

**TREATISE ON  
SOLID STATE CHEMISTRY**

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**Volume 1  
The Chemical Structure  
of Solids**

# TREATISE ON SOLID STATE CHEMISTRY

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## Volume 1 The Chemical Structure of Solids

Edited by  
**N. B. Hannay**

*Vice President  
Research and Patents  
Bell Laboratories  
Murray Hill, New Jersey*

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**Volume 1  
The Chemical Structure  
of Solids**

## **TREATISE ON SOLID STATE CHEMISTRY**

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- Volume 1 • The Chemical Structure of Solids
- Volume 2 • Defects in Solids
- Volume 3 • Crystalline and Noncrystalline Solids
- Volume 4 • Reactivity of Solids
- Volume 5 • Changes of State
- Volume 6 • Surfaces

## *Foreword*

The last quarter-century has been marked by the extremely rapid growth of the solid-state sciences. They include what is now the largest subfield of physics, and the materials engineering sciences have likewise flourished. And, playing an active role throughout this vast area of science and engineering have been very large numbers of chemists. Yet, even though the role of chemistry in the solid-state sciences has been a vital one and the solid-state sciences have, in turn, made enormous contributions to chemical thought, solid-state chemistry has not been recognized by the general body of chemists as a major subfield of chemistry. Solid-state chemistry is not even well defined as to content. Some, for example, would have it include only the quantum chemistry of solids and would reject thermodynamics and phase equilibria; this is nonsense. Solid-state chemistry has many facets, and one of the purposes of this *Treatise* is to help define the field.

Perhaps the most general characteristic of solid-state chemistry, and one which helps differentiate it from solid-state physics, is its focus on the chemical composition and atomic configuration of real solids and on the relationship of composition and structure to the chemical and physical properties of the solid. Real solids are usually extremely complex and exhibit almost infinite variety in their compositional and structural features.

Chemistry has never hesitated about the role of applied science, and solid-state chemistry is no exception. Hence, we have chosen to include in the field not only basic science but also the more fundamental aspects of the materials engineering sciences.

The central theme of the *Treatise* is the exposition of unifying principles in the chemistry, physical chemistry, and chemical physics of solids. Examples are provided only to illustrate these principles. It has, throughout, a chemical viewpoint; there is, perforce, substantial overlap with some areas of solid-

## *Foreword*

state physics and metallurgy but a uniquely chemical perspective underlies the whole. Each chapter seeks to be as definitive as possible in its particular segment of the field.

The *Treatise* is intended for advanced workers in the field. The scope of the work is such that all solid-state chemists, as well as solid-state scientists and engineers in allied disciplines, should find in it much that is new to them in areas outside their own specializations; they should also find that the treatment of their own particular areas of interest offers enlightening perspectives.

Certain standard subjects, such as crystal structures, have been omitted because they are so well covered in many readily available standard references and are a part of the background of all solid-state scientists. Certain limited redundancies are intended, partly because they occur in different volumes of the series, but mainly because some subjects need to be examined from different viewpoints and in different contexts. The first three volumes deal with the structure of solids and its relation to properties. Volumes 4 and 5 cover broad areas of chemical dynamics in bulk solids. Volume 6 treats both structure and chemical dynamics of surfaces.

N.B.H.

## *Preface to Volume 1*

No aspect of chemistry is more fundamental to the science than is the study of the nature of the chemical bond. Solids exhibit the complete range of bonding behavior and offer opportunity, therefore, for gaining special insight into the nature of interatomic binding forces. The regularity of many solids facilitates experimental and theoretical examination of chemical bonds and allows the interpretation of the properties of solids in fundamental atomic terms. This volume is concerned with these aspects of solid-state chemistry. Thus it furnishes a fundamental basis for later volumes.

