYSICAL PERFORMANCE; I.E.,

- CREEP
- ELONGATION
- FATIGUE
- TEAR
- RUPTURE
- MODULUS OF ELASTICITY
- HEAT DISTORTION TEMPERATURE

MECHANICAL ENERGY LOSS SPECTRUM FOR POLYPROPYLENE AT 1 CYCLE PER SECOND

1. MELTING POINT
2. GLASS TRANSITION
3. IN CHAIN MOTION OF 4-8 CARBON ATOMS
4. MOTION OF $CH_3$-SIDE GROUP IN CRYSTALS
5. MOTION OF $CH_3$-SIDE GROUP IN AMORPHOUS AREAS
6. CRYSTALLINE-AMORPHOUS INTERACTIONS
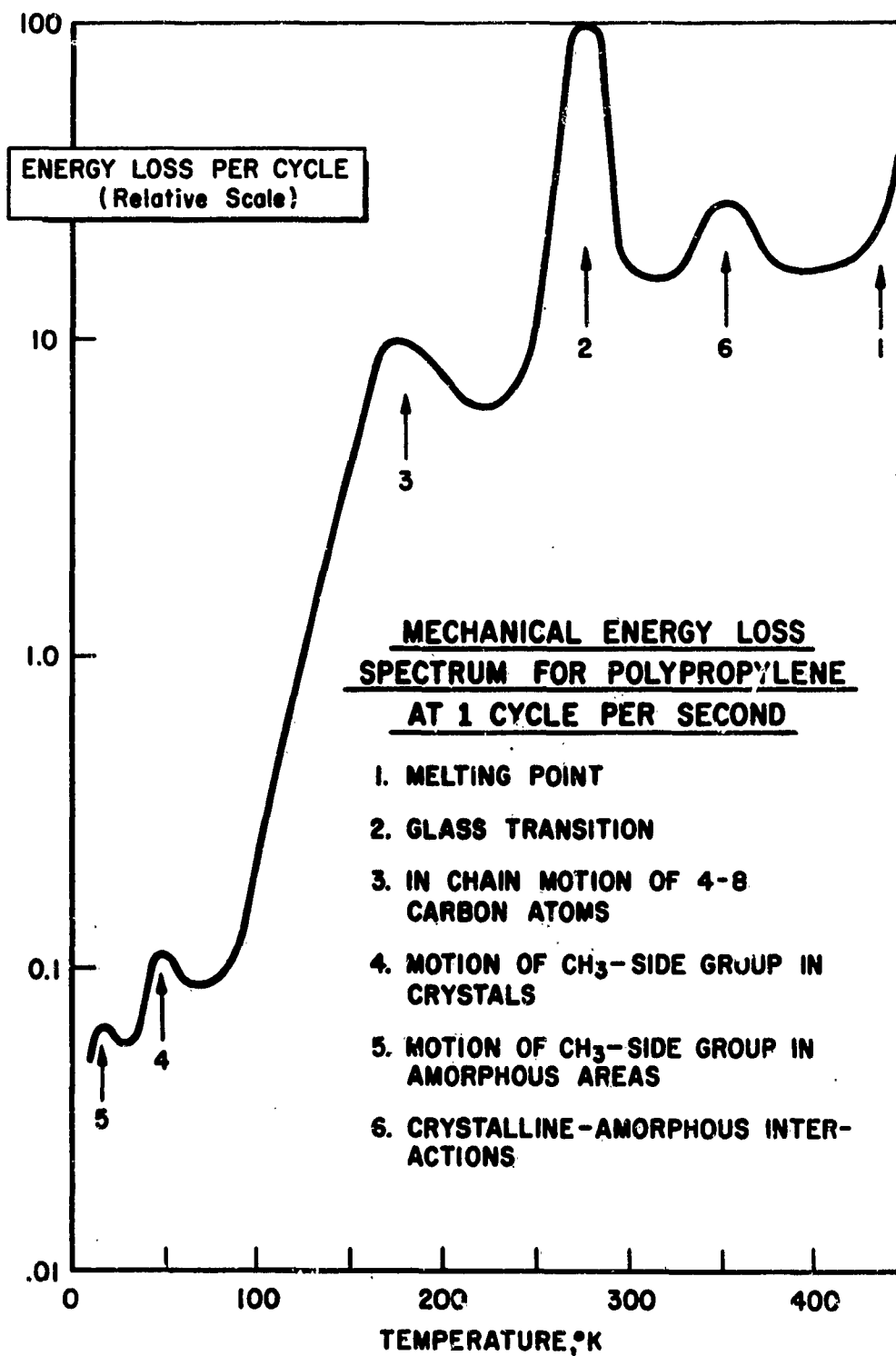
- THERMAL EXPANSION COEFF~~~ENTS
- DIELECTRIC LOSS

ETC., IS EXTREMELY DEPENDENT ON THE LOCATION OF THE MEA
SURING TEMPERATURE RELATIVE TO SUCH LOSS PEAKS.

SUCH A SPECTRUM RESULTS FROM A NUMBER OF BASIC CHAR-
ACTERIZATION PARAMETERS:

- CHEMICAL COMPOSITION
- INTERMOLECULAR FORCES
- BOND ANGLES
- BOND ENERGETICS
- CHAIN CONFIGURATION
- ORIENTATION
- CRYSTALLINITY
- FREE VOLUME

ETC., AND YET, AT THE PRESENT TIME, CANNOT BE COMPUTED
FROM THESE PARAMETERS.

Many polymer scientists feel strongly that such spectra, which give the
melting and glass temperatures as well as other relaxation regions, are
truly a part of polymer characterization. It is felt equally strongly by
many polymer scientists that thermodynamic properties such as melting
point, heat content, etc., as well as optical properties, should be part of
the characterization portfolio.

Once again the charter of this panel was to select a set of characteriza-
tion parameters with a two-fold purpose:

1. Permit an accurate description of a given polymer sample.

2. Hopefully, permit the calculation of some physical properties.

Our list of parameters, as given in Section III, is believed to be necessary and sufficient for "1." above but is not currently sufficient for "2." Our list is not intended to exclude the use of additional physical measurements.

