SOLID STATE
PHYSICS

Advances in
Research and Applications

Editors

HENRY EHRENREICH

DAVID TURNBULL

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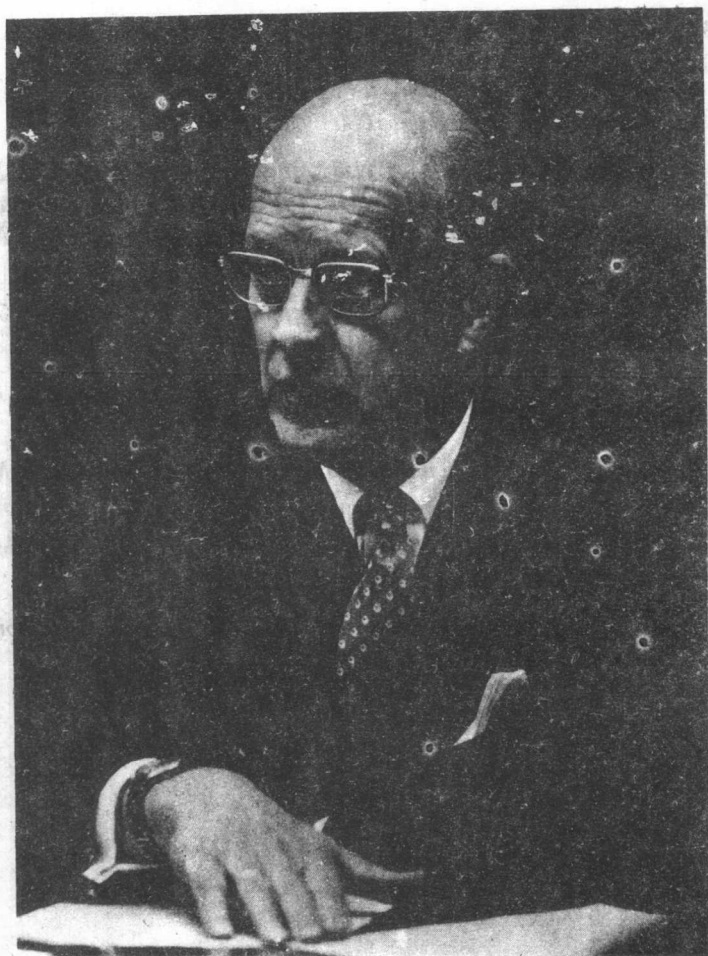
Frederick Seitz

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Foreword

This volume marks the transition of Frederick Seitz's role in this publication from that of active coeditor to founding editor.

Seitz's treatise on "The Modern Theory of Solids," published in 1940, played a major, perhaps the major, part in distinguishing and delineating the then fledgling discipline of solid state physics. It became a prime source of instruction and inspiration to a whole generation of solid state scientists. As the field grew and flourished following World War II, Seitz felt a pressing need to revise and expand the treatise. However, it seemed that the scope and magnitude of the task required had become too large for any one person to encompass in a single volume. Paraphrasing, remarks in his biographical notes [see "The Beginnings of Solid State Physics" (N. F. Mott, ed.), *Proc. R. Soc. London, Ser. A* **371**, 84–99 (1980)], this situation contrasted sharply with that in the 1930s, when the total volume of experimental and theoretical literature dealing with the properties of solids was sufficiently limited that it was possible to become familiar with essentially every significant paper in the areas covered in "The Modern Theory of Solids." Faced with the new situation, he concluded that the need for coverage might better be met by a multivolume work consisting of comprehensive and in-depth treatments of basic topics by a number of experts, and one of us (D.T.) accepted his invitation to join in the planning and editing of such a series. The late Kurt Jacoby, then vice president of Academic Press and a former Akademische-Verlag editor and refugee from Germany, enthusiastically encouraged the project and arranged to have the volumes published by Academic Press, beginning in 1955. Later, in 1967, the other of us (H.E.) accepted an invitation to share in the editorial responsibilities.

