

**TREATISE ON
SOLID STATE CHEMISTRY**

**Volume 4
Reactivity of Solids**

TREATISE ON SOLID STATE CHEMISTRY

Volume 4 Reactivity of Solids

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**TREATISE ON
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Volume 4
Reactivity of Solids

TREATISE ON SOLID STATE CHEMISTRY

- 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 6A • Surfaces I
- Volume 6B • Surfaces II

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 4

Changes in the chemical state of solids take many forms, yet they all have certain common characteristics. Our concern is not only with the detailed nature of the initial and final states, but also with the kinetics and mechanisms describing the chemical change. This volume covers a great variety of "chemical reactions," where we have taken the term in its broadest context. The subject matter of this volume is complementary to that of Volume 5, which also deals with changes of state but where the changes are generally physical in nature, rather than chemical. Chemical reactions on surfaces are reserved for Volumes 6A and 6B.

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