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## LIST OF ILLUSTRATIONS FOR PART II OF SECTION VI

## III. SURVEY OF THE STATE OF THE ART ON THE
## CHARACTERIZATION OF POLYMERS

### A. THE QUESTIONNAIRE: EXPLANATION AND CRITIQUE

The Panel drew up a list of characterization parameters of importance
for polymers. These were grouped under the broad categories of Compo-
sition and Organization of Solid with various subheadings. For each param-
eter, respondents were asked to rate the present state of the art as good,
fair, or bad. They were then asked whether new instruments, new theory,
or more research effort were needed. The third question was the extent
to which the present art is used. Finally, specific comments and sugges-
tions were solicited.

The Panel accepted a concept of characterization in terms of composition,
structure, and cohesive forces. In principle, the properties of a material
can be derived from such a characterization, but this is generally beyond
the state of the art for polymers. Many of the 70 polymer scientists who
were contacted visualize characterization in terms of melting points,
glass temperatures, densities, and the like, and this was reflected in their
comments.

An attempt was made to distinguish between the state of the art (Column A)
and the extent to which it is properly used in publications and reports
(Column C). In some responses, there was such a high correlation between
these two ratings that it is suspected that this distinction was not well
understood. However, in some areas, such a correlation is considered
valid.

Answers to the question, "What is needed?" (Column B), seem to reflect
the taste of the individuals. Some saw many needs for new instruments
while others tended to favor theoretical approaches.

For many areas, those with the greatest knowledge and experience
tended to give a lower rating to the state of the art than other respondents.
Some weight has been given to individual experience in the compilation
of comments which follows.

In spite of these difficulties, there was a gratifying degree of consistenc
in the responses from various laboratories, and we believe that a true
consensus among polymer scientists has emerged.

B. STATISTICAL SUMMARY

| | A. State of Art | B. What is needed? | C. Extent of Using Present Ability | D. Number of Responses |
|---|---|---|---|---|
| | G = Good | I = New Instrum.* | | |
| | F = Fair | T = New Theory | | |
| | B = Bad | E = More Res. Effort | H = High | |
| | | No. of Responses I, T, E | M = Med. L = Low | |

1. Composition
  1.1 Homopolymers
    1.1.1 Chemical composition

| | A. | B. | C. | D. |
|---|---|---|---|---|
| Elemental | G | 13, 0, 9 | H | 59 |
| Monomer | G-F | 9, 0, 9 | H-M | 51 |
| Solid additives | G-F | 8, 3, 19 | M | 44 |
| Plasticizers | F | 7, 5, 14 | M | 41 |
| Minor impurities | G | 17, 0, 27 | M-L | 49 |

    1.1.2 Molecular weight

| | A. | B. | C. | D. |
|---|---|---|---|---|
| distribution | F | 5, 4, 6 | M | 15 |
| Broad distribution | F | 41, 18, 40 | M | 57 |
| Low M. W. components (deliberate & accidental) | F | 25, 6, 25 | M-L | 46 |

    1.1.3 Detailed chain structure

| | A. | B. | C. | D. |
|---|---|---|---|---|
| Branching | F-B | 17, 35, 48 | M | 53 |
| Tacticity | F | 16, 15, 36 | M | 58 |
| Chemical variations (end groups, double bonds, head-to-tail, etc.) | F | 20, 10, 44 | M | 51 |
| Cross-links & network topology | F-B | 18, 38, 48 | M | 57 |

  1.2 Copolymers
    1.2.1 Chemical composition

| | A. | B. | C. | D. |
|---|---|---|---|---|
| Elemental | G | 9, 1, 3 | H-M | 41 |
| Monomer | G-F | 11, 3, 9 | H-M | 39 |
| Solid additives | G-F | 8, 2, 10 | M | 41 |
| Plasticizers | F | 3, 5, 11 | M | 39 |
| Minor impurities | F | 12, 7, 12 | M-L | 32 |

    1.2.2 Molecular weight distribution

| | A. | B. | C. | D. |
|---|---|---|---|---|
| Broad distribution | F-B | 21, 19, 37 | M-L | 37 |
| Low M. W. components (deliberate & accidental) | F-B | 13, 6, 21 | M-L | 32 |

* Instruments

| | A.<br>State of<br>Art<br>G = Good<br>F = Fair<br>B = Bad | B.<br>What is needed?<br>I = New Instrum.<br>T = New Theory<br>E = More Res.<br>Effort<br>No. of Responses<br>I, T, E | C.<br>Extent of<br>Using<br>Present<br>Ability<br>H = High<br>M = Med.<br>L = Low | D.<br>Number of<br>Responses |
|---|---|---|---|---|
| **1.2.3 Detailed chain structure** | | | | |
| Branching | G | 13, 21, 31 | M-L | 31 |
| Tacticity | F-B | 10, 20, 32 | M | 36 |
| Chemical variations<br>(end groups, double<br>bonds, head-to-tail, etc.) | F-B | 17, 32, 38 | M-L | 38 |
| Cross-links & network<br>topology (Same as 1.1.3) | | | | |
| **1.2.4 Others** | | | | |
| Identity of (chain) units | F | 11, 3, 28 | M | 34 |
| Proportion | F | 11, 4, 30 | H-M | 42 |
| Sequence | F-B | 20, 18, 35 | M-L | 48 |
| Branches; grafts | F-B | 18, 11, 33 | M-L | 35 |
| **1.3 Polyblends (e.g. ABS, impact polystyrene, polypropylene + PIB)** | | | | |
| **1.3.1 Chemical composition** | | | | |
| Elemental | G-F | 5, 2, 3 | H | 32 |
| Monomer | F | 2, 2, 9 | M | 27 |
| Solid additives | F | 4, 2, 17 | M | 25 |
| Plasticizers | F | 1, 3, 16 | M | 26 |
| Minor impurities | F-B | 3, 3, 6 | M-L | 25 |
| **1.3.2 Molecular weight distribution** | | | | |
| Broad distribution | F-B | 18, 7, 22 | M-L | 37 |
| Low M. W. components<br>(deliberate & accidental) | F-B | 13, 5, 17 | M-L | 21 |
| **1.3.3 Detailed chain structure** | | | | |
| Branching | F-B | 12, 5, 20 | M-L | 26 |
| Tacticity | F-B | 9, 7, 19 | M-L | 24 |
| Chemical variations<br>(end groups, double<br>bonds, head-to-tail, etc.) | F-B | 10, 4, 13 | M | 20 |
| Cross-links & network<br>topology | B | 9, 8, 17 | L | 21 |