Seitz's broad perspective and extraordinary profundity as an author and editor reflect a scientific career distinguished by major contributions to all of the principal branches of condensed phase science. He was one of the small group who pioneered the development of modern solid state theory. His paper, in collaboration with Wigner, deriving from first principles the cohesive energy and other electronic properties of metallic sodium, stands as a major landmark in this development. His later research ranged over the entire field of solid state science, and the resulting contributions, especially those on the nature and operation of point and line imperfections in crystals, decisively influenced the modern development of solid state chemistry and physical metallurgy as well as solid state physics.

As may be apparent from his versatility in the practice of research, he perceived condensed phase science as a unified whole, embracing the more

applied fields of metallurgy and ceramics as well as the physics of solids. This catholicity of outlook motivated his effective promotion of inter-disciplinary cooperation in the broad professional community as well as within the universities with which he was affiliated. It has been central to the editorial policy of this series. To implement this policy the editors have sought contributions, from experts distributed throughout the international community, over the whole spectrum, experimental and theoretical, of condensed phase science, using significance, depth, and timeliness as the principal criteria of acceptability.

The scientific community is deeply indebted to Frederick Seitz both for his pioneering research on solids and for his notable achievements as a scientific statesman. It has been a high privilege for us to have been associated with him as coeditors of this series.

DAVID TURNBULL
HENRY EHRENREICH

Preface

In this volume, Samara reviews the experience on the dependence of solid state ionic conductivity on hydrostatic pressure and its theoretical interpretation. He shows that the pressure results permit evaluation of the elastic volume relaxations in the formation and motion of point structural defects and often lead to identification of the dominant transport mechanism from among the various competing ones. In the second article, Peeters and Devreese review the theory of the polaron and its mobility. They present a comprehensive contemporary treatment of the role of polarons in charge transport processes. This subject has been previously discussed in Volume 21 of this series in an article by Appel.

In the following article, Callaway and March present a critical review of the foundations, achievements, and limitations of density functional methods in determining inhomogeneous electron distributions in atoms, molecules, and solids. Some applications of these methods are described. Application of the methods to surface problems had been reviewed by N. D. Lang in Volume 28 of this series.

The recent discovery of the tremendous enhancement of Raman scattering at roughened surfaces has stimulated much experimental and theoretical investigation. The fourth article in this volume, by Wokaun, reviews these investigations and presents evidence that the enhancement reflects a general electromagnetic phenomenon. Wokaun proposes a general mechanism involving localized surface plasmons, which may make a major contribution to the enhancement.

The theory of excitons was reviewed in Supplement 5 (1963) to this series by R. S. Knox. More recent contributions to the theory are reviewed in the final article in this volume, by Singh. He presents a treatment directed at unifying the physical and chemical approaches, as exemplified by the Wannier and Frenkel theories, and describes various radiationless processes of excitons in inorganic as well as organic crystals.

HENRY EHRENREICH
DAVID TURNBULL

Supplements

Supplement 1: T. P. DAS AND E. L. HAHN
Nuclear Quadrupole Resonance Spectroscopy, 1958

Supplement 2: WILLIAM LOW
Paramagnetic Resonance in Solids, 1960

Supplement 3: A. A. MARADUDIN, E. W. MONTROLL, G. H. WEISS, AND
I. P. IPATOVA, Theory of Lattice Dynamics in the Harmonic
Approximation, 1971 (Second Edition)

Supplement 4: ALBERT C. BEER
Galvanomagnetic Effects in Semiconductors, 1963

Supplement 5: R. S. KNOX
Theory of Excitons, 1963

Supplement 6: S. AMELINCKX
The Direct Observation of Dislocations, 1964

Supplement 7: J. W. CORBETT
Electron Radiation Damage in Semiconductors and Metals, 1966

Supplement 8: JORDAN J. MARKHAM
F-Centers in Alkali Halides, 1966

Supplement 9: ESTHER M. CONWELL
High Field Transport in Semiconductors, 1967

Supplement 10: C. B. DUKE
Tunneling in Solids, 1969

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Optical Modulation Spectroscopy of Solids, 1969

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High-Pressure Studies of Ionic Conductivity in Solids

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I. Introduction

There has been a great deal of renewed interest in the past several years in the study of ionic charge transport (or conductivity) in solids. This interest derives not only from the need to develop advanced solid state batteries but also from the challenging physics involved, especially in the case of fast ion (or superionic) conductors.

