TREATISE ON SOLID STATE CHEMISTRY

Volume 3
Crystalline and Noncrystalline Solids

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Crystalline and Noncrystalline Solids

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PLENUM PRESS • NEW YORK-LONDON

Library of Congress Cataloging in Publication Data

Hannay, Norman Bruce, 1921-
Crystalline and noncrystalline solids.

(His Treatise on solid state chemistry; v. 3)
Includes bibliographical references and index. 1. Crystallography. 2. Solids. I. Title.
QD478.H35 vol. 3 [QD905.2] 541.'042'1s [548'.8]
ISBN 0-306-35053-X 76-18863

Seven-volume set: ISBN 0-306-35050-5

Published by Plenum Press, New York
A Division of Plenum Publishing Corporation
227 West 17th Street, New York, N.Y. 10011

Printed in the United States of America

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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-

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 3

Volumes 1 and 2 of this Treatise were concerned with both perfect and imperfect crystalline solids, all exhibiting simple crystal lattices and with the imperfect solid taken to mean a solid with a modest concentration of simple defects, i.e., point defects or dislocations. Certain classes of solids, including major classes of practical materials, fall outside the range covered by this structural description. The reason for this varies widely; thus, periodic structural features can be used to distinguish unusual classes of crystalline solids, the solid can be built up from molecular units, the defects can be extended in nature, or the solid may exhibit a semicrystalline or a completely amorphous structure. In this volume, several classes of solids of this type are examined.

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Metastable Phases Produced by Rapid Quenching from the Vapor and the Liquid

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1. Introduction

1.1. Definition

Though some metastable phases are obtained readily, e.g., common inorganic oxide glasses or some phases present in many varieties of steels, the phases of interest here are those which can be obtained only through the use of high effective quenching rates from the vapor or liquid phase. This includes many thin-film phases obtained by evaporation or sputtering and not-so-thin film phases obtained by rapid cooling from the melt and by electrodeposition from a liquid electrolyte. In the case of evaporation or sputtering of a metal, the substrate is exposed to a gaseous ambient containing metal as well as nonmetal atoms, whereas in the case of rapid quenching from the melt and electrodeposition, the ambient of the substrate is made up of a crystallographically uncorrelated assembly of atoms in the liquid phase or in solution.

* Communication No. 9.