| | A. State of Art<br>G = Good<br>F = Fair<br>B = Bad | B. What is needed?<br>I = New Instrum.<br>T = New Theory<br>E = More Res.<br>Effort<br>No. of Responses<br>I, T, E | C. Extent of Using Present Ability<br>H = High<br>M = Med.<br>L = Low | D. Number of Responses |
|---|---|---|---|---|
| 1.3.4 Others | | | | |
|     Identity of (chain) units | F | 9, 5, 17 | M-L | 24 |
|     Proportion | F | 9, 5, 13 | M | 21 |
|     Sequence | F-B | 13, 10, 18 | M-L | 21 |
|     Branches; grafts | B | 12, 5, 19 | M-L | 27 |
| 1.3.5 Nature of interfaces | B | 24, 26, 41 | M-L | 43 |
| 1.3.6 Domain size | F-B | 16, 14, 36 | M-L | 43 |
| 1.4 Composites (not covered) | | | | |
| 2. Organization of Solid | | | | |
| 2.1 Noncrystalline (include both glasses & rubbers) | | | | |
| 2.1.1 Chain orientation | F-B | 14, 21, 30 | M-L | 40 |
| 2.1.2 Volume considerations | | | | |
|     Holes | G-F | 12, 21, 25 | M-L | 37 |
|     Free volume | F | 8, 22, 20 | M | 25 |
|     Deviations from equilibrium | F | 10, 20, 22 | M-L | 25 |
| 2.1.3 Entanglement | F-B | 10, 32, 28 | M-L | 40 |
| 2.1.4 Strain | F | 12, 14, 24 | M | 39 |
| 2.1.5 Local order | B | 16, 23, 32 | L | 41 |
| 2.1.6 Flaw structure, defects | F-B | 14, 15, 29 | M-L | 36 |
| 2.1.7 Voids | F-B | 10, 9, 26 | M-L | 38 |
| 2.1.8 Inter- and intra- (chain) potentials, barriers | F-B | 11, 24, 23 | M | 42 |
| 2.2 Crystalline | | | | |
| 2.2.1 Chain orientation | G-F | 8, 5, 14 | H-M | 34 |
| 2.2.2 Volume considerations | | | | |
|     Holes | F-B | 1, 7, 7 | M-L | 19 |
|     Free volume | F-B | 0, 5, 8 | M-L | 16 |
|     Deviations from equilibrium volume | F-B | 2, 4, 8 | M-L | 16 |
| 2.2.3 Entanglement | F-B | 3, 8, 8 | M-L | 18 |
| 2.2.4 Strain | F-B | 2, 6, 10 | M-L | 21 |
| 2.2.5 Local order | F-B | 6, 8, 12 | M-L | 22 |
| 2.2.6 Flaw structure, defects | F-B | 4, 8, 13 | M-L | 26 |

| | | A.<br>State of<br>Art<br>G = Good<br>F = Fair<br>B = Bad | B.<br>What is needed?<br>I = New Instrum.<br>T = New Theory<br>E = More Res.<br>Effort<br>No. of Responses<br>I, T, E | C.<br>Extent of<br>Using<br>Present<br>Ability<br>H = High<br>M = Med.<br>L = Low | D.<br>Number of<br>Responses |
|---|---|---|---|---|---|
| 2.2.7 | Voids | F-B | 4, 5, 10 | M-L | 18 |
| 2.2.8 | Inter- and intra- (chain) potentials, barriers | F-B | 2, 1, 10 | M | 21 |
| 2.2.9 | Fractional crystallinity | F | 10, 17, 20 | H-M | 48 |
| 2.2.10 | Defects within crystals | F-B | 13, 20, 26 | M | 44 |
| 2.2.11 | Crystal domain orientation | F | 9, 8, 21 | M | 41 |
| 2.2.12 | Structure of unit cell | G-F | 7, 6, 10 | H-M | 28 |
| 2.2.13 | Secondary structure – crystallites | F-B | 1, 3, 7 | M | 7 |
| | Lamellae | G-F | 5, 5, 21 | M | 37 |
| | Interlamellar regions | F-B | 10, 21, 29 | M-L | 38 |
| | Interlamellar links | F-B | 0, 18, 27 | L | 34 |
| | Other crystals | F-B | 4, 3, 10 | M-L | 14 |
| 2.2.14 | Tertiary structure – aggregation of crystallites | F | 7, 8, 13 | M | 23 |
| | Spherulites | G-F | 8, 8, 13 | H M | 38 |
| | Disordered regions | F-B | 12, 14, 22 | M-L | 40 |
| | Tie molecules | B | 11, 16, 28 | M-L | 31 |

## C. DETAILED COMMENTS

### 1. Homopolymers

The state of the art for characterizing the chemical composition of polymers is generally good. Better methods are needed for the determination of hydrogen, oxygen, and fluorine. There is a continuing need for improved speed and economy in the basic techniques of chemical analysis. Characterization of solid additives, plasticizers, and minor impurities involves many problems and is all too frequently neglected. These components frequently have major effects on physical properties and stability.

There is a great need for improved characterizations of molecular weight distribution, but recent progress in gel permeation chromatography and novel fractionation techniques leads us to expect considerable improvement in speed, accuracy, and reliability over the next few years. Insoluble and intractable polymers constitute an area of special need. Materials such as fluorocarbon polymers and highly aromatic polymers which are designed to serve under severe conditions frequently cannot be characterized by the usual solution techniques. The need for nonsolution characterization methods applies not only to molecular weight but also to other aspects of chain structure such as tacticity and branching.

Large quantities of pure, narrow fractions would be valuable aids in solving many characterization problems.

The presence of low molecular components such as monomer, linear and cyclic oligomers, and moisture is of great importance. Here, the problem is primarily to increase awareness and improve the utilization of existing knowledge.