Ionic charge transport and, more generally, ionic diffusion in solids result from the existence and motion of crystalline defects. These can be either extrinsic defects, which are associated with the presence of chemical impurities (dopants) and lattice imperfections, or intrinsic defects. Any solid has at a given temperature an equilibrium concentration of intrinsic defects (usually vacancies or interstitials) which is controlled by a Boltzmann factor. Because ionic conduction and diffusion are generally sensitive to this thermal equilibrium concentration of intrinsic defects, they are called activated processes.

1

The situation is quite interesting in the case of fast ion (superionic) conductors. These materials are characterized either by the availability of a very large number of normally vacant lattice sites (i.e., a defect structure) or by an essentially complete disorder of the mobile ionic species. These mobile ions are distributed randomly over a large number of sites, and the magnitude of the conductivity indicates that nearly all of them must contribute to the conductivity. The activation energy for ionic motion in the superionic regime is usually small (~ 0.1 eV).

Ionic conductivity and diffusion have been studied extensively in a variety of ionic crystals at atmospheric pressure, and in many cases the mechanisms for the transport processes in terms of point defects have been established.[1,2] Experimental results have generally been successfully interpreted in terms of absolute reaction-rate theory.[1-3]. In this theory the elementary diffusive jump is likened to a transition, in thermal equilibrium, between a ground state corresponding to the equilibrium lattice position of the mobile species and an excited state corresponding to the saddle-point position. The basic assumption underlying the use of this theory in diffusive processes is that there exists a well-defined transition (excited) state whose lifetime is sufficiently long compared to lattice thermal relaxation time that it makes sense to define the thermodynamic properties of the excited state. Although the theory has been criticized on this assumption and on other counts,[4] its general success in interpreting experimental results provides strong support for the usefulness and, perhaps, validity of the equilibrium statistical mechanical treatment of the diffusion process in many systems.

There has been a considerable number of studies of the effects of hydrostatic pressure on ionic conductivity and other related ionic transport processes. Both the formation and the motion of lattice defects which determine the conductivity normally depend exponentially on pressure. Most of the early pressure work was on NaCl and the silver halides, whereas recent work has extended these studies to a broader range of materials that includes fast ion conductors. The results are reviewed briefly in Part III. In all of these studies pressure is found to be a complementary variable to temperature in

[1] See, e. g., A. B. Lidiard, in "Handbuch der Physik" (S. Flügge, ed.), Vol. 20, p. 246. Springer-Verlag, Berlin and New York, 1957; see also C. Kittel, "Introduction to Solid State Physics," Chapter 18. Wiley, New York, 1966.

[2] L. W. Barr and A. B. Lidiard, in "Physical Chemistry: An Advanced Treatise" (W. Jost, ed.), Vol. 10, p. 151. Academic Press, New York, 1970.

[3] C. Zener, in "Imperfections in Nearly Perfect Crystals" (W. Shockley, ed.), p. 289. Wiley, New York, 1950; Acta Crystallogr. 2, 163 (1949); C. Wert and C. Zener, Phys. Rev. [2] 76, 1169 (1949).

[4] D. Lazarus and N. H. Nachtrieb, in "Solids Under Pressure" (W. Paul and D. M. Warschauer, eds.), Chapter 3. McGraw-Hill, New York, 1963.

trying to understand the mechanisms of ionic conduction. In some cases, as we shall see later, pressure turns out to be an essential variable. In ionic conductivity and other defect-dominated properties in general, it is important to know the elastic volume relaxation associated with the formation of lattice defects as well as the lattice relaxation accompanying the diffusive motion of these defects. Measurements of the hydrostatic pressure depen- dence of the ionic conductivity give, in principle, direct information about these volume relaxations, and this information can in turn be used to under- stand better the mechanisms of ionic transport and to test the validity of proposed models. These aspects are prominently featured in present review article. Pressure studies also provide a better understanding of the nature of the energy barriers associated with ionic transport and are, in addition, important to the understanding of the phase transitions observed in many ionic conductors.

