PHYSICAL CHEMISTRY

An Advanced Treatise

VOLUME X / Solid State

Edited by

WILHELM JOST

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WILHELM JOST
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Göttingen, Germany

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Foreword

In recent years there has been a tremendous expansion in the development of the techniques and principles of physical chemistry. As a result most physical chemists find it difficult to maintain an understanding of the entire field.

The purpose of this treatise is to present a comprehensive treatment of physical chemistry for advanced students and investigators in a reasonably small number of volumes. We have attempted to include all important topics in physical chemistry together with borderline subjects which are of particular interest and importance. The treatment is at an advanced level. However, elementary theory and facts have not been excluded but are presented in a concise form with emphasis on laws which have general importance. No attempt has been made to be encyclopedic. However, the reader should be able to find helpful references to uncommon facts or theories in the index and bibliographies.

Since no single physical chemist could write authoritatively in all the areas of physical chemistry, distinguished investigators have been invited to contribute chapters in the field of their special competence.

If these volumes are even partially successful in meeting these goals we will feel rewarded for our efforts.

We would like to thank the authors for their contributions and to thank the staff of Academic Press for their assistance.

HENRY EYRING
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WILHELM JOST

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Preface

Texts on physical chemistry generally provide a thorough introduction into thermodynamics and statistical mechanics of solid crystals, their optical behavior, the nature of the metallic state, the crystal structure of simple and complicated inorganic and organic crystals.

The last decades brought a tremendous increase in our understanding of solid state phenomena outside the traditional scope, and a rapid development of practical applications.

This holds especially for the disordered solid state and is perhaps most pronounced in the field of semiconductors. Consequently, in this treatise properties of the ideal solid state are considered sufficiently well known and basically understood, and the emphasis in this volume is laid upon fields with conspicuous recent progress. Thus there are treated advanced methods in crystal structure analysis, including some results of neutron diffraction, dislocations in solids, defects in ionic crystals, order–disorder transformations, fundamentals of semiconductors, including surface effects and organic semiconductors, photoconductivity of semiconductors, and finally precipitation of solids and aging.

WILHELM JOST

January, 1970

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Chapter 1

Diffraction of X-Rays, Electrons, and Neutrons on the Real Crystal

ALARICH WEISS
AND
HELMUT WITTE

I. Introduction

Diffraction methods are probably the most powerful and most important methods for studying crystallized matter, since the geometrical arrangement of atoms, ions, and molecules in crystals is found using them. Furthermore, the resolving power of the diffraction methods is high enough to reveal the distribution of charges within the unit cells of the crystals. Knowledge of the arrangement of the atoms is the basis of practically all other theoretical and experimental studies of the solid state.

It is known from classical optics that in principle diffraction methods are insensitive to the small statistical disturbances of a grating. Therefore the diffraction methods applied to the crystal lattice are basically insensitive to small irregularities in the crystal lattice. This is the reason the use of first-order theories of diffraction applied to crystal structure determination leads to a reasonably good fixation of the positions of the atoms in the elementary cell. As long as only atomic positions and interatomic distances with an accuracy of 0.1% are of interest, first-order diffraction theory can be applied.

All periodic disturbances of the ideal lattice such as phonons, the ordering of scattering particles (superstructures, long-range order), and the ordering of spins (magnetic structures) may be studied with considerable success by the different diffraction methods. A careful experimental and theoretical consideration of higher-order diffraction effects also permits the study of complete or partial statistical deviations from the ideal arrangement of the scattering particles within the macroscopic crystal.

Following the work by von Laue *et al.* (1912, 1913) the possibility of studying atomic arrangements in crystals by diffraction methods has been established. Whenever a beam of electromagnetic waves or of particles of appropriate wavelength, i.e., of wavelengths comparable with the atomic distances in the crystal lattice, travels through a crystal diffraction can occur. The resulting three-dimensional diffraction pattern is in geometry and amplitude a Fourier transform of the distribution of the scattering matter in the crystal. This scattering matter may be the electrons (in the case of X-ray diffraction), the electrons and nuclear charges (in the case of electron diffraction), or the nuclei and resultant spins (electron spins and nuclear spins) in the case of neutron diffraction. The two important features of the diffraction pattern, the diffraction

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