The problems of detailed chain structure include branching, tacticity, and chemical variations such as end groups, double bonds, and head-to-head

vs. head-to-tail sequences in vinyl polymers. Simpler and more reliable methods are needed for the determination of branching, especially small numbers of long branches. Considerable emphasis should be given to theory in this field. The greatest advances in measurements of tacticity have involved nuclear magnetic resonance. Needs include simpler, faster, and more reliable methods and techniques for the characterization of longer sequences than are revealed at present. This may require the use of other measurements in conjunction with NMR.

· The kinetic theory of rubber elasticity is one of the greatest achievements of polymer science. Analogous to the kinetic theory of gases, it combines esthetics with utility. Nevertheless, present knowledge is considered unsatisf. ory. The density of cross-links has been emphasized but topological details such as the distribution of chain lengths between cross-links and interlocking loops have not been adequate'y treated. The characterization of very highly cross-linked systems such as thermosetting resins is in its infancy.

2. Copolymers

The state of art for the characterization of copolymers and polyblends is similar to that for homopolymers but somewhat inferior because of the greater structural complexity. For example, it is more difficult to determine the molecular weight distribution because fractionation can occur by chain composition as well as by molecular weight.

The determination of the proportions of the various monomer units is usually fairly good, although this can be quite difficult with chemically similar monomers. The problem of monomer sequences is similar to that of tacticity. Here again, much has been done on the characterization of short sequences with NMR. Experience with biological polymers shows

the importance of the structure of longer sequences. This is an area of
great need.

### 3. Polyblends

Polyblends are mixtures of imperfectly compatible polymers, usually
consisting of a rigid and a rubbery component. The nature of the interfaces
and the size of the domains are variables of critical importance, but they
are not well characterized at present. In many cases, the interfaces
involve chemical cross-linking between the components as well as physical
adsorption. Both kinds of interactions should be better characterized.
Also needed are improved microscopic techniques for the characterization
of very small particles and their agglomerates.

### 4. Composites

Composite structures, such as glass-fiber reinforced plastics, were
not included in this study. Being multicomponent systems, they involve
some of the same problems as polyblends. Studies of chemical and physical
structure at interfaces (polymer-air, polymer-polymer, and polymer-
substrate) are badly needed.

### 5. Organization of Solids

The state of the art for characterizing most parameters related to the
organization of solids is fair or bad. This is especially true for non-
crystalline glasses and rubbers. Polymers share with other forms of
matter the inadequacy of the present theories of the liquid state. The
concept of free volume has frequently been used with profit, but its meaning
is not clear and some have questioned its validity. There is a need for
better terminology and improved relationships between theory and experiment.

The local order in amorphous polymers is even more uncertain than
that in simple, low molecular liquids. In addition to the usual radial distri-
bution function, the correlation of the orientation of segments of neighboring
chains should be defined. These areas are almost untouched. Suggested

experimental approaches include x-ray and neutron scattering. There is considerable evidence for degrees of order between amorphous and crystalline structures. Liquid crystals, paracrystals, and one- and two-dimensional order have been discussed. While research in this area is more difficult than with more perfectly ordered structures, intermediate degrees of order are common in useful materials. There is great need for improvements in theory, experimental characterization, and standard terminology. This is an opportunity area.

The concept of chain entanglements has frequently been used to explain the viscoelastic properties of molten polymers. The present state of the art is highly unsatisfactory, and different methods frequently give conflicting results for the concentration of entanglements. Some workers believe that the importance of entanglements has been overemphasized. The major need is for improved theory.

Work on inter- and intra-chain potentials and barriers to rotation has increased in recent years, but much remains to be done. The conformation of polyethylene chains in dilute solutions and cross-linked rubbers has been correlated, but this has not been done for most polymers. It seems better to measure polymers directly rather than rely on extrapolations from short chain molecules. More measurements of internal pressure would be helpful in unraveling inter- and intra-molecular interactions. In many cases, the stable rotational states need to be more clearly defined.

6. Crystallography

The greatest progress in characterizing the organization of solid polymers has been made by applying the established techniques of crystallography. For the present purposes, primary crystalline structure is defined as the structure of the unit cell, secondary structure is the crystallite, and tertiary structure involves aggregates of crystallites such as spherulites.

The fraction crystallinity is widely recognized as having an important
effect on physical properties, and it is reported more frequently than most
other parameters. While the importance of a variable which distinguishes
among various degrees of order is clear, its meaning and measurement
are less so. Originally, semicrystalline polymers were thought to be divid-
ed into two phases which had the properties of perfect crystals and super-
cooled melt. More recently it has been thought that many materials are
almost entirely crystalline but that the crystals are imperfect in varying
degrees. In view of this, it is not surprising that different methods for
determining fraction crystallinity sometimes give conflicting results.
The situation is fairly good for polyethylene, but many other polymers pose
serious difficulties. There is a need for improved understanding of the
relationships of the various crystallinity-dependent properties to structure.
A more specialized need is that of methods for the determination of very
low levels of crystallinity in rubber.

Present methods for the determination of the structure of the unit cell
from diffraction patterns are considered adequate in principle, but there
is a need for speed and automation. For polymers, the diffraction maxima
are typically quite broad. This broadening can be due to crystalline imper-
fections or to small crystalline size. More work is needed to assess the
importance of these factors in various cases.

It is now believed that polymers crystallize mostly in lamellae in which
the chains are folded back and forth every hundred or so chain atoms.
While a great deal of work has been done on the characterization of lamellae,
continuing effort is amply justified. One outstanding problem is the imper-
fect correlation between the estimates of crystalline size from low angle
x-ray diffraction and electron microscopy. Another is the characterization

of lamellar surfaces, interlamellar regions, and interlamellar links. Recent studies indicate that under certain conditions extended-chain crystals can be formed and this is also an important subject to investigate.

Much has been done to describe the structure of spherulites, but better theories are needed to explain their formation. In some instances, polymers can crystallize without the formation of detectable spherulites. There is a need for better characterization and understanding of nonspherulitic tertiary crystalline structure.