In the present article we shall review and discuss hydrostatic pressure studies performed on a variety of ionic conductors. There appear to be no earlier reviews of the subject except for a very brief recent account by the author.[5] Two early reviews by Lazarus and Nachtrieb[4] and Keyes,[6] are relevant; however, at the time these reviews were published, very little information on pressure work on ionic conductivity was available. The em- phasis of the present review is on experimental results and their interpretation in terms of relevant concepts and theory. It is not our intention to give a com- plete summary of all of the available literature; rather, we shall dwell on examples which illustrate special features or show systematic trends or both. Much of the available pressure work has been on relatively simple materials and crystal structures because these are amenable to theoretical treatment. Some of the materials investigated (e.g., PbF_2 and the thallous halides) are especially interesting because, among other properties, they possess large dielectric constants and also exhibit relatively soft, low-lying phonon modes. These factors are important in relation to ionic conduction because the larger the dielectric constant of an ionic crystal, the lower the energy of formation of lattice defects. Also, physically, ionic transport occurs by hopping motion across an energy barrier, and this barrier might be expected to become smaller the "softer" the lattice. We shall examine the evidence for the connection between these properties and the transport properties.

This review is organized as follows. We begin Part II with a brief theo- retical background giving some of the concepts and results necessary for the

[5] G. A. Samara, in "High Pressure Science and Technology" (B. Vodar and P. Marteau, eds.), p. 454. Pergamon, Oxford, 1980.

[6] R. W. Keyes, in "Solids Under Pressure" (W. Paul and D. M. Warschauer, eds.), Chapter 4. McGraw-Hill, New York, 1963; J. Chem. Phys. 19, 467 (1959).

analysis and interpretation of the results to be presented in later sections. Part III reviews the pressure results and their interpretation. For this purpose it was found most convenient to divide the substances of interest into several groupings as follows: alkali halides (both NaCl and CsCl types), silver halides, thallium halides, fluorites and related structures, and fast ion conductors. Finally, Part IV provides some overall evaluation of the results, concluding remarks, and suggestions for future work. Throughout this review the pressure unit used is the giga pascal (GPa), or 10^9 P. This is an SI unit of pressure: 1 GPa = 10 kilobar (kbar) = 10^{10} dyn cm^{-2}.

II. Theoretical Background

1. LATTICE DEFECTS

The simplest and, for our present consideration, most important lattice imperfections are vacancies and interstitials. A lattice vacancy is known as a Schottky defect. A Schottky defect is formed in a perfect crystal by moving an ion from a lattice site in the interior to a lattice site on the surface of the crystal. At any given temperature, a certain equilibrium number of lattice vacancies is always present in a crystal because the entropy is increased by the presence of disorder in the lattice. To keep the crystal electrostatically neutral on a local scale, it is usually energetically favorable in ionic crystals to form roughly equal numbers of separated positive and negative ion vacancies (so-called Schottky pairs). It is easy to show that the concentration n of such pairs is[1]

$$n = N \exp(-\Delta G_f^v/2kT), \tag{1.1}$$

where N is the number of ions (sites) per unit volume, and ΔG_f^v is the Gibbs free energy of formation of a pair.

Another type of lattice defect is the Frenkel defect. In this case an ion is moved from a lattice site to an interstitial position, a normally unoccupied lattice position. The concentration of Frenkel defects is again easily shown to be given by[1]

$$n = (NN')^{1/2} \exp(-\Delta G_f^i/2kT), \tag{1.2}$$

where N is the number of lattice sites, N' is the number of interstitial sites (both per unit volume), and ΔG_f^i is the Gibbs free energy for the formation of the interstitial.

Equations (1.1) and (1.2) are obtained in the limit $n \ll N$ and as such are thus strictly not valid for ionic conductors in the superionic regime where n approaches N.

The production of Schottky defects lowers the density of the crystal because the volume is increased without an increase in mass. The production of Frenkel defects, on the other hand, does not to first order change the volume of the crystal, and thus the density remains nearly unchanged. On this basis pressure can be expected to cause a relatively large suppression of the formation of Schottky defects. We shall show evidence for this later.