The ideal solid would be perfectly ordered and geometrically regular, chemically pure and stoichiometric. No real solid is found in this state, and some of the most interesting and important properties of solids depend upon departure from the ideal. The study and control of these deviations from the perfect solid are a principal concern of solid-state chemists. Later volumes of the *Treatise* will be concerned with defects in solids in relation to physical and chemical properties. Here we lay the foundation by examining the nature of defects and the equilibria controlling their concentrations. In addition, the characterization of solids is included; it would seem almost self-evident that the measurement of departures of a solid from the ideal chemical and geometrical state is a *sine qua non* in the study of the imperfect solid, yet it has all too often been overlooked or treated casually.

N.B.H.



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## *Chemical Bonds in Solids*

*J. C. Phillips*

*Bell Laboratories*

*Murray Hill, New Jersey*

### **1. Why Solids Are Different from Molecules**

Most of the ideas about chemical bonds that are contained in the collective wisdom of science have been refined inductively from the great body of chemical knowledge concerning the structure, properties, and reactivities of molecules in gases. Therefore to discuss chemical bonding of atoms in solids, one begins by stressing how it differs from chemical bonding of molecules in gases. Above all, most solids are much denser than corresponding molecules. For example, in the diatomic molecule  $\text{Na}^+\text{Cl}^-$  each ion has one nearest neighbor, but in the  $\text{Na}^+\text{Cl}^-$  crystal each ion has six nearest neighbors. The diatomic molecule has a dipole moment, which is important in many properties. The diatomic crystal has no permanent dipole moment. Generally speaking, the symmetry of the crystal is much higher than that of the molecule. Most solids are “three dimensional”; those solids that are composed of layers and chains of atoms exhibit many molecular characteristics, while most of what we have to say applies to chemical bonds in “three-dimensional” solids. The cases of layers, chains, and surfaces are special and are treated as such elsewhere in these volumes.

The formation of chemical bonds between atoms brings about a redistribution of electronic charge relative to a simple superposition of atomic charge densities. One may characterize many of the properties of an atom in two ways: by its ground-state charge distribution (which determines the atomic size), and by the accessibility of its first



few excited states. When a second atom interacts with the first one the interaction can be thought of primarily as an electric dipole one, which polarizes the first atom and leads to partial occupation of excited states. Much of the polarizability of an isolated atom is associated with excitations into the ionization continuum. In a molecule some of the oscillator strength associated with ionization of the atoms is transferred to bonding  $\rightarrow$  antibonding excitations. Non-bonded or lone-pair electrons on the “outside” of the molecule retain a large part of their oscillator strength in ionization processes. (This accounts in part for some of their special properties.) In the solid, on the other hand, except for atoms on or very near the surface, almost all the oscillator strength is associated with excitation of the atoms *considered as part of the medium*. Thus while the identity and properties of atoms are partially preserved in low-polarizability molecules, great care should be exercised in extending atomistic concepts into the discussion of chemical bonding in much more highly polarizable solids.

As a simple illustration of this theme, consider the specific problem of the crystal structures of the alkali halides. These are the simplest salts known, and chemical theories of their properties are discussed at greater length in Section 3.1. However, the structures of these very simple ionic crystals illustrate in the most direct way how much different solids are from molecules.

The compounds of formula  $M^+X^-$  are expected to be well represented by electrostatic models because the electronic configurations of the cations  $M^+$  and the anions  $X^-$  are isoelectronic to those of inert gases such as Ne and Ar. It now seems reasonable to discuss alternative crystal structures in terms of mechanical models based on electrostatic attractions of rigid spheres. So long as the cation and anion sphere radii are nearly equal, the crystal structure favored by this model will be one with the largest possible number of oppositely charged ions coordinated around each central ion. This is the CsI structure (eightfold coordination, with each ion surrounded by oppositely charged ions located at the corners of a cube centered on the first ion). However, a simple geometric calculation shows that when the radius ratio  $\rho = r_+/r_-$  of the sphere radii is less than 0.732 the eight anions will come into mutual contact, thereby determining a larger cation–anion separation than would have been fixed by cation–anion repulsion alone. As a result, the NaCl structure (sixfold coordinated, nearest neighbors centered on cube faces) will be favored. Finally, when  $\rho = 0.414$  the six anions come into contact, and again