## IV. AN EXAMPLE OF A MAJOR EFFORT AT POLYMER CHARACTERIZATION: THE NATIONAL BUREAU OF STANDARDS, STANDARD POLYSTYRENE SAMPLES, NO. 705 AND NO. 706

The Polymer Division of the National Bureau of Standards (NBS) is currently furnishing at cost small quantities of two standard polystyrene samples. Number 705, prepared by anionic polymerization with butyl lithium as a catalyst, has a narrow molecular weight distribution. Number 706, prepared thermally at 140°C, has a broad molecular weight distribution. These samples formed the background for Figures 2 and 4 in Section II-B.

Dr. Donald McIntyre, Chief of the Polymer Solutions Section in the Polymer Division of the NBS has kindly supplied the Panel with the Bureau data which are reproduced here in the form of Tables II and III. In reference to the Statistical Summary Table in Section III-B, it is seen that of the four pertinent sections

> Chemical composition
>
> Molecular weight distribution
>
> Detailed chain structure
>
> Organization of Solid (noncrystalline)
>
> (not pertinent for the purpose of the Bureau),

only the first two are covered on these two samples. Several additional properties, not listed by the Panel as characterization parameters, are given. This is not intended as a criticism of the Bureau effort; on the contrary, the Bureau is to be commended for its pioneering effort in having started this program five years ago.

Samples of these polymers have gone to many polymer scientists who are carrying out numerous physical measurements on them. Once all such information is assembled, these will probably be the most thoroughly studied, well-characterized polymers in existence.

It should be recognized that because these were to be certified standard samples, intended for wide distribution and with the reputation of the National Bureau of Standards behind them, considerably more time was spent in repeating and cross-checking than would normally be required. Thus, making 12 osmotic pressure, 9 light scattering, and 22 ultracentrifuge runs, as in Table II is far more effort than is normally necessary.

The Panel is greatly indebted to Dr. McIntyre who supplied us with this data to suit our deadline and well ahead of the time which he had scheduled for completion of his final report on this subject.

TABLE II
POLYSTYRENE STANDARD SAMPLE 705
Narrow Molecular Weight Distribution

| Characterization Parameters | Value(s)* | Standard Deviation of Averages* | Number of Determinations |
|---|---|---|---|
| **Chemical** | | | |
| 1. elemental analysis | | | |
| carbon | 92.07, 92.23, 92.24% | | |
| hydrogen | 7.75, 7.69, 7.74% | | |
| lithium | 0.005, 0.004% | | |
| 2. ash | 0.034, 0.037% | | |
| 3. volatiles | 0.51, 0.37, 0.69% | | |
| **Molecular Weight** | | | |
| 1. $\overline{M}_n$ (osmotic pressure) | 170,900 | 580 | 12 |
| 2. $\overline{M}_w$ (light scattering) | 179,300 | 740 | 9 |
| 3. $\overline{M}_w$ (equilibrium ultra-centrifugation) | 189,800 | 2100 | 22 |
| 4. $\overline{M}_z$ (equilibrium ultra-centrifugation) | 202,200 | 4420 | 22 |
| **Molecular Weight Distribution** | | | |
| 1. fractionation (liquid-liquid separation) | 1 determination | | |
| number of fractions | 36 | | |
| $\overline{M}_z:\overline{M}_w:\overline{M}_n$ | 1.12:1.07:1 | | |
| 2. extractions | | | |
| Number of extractions in boiling ethanol, iso-propanol, n-propanol | not detectable beyond volatile content | | |
| **Physico-Chemical** | | | |
| 1. intrinsic viscosity (m$\ell$/g) | | | |
| benzene, 25°C. | 74.3 | 0.18 | 5 |
| benzene, 35°C. | 74.4 | 0.23 | 13 |
| cyclohexane, 35°C. | 35.4 | 0.24 | 6 |
| 2. refractive index increment, dn/dc (m$\ell$/g) | 0.1705 | | |
| 3. partial specific volume, $\overline{V}$ | 0.928 | | |
| 4. specific extinction coefficient ($\epsilon$) 2615 Å | 20.89 | | |

* If the number of determinations was small, the several numerical values are given rather than calculating a standard deviation.

TABLE III
POLYSTYRENE STANDARD SAMPLE 706
Broad Molecular Weight Distribution

| Characterization Parameter | Value(s)* | Standard Deviation of Averages* | Number of Determinations |
|---|---|---|---|
| **Chemical** | | | |
| 1. elemental analysis | | | |
| carbon | 92.05, 92.05% | | |
| hydrogen | 7.75, 7.63% | | |
| 2. ash | <0.001, <0.001% | | |
| 3. volatiles | 0.73, 1.01, 0.67, 0.91% | | |
| **Molecular Weight** | | | |
| 1. $\overline{M}_n$ (osmotic pressure) | <136,000 | | |
| 2. $\overline{M}_w$ (light scattering) | 257,800 | 930 | |
| 3. $\overline{M}_w$ (equilibrium ultra-centrifugation) | 288,100 | 9600 | 4 |
| 4. $\overline{M}_z$ (equilibrium ultra-centrifugation) | 565,000 | 13,400 | 4 |
| **Molecular Weight Distribution** | | | |
| 1. fractionation (liquid-liquid separation) | 1 determination | | |
| number of fractions | 44 | | |
| $\overline{M}_z:\overline{M}_w:\overline{M}_n$ | 2.9:2.1:1 | | |
| 2. accumulative amounts | | | |
| extracted in boiling | 1 determination | | |
| ethanol | 0.8%, $M_n$ ~500 | | |
| isopropanol | 1.6% | | |
| n-propanol | 7.9% | | |
| **Physico-Chemical** | | | |
| 1. intrinsic viscosity (m$\ell$/g) | | | |
| benzene, 25°C. | 93.7 | 0.19 | 17 |
| cyclohexane, 35°C. | 39.5 | 0.10 | 4 |

* If the number of determinations was small, the several numerical values are given rather than calculating a standard deviation.

## V. RECOMMENDATIONS

### A. INTRODUCTION

In this concluding section, eleven recommendations are set forth on the following topics:

1. Detailed Polymer Chain Structure

2. Polymer Molecular Weight Distribution

3. Supermolecular Order in Amorphous Polymers

4. Structure in Semicrystalline Polymers

5. Network Topology

6. Intractable Polymers

7. Polyblend Composition and Structure

8. Model Compound Study

9. Characterization Education and Encouragement

10. Characterization Newsletter

11. Research Project Philosophy

Recommendations 1 through 8 deal specifically with polymer characterization research areas deserving special intensive effort during the coming five-to-ten-year period. Recommendations 9 through 11 are concerned with educational and information dissemination aspects of the characterization problem. Within each recommendation an attempt will be made to indicate

(a) the nature of the material characteristic involved,

(b) relevance of the characteristic to physical properties and polymer use,

(c) some measurement methods and research tools presently employed, and

(d) possible intermediate gains during research prosecution.