Controlled concentrations of vacancies and interstitials can often be introduced by doping an ionic crystal with aliovalent impurities. For example, doping NaCl with $CaCl_2$ would cause the Ca^{2+} ion to go in substitutionally for the Na^+ ion. The requirement of charge neutrality would also cause the creation of a Na^+ vacancy. On the other hand, doping NaCl with, e.g., Na_2S, would cause the S^{2-} ion to go in substitutionally for the Cl^- ion and would result in the formation of a Cl^- vacancy.

2. TEMPERATURE DEPENDENCE OF THE CONDUCTIVITY

The conductivity of a solid ionic conductor can be written as

$$\sigma = \sum_j n_j q_j \mu_j, \tag{2.1}$$

where n_j, q_j, and μ_j are the concentration, electrical charge, and mobility, respectively, of the jth mobile charge carrier, and the summation is over the different types of charge carriers. The temperature dependence of σ arises from the temperature dependence of n or μ or both. In general, the temperature dependence of n can be quite complicated since it can be influenced by the relative amounts of intrinsic defects and impurities as well as by the possible association and/or precipitation[1] of these impurities and defects.

In the extrinsic regime n is determined by the concentration of impurities; however, in the intrinsic regime the concentration of intrinsic defects is given by either Eq. (1.1) or (1.2), which can be rewritten in the form

$$n = N \exp(\Delta S_f/2k) \exp(-\Delta H_f/2kT), \tag{2.2}$$

with a similar expression for Eq. (1.2). Here, ΔS_f and ΔH_f are the entropy and enthalpy, respectively, associated with the formation of the defects.

Not only is the concentration of intrinsic defects an activated process, but so is the motion of defects as well, since work is required to move the defect from its equilibrium position of minimum energy to the saddle point which

separates it from another position of minimum energy. The rate at which a defect traverses a barrier is

$$1/\tau = \nu \exp(-\Delta G_m/kT), \tag{2.3}$$

where ΔG_m is the free energy required to *move* the defect across the energy barrier, and ν is the vibrational (or attempt) frequency of the defect in the direction which carries it over the barrier. Note that ν is usually a difficult quantity to estimate since it relates to a defective region of the crystal. A useful approximation is to equate ν with the Debye frequency for cases where the diffusing species has a comparable mass to the atoms of the host crystal.[6]

The diffusion coefficient (isotropic case) is given by

$$D = Ar^2\tau^{-1}, \tag{2.4}$$

where A is a dimensionless geometrical factor (of order unity) which depends on the lattice type and transport mechanism, and r is the jump distance. The mobility μ of a given species is related to the diffusion coefficient D of that species through the Nernst–Einstein relation

$$D = \mu kT/q, \tag{2.5}$$

where q is the electric charge of the species. Since D is given by[3]

$$D = A\nu r^2 \exp(-\Delta G_m/kT), \tag{2.6}$$

the temperature dependence of μ is given by

$$\mu = \left(\frac{Aq\nu r^2}{kT}\right)\exp\left(-\frac{\Delta G_m}{kT}\right) = \left(\frac{Aq\nu r^2}{kT}\right)\exp\left(\frac{\Delta S_m}{k}\right)\exp\left(-\frac{\Delta H_m}{kT}\right), \tag{2.7}$$

where the subscript m denotes mobility.

The conductivity σ in the *intrinsic* regime where one mobile species dominates can then be written as

$$\sigma T = \left(\frac{ANq^2\nu r^2}{k}\right)\exp\left(\frac{\Delta S_f}{2k} + \frac{\Delta S_m}{k}\right)\exp\left(-\frac{\Delta H_f}{2kT} - \frac{\Delta H_m}{kT}\right). \tag{2.8}$$

In dealing with experimental data, Eq. (2.8) is more commonly written as

$$\sigma T = \sigma_0 \exp(-E/kT), \tag{2.9}$$

where it is seen that the preexponential factor σ_0 is

$$\sigma_0 = \left(\frac{ANq^2\nu r^2}{k}\right)\exp\left(\frac{\Delta S_f}{2k} + \frac{\Delta S_m}{k}\right), \tag{2.10}$$