No attempt will be made to predict ultimate results of the recommended programs since it is the firm belief of the Panel that scientific and technological advances evolving through current research efforts can change completely within a few years the goals toward which the research was initially projected.

The listed recommendations are in large measure the result of this panel's interpretation of the responses to and comments on the Characterization Parameters for Polymers questionnaire presented in Section III of this report. In addition to the questionnaire-derived recommendations, there are interjected research area recommendations developed by deliberations of the Panel. Column B in the questionnaire summary may be consulted for an indication of response load and relative needs according to the opinions of the responding experts.

It cannot be emphasized too strongly that the present report concerns itself solely with the chemical and physical characterization of polymers in terms of their molecular structures and modes of molecular arrangement into bulk polymer systems. Characterization is an essential first step in understanding and correlating fundamental characteristics of polymers with their physico-chemical behavior and their technological utility. Polymer properties such as chemical stability, processibility, modulus and strength, etc., can be studied profitably only within a framework of well-characterized initial polymer materials and successful analysis of changes which occur in the basic molecular and aggregate structures in response to environmental forces.

It is therefore recommended that special emphasis and support be given to research in eleven areas of polymer characterization, divided into two categories, given as "B." and "C." below.

## B. RECOMMENDATIONS ON POLYMER CHARACTERIZATION RESEARCH

### 1. Detailed Polymer Chain Structure.

The chemical identities, locations, and spatial configurations of the units which make up polymer chain structures need more exact and facile analysis. In chains containing more than one type of unit (copolymers, terpolymers, etc.), not only the relative amounts of the chemically different units are important but the distribution of repeating sequence lengths needs to be known. For instance, polymers containing two chemically different units may be rubbery or rigid depending on whether the units of one type occur in long sequences (block copolymers) or occur randomly distributed throughout the chain (statistical copolymers). Even in homopolymers (polymers containing a single type of chemical chain unit), the spatial arrangement of side groups in successive units needs specification. The ability of some polymers to crystallize is dependent upon a high degree of spatial order (stereoregularity) of the groups in successive units. Correlation of physical properties of polymer samples from different sources can be extremely difficult and misleading if proper characterization of the molecular "fine structure" is not available.

Methods presently available to analyze detailed polymer chain structure differ according to polymer chemical type and complexity. Synthetic and analytic determination of amino acid sequences in biologically important molecules is a good example of chemical analyses coupled with chromatographic separations, infrared spectroscopy, and model compound study. Chemical degradations of susceptible units in copolymers have allowed assignment of unit sequence sizes in copolymers through analysis of the chain degradation products. Nuclear magnetic resonance (NMR) spectroscopy has been the most powerful tool in establishing the spatial (configurational) order of side groups in homopolymers. Even here ambiguity exists

in many instances and an assignment of structure requires a combination of NMR, infrared, and x-ray evidence and some inductive reasoning.

Improved ability to characterize polymer chain structure will assist in evaluating the mechanisms of polymerizations, the factors influencing the aggregation of polymer molecules into supermolecular random or ordered structures, and the interplay of detailed chemical composition with engineering properties of the bulk materials.

2. Polymer Molecular Weight Distribution

As was indicated in Section II of this report polymers are comprised not of molecules of a single size, but rather of normally broad ranges of molecular size. The analysis of molecular weight distributions by fractionation and determination of average molecular weights has proceeded from the earliest recognition of this factor in the late thirties and early forties. The essentially equivalent chemical nature of the different size species (homologs) within a polymeric material has made sharp, clear separation and analysis of the polymer molecules according to molecular weight difficult. Separations have depended upon small differences in thermodynamic interactions (chemical potentials, partial free energies) or upon small differences in transport properties (sedimentation, diffusion, viscosity, etc., of solutions). Physical chemical methods of deter ining average molecular weights (moments of the distributions) by dilute solution techniques such as light scattering, ultracentrifugation, viscometry, and osmometry are reasonably well developed although standardization among laboratories and reproducibility need improvement. The recent advent of gel permeation chromatography (GPC) offers one of the first rapid displays of a function of a polymer molecular weight and/or molecular size distribution.

The greatest need is the development of new rapid, inexpensive methods of molecular weight distribution analysis. Such methods would permit quick

feedback of information to synthesis groups of both large and small research
and development organizations. On-line control of polymer molecular
weight distribution in production facilities could result. Research pointed
toward understanding the controlling factors in new molecular weight
display methods should be supported to serve as a basis for further tech-
nological advances. Special help is needed for high melting polymers and
for water-soluble polymers.

The importance of molecular weight distribution to the bulk chemical
and physical properties of polymers has received increased attention
during the past decade. Low molecular weight polymer or nonpolymer
impurities can greatly affect the thermal, chemical, and radiation stability
of a material. The degree of Newtonian behavior of polymer melt flow is
now known to be closely related to the molecular weight distribution breadth
and shape. Polymer processibility is thereby greatly influenced. The degree
of stress retention (elastic memory) in molded plastic artifacts is related
directly (although at present not quantitatively) to the flow characteristics
of the melt. The effects of molecular weight distribution upon ductility,
brittle fracture, crazing, crystallization kinetics and morphology, and
many ultimate property manifestations can be determined only through
careful, accurate, and complete distribution characterizations.

3. Supermolecular Order in Amorphous Polymers

The term "amorphous polymer" means literally a polymer having no
structural order beyond that of the arrangement of chemical groups in the
molecular chains. However, there are known to be varying degrees of
order or molecular aggregates and alignments even in the most "amorphous"
polymers. The nature, extent, and quantitative description of these degrees
of order deserve research support. Without such characterization, the

properties of glassy polymers cannot be correlated satisfactorily. Even rubbery polymers exhibit "anomalous" physical behaviors which may require supermolecular order characterization to clarify.

Unintentional residual stresses in extruded or molded plastic articles were mentioned in considering effects of molecular weight distribution on melt processing. Such stresses are the result of nonrelaxed orientations (residual supermolecular order) in the processed polymer. Intentional orientation is also possible through cold-drawing operations in processing. A polymer may thereby be strengthened in a single direction (drawn fiber) or biaxially in a plane (oriented film). Although the effect is greater in semicrystalline polymers, some advantage thereby can be achieved in amorphous polymers. Even beyond the obvious orientation and mechanical anisotropy which may be introduced into amorphous polymers by external forces, there is reason to suspect that a degree of natural order, dictated purely by local internal molecule-to-molecule force fields, exists. Characterization of, or disproof of, such "innate order" can contribute strongly to the understanding of the macroscopic behavior of polymers.

Characterization of supermolecular order in amorphous polymers is at present attempted principally by optical (polarized light) observations and rheological (stress relaxation) measurements. New measuring methods and quantitative order parameters need to be formulated in order to advance in this area.

### 4. Structure in Semicrystalline Polymers

Detailed characterization of the supermolecular states of aggregation in semicrystalline polymers is vital. Concentration should focus on structures achieved by the crystallization of polymers from their molten states. Primary structure (crystal lattice parameters and repeat units), secondary

structure (crystal lamellae, fold surfaces) and tertiary structure (arrange-
ment of lamellae in spherulites, interlamellar region material, spherulite
contact regions, amorphous polymer content and condition) are descriptive
terms applied to semicrystalline polymer structural content. There is
today a large research effort being directed to understand this area.
Support is important now and in the immediate future although the need
for special emphasis could disappear in the coming five years.

Semicrystalline polymers constitute the basis of all high-strength poly-
mer fibers and films. Uniaxial or biaxial orientation imposed during
processing produces large increases in tensile strength and other desirable
properties. Control of crystal nucleation to the extent of introducing large
numbers of crystal nuclei and consequently large numbers of small spheru-
lites enhances the strength. Characterization of the microscopic and sub-
microscopic structures in these polymers will aid both in process improve-
ments and in establishing uniformity of end products.

Several experimental methods have been applied to characterize the
primary, secondary, and tertiary structures. X-ray diffraction and electron
diffraction give information concerning the crystal cell units. Low-angle
x-ray diffraction and thermodynamic measurements have given information
on the secondary (lamellar) structures. Some attempts to characterize
lamellar surfaces have been performed by infrared observations, selective
radiative cross-linking, and selective oxidation. Light optics are applicable
to the observation and characterization of spherulite structures. Rapid
advances are now taking place in the observational techniques (e.g., low
voltage electron beams, improved electron microscopy, simpler calori-
metric arrangements) and ad hoc theory formulations are possible thereby.

## 5. Network Topology

There is now need to know the detailed structure of three-dimensional polymer networks. These networks are exemplified by cured rubbers and thermoset or otherwise cross-linked plastics. The available theoretical bases for describing such nets rely mainly upon a random disposition of tie points (cross-link or branch points) throughout the material. Such assumptions lead to models of the networks which have known distributions of elastic chain lengths which can be treated by statistical thermodynamic analyses. Unfortunately, the sequential (noninstantaneous) methods by which the polymeric networks are produced chemically lead to actual network structures of unknown complexity. Methods of analysis and theories of structuration of actual networks require development. Just as the importance of molecular weight distribution shape upon physical properties of thermoplastics has recently become recognized, there is now developing a realization of the possible intimate relation of network topology to the physical properties of thermosets and cured rubbers.

In a sense two fairly distinct classes of polymeric network materials exist. One is the cured rubber network which has about 0.5 to 3% of its units involved in cross-link junctions. The second class is comprised of rigid thermoset polymers normally formed by condensation reactions of multi-functional monomers giving rise to "cross-link junctions" involving perhaps more than 20% of the units. Network topology characterization methods of differing sorts may be necessary for the loosely and tightly cross-linked nets.

The present state of network characterization customarily involves analysis of solubles extraction, gel swelling, and elastic response data on the materials using random cross-link disposition theory to systematize the findings. Some networks are studied by synthesis or degradative analysis

procedures tailored to minimize deviations from random statistical structure obedience. Even here, however, resort to a theoretical model is used in the analyses.

### 6. Intractable Polymers

The emphasis upon discovery and development of polymers capable of withstanding extreme environments (high temperature, low temperature, corrosive atmospheres and fluids, exotic fuels and lubricants, intense radiation fields, etc.) has created a distinct characterization problem within the past decade. A large fraction of such polymers are high melting or infusible below decomposition temperatures and are solvent resistant. Such polymers are here termed intractable. Many characterization methods rely upon dissolving polymers to low concentrations and studying the properties of the resultant solutions. For intractable polymers, special experimental approaches need to be devised for characterization at the molecular level. Even supermolecular instrumental methods and bulk spectroscopic techniques often require sample preparations made difficult by the chemical and physical resistance of these polymers. Support should be extended to all reasonable proposals of novel experimental and conceptual approaches to the characterization of intractable polymers.

### 7. Polyblend Composition and Structure

The characterization of polyblends (materials containing two or more polymers intimately blended) has the same complexity as that of individual polymer characterization plus the added difficulties of polymer species chemical heterogeneity and compatibility. Due to the tendency of a polymer to be immiscible with another polymer, most polyblends exhibit two-phase or multiphase microstructure. The morphology of polyblends at all levels of subdivision needs research. New, rapid methods are needed to separate

polyblends into their constituent molecular species and to analyze these species. Unambiguous analysis without separation would be an even more desirable goal.

Technology has capitalized upon synergistic combinations of polymers to achieve desired mechanical properties. A well-known class of polyblends is that of high-impact plastics. These in general consist of glassy polymer matrices containing a dispersion of small spherical particles (e.g., .5-100 micron diameter) of rubbery polymer. See Figures 6 and 7 in Section II-C-6. The polyblend retains essentially the high modulus (rigidity) of the glassy polymer, but has increased impact strength due to the energy dissipation ability of the rubbery inclusions. The growth of graft and block copolymer synthesis and technology is rapidly expanding the number and complexity of useful polyblends. Characterization research has not been able to keep pace with this growth. Separation procedures in polyblend analysis consist almost entirely of differential solubility techniques. Pyrolysis coupled to vapor phase chromatography has proven useful in identifying the constituent polymers. Discrimination between mixtures of pure polymers, mixtures of polymers and their block copolymers, or pure block copolymers has been difficult.

Gains in ability to characterize polymer blends will have immediate impact in modern materials technology.

### 8. Model Compound Study

The characterization and study of low molecular weight compounds which can serve as nonpolymeric analogs of polymers deserve increased attention. There exists in all polymer characterization efforts a need to separate phenomena arising simply from the chemical nature and local structure of a polymer from those phenomena that are peculiar to the high

molecular weight and chain structure per se. This is very important to dispel misconceptions and confusions which are prevalent in interpreting polymer behavior. All too often investigators studying polymers lose perspective. Not having at hand knowledge of basic characteristics of low molecular weight analogs, the investigator may be prone to invoke unwise speculative correlations between observations and polymeric structure.

The value of model compound research lies in part in the increased ease and variety of measurements which are accessible. Although a well-developed art (or science) exists for handling and manipulating polymeric materials for characterization, their intrinsic high viscosity, diffuse phase transitions, and nonvolatility complicate physical measurements.

## C. RECOMMENDATION ON EDUCATIONAL AND INFORMATION DISSEMINATION ASPECTS OF CHARACTERIZATION

### 9. Characterization Education and Encouragement

Fundamental to advances in sophisticated polymer technologies is the education of research and development personnel in the necessity for careful, complete, and accurately reported characterization of the materials with which they work. The amount of research data rendered valueless due to lack of knowledge of polymer purity, structure, and handling history is enormous. In the early years of polymer research and development, some value accrued from establishment of the gross physical and chemical behavior of poorly characterized polymers. The lack of characterization was excusable upon the bases of instrumentation limitations, manpower limitations, and inadequacy of theoretical framework. Present and future rapid development in polymer utilization demand characterization sophistication at least commensurate with the property measurement sophistication now in place.

Throughout the present report no indication has been given of the numerical accuracy and reproducibility of measurements employed in characterizing

polymers. (Section IV on a specific polymer molecular characterization is excepted.) The omission of quantitative specifications was intentional for two reasons. First, the approach of this panel was to attack the characterization problem from the angle of characteristic parameters of the polymers rather than from the measurement tools and methods involved. A critical evaluation of the tool and method capabilities in quantitative terms is indeed in order. Such evaluation should proceed from formal conferences (with documented proceedings) comprised of working specialists in the measurement fields. The second reason for this panel's omission of quantitative specification of polymer characterization is the present incompleteness of data. Indeed, the questionnaire formulation of characteristic parameters required extensive deliberation. Having delineated the areas, future advance should now be facilitated.

Reporting of quantitative characterization of polymers can be encouraged by publication referee insistence upon it. Although thorough characterization cannot be required for every material, a referee's knowledge of minimum requirements to specify the nature and state of samples relevant to the physical properties is a reasonable assumption. Gradual increase in characterization completeness should accrue from referee pressure.

The necessity for characterization needs more emphasis in the curricula of Materials Science Departments of our University and Technology Institute training grounds. Such emphasis can be fostered by requirement in research project funding that characterization is a necessity. In some respects, increase in interdisciplinary efforts is needed to foster polymer characterization and property study coupling. In the past, physicists and engineers have often been willing to study extensively polymers of ill-defined chemical composition. Similarly, chemists have studied polymer reactions without

definition of physical state properties which could greatly affect the chem-
ical processes. These fragmented, poorly controlled research practices
must be minimized.

### 10. Characterization Newsletter

Serious consideration should be given to the establishment of a charac-
terization newsletter to speed the dissemination of characterization develop-
ments and to encourage an awareness of characterization need in the field
of polymer research and development. A study group should be formed to
determine the best and most effective mode of publishing such a newsletter.
This publication might be inserted as an intrinsic, concise section in an
existing technical journal or separately as a "flyer" of sufficient brevity
and attractiveness to invite perusal and action.

### 11. Research Project Philosophy on Funding Research Projects

It is recommended that polymer research projects supported by govern-
ment funds be tailored for longer periods to allow sufficient character-
ization of starting materials and end materials. The lengthened research
period should not simply allow for more characterization but require such
characterization both in the proposal and in the reporting. Only by such a
requirement can the results of the research be used and correlated at a
future date with research on similar materials at the same or other loca-
tions. In addition to increased value of the research findings in specific
supported projects, the realization of the value of improved characterization
will foster characterization in other areas of an institution's operations.
An educational function is served by the characterization requirement.

This means that those who read and approve research contract proposals
should insist on more attention being given to characterization.

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13. ABSTRACT

The term, Characterization, as used in this report means essentially a description of those features of the composition and structure (including defects) of a material that are significant for a particular preparation, study of properties, or use, and suffice for reproduction of the material. Such work on characterization is, at present, fragmented as a field. While practically every laboratory using materials makes some specialized measurements which may partially define a material, rarely (if ever) do we get independently and thoroughly characterized materials. In a word, materials characterization, the cornerstone of materials science, is a neglected field. This committee, charged with making a detailed study of characterization in terms of composition, structure, defects, polycrystals, and polymers, has documented the state of the art in our ability to prepare a material, analyze it (composition, structure, and defects), and in turn to correlate these to property measurements. The study also assesses the situation surrounding some of the greatest needs for characterization; e.g., (a) better techniques and instruments, or more and better use of existing techniques and instruments, (b) better characterization for improved preparation of materials, or for improved study of materials, or for improved use of materials, and (c) more accurate and detailed characterization of materials in general, or just certain features of certain materials. (U)

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| Materials Character | | | | | | |
| Characterization of Materials | | | | | | |
| Properties of Materials | | | | | | |
| Analytical Techniques Used in Materials Characterization | | | | | | |
| Characterization of Materials in Terms of Composition, Structure, Defects | | | | | | |
| Characterization of Polycrystalline Materials | | | | | | |
| Characterization of Polymers | | | | | | |
| Characterization of Single Crystals | | | | | | |
| Relation of Properties of Materials to the Character of Materials | | | | | | |