M. Ali Omar

ELEMENTARY SOLID STATE PHYSICS

固态物理学基础

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بسم الله الرحمن الرحيم

To my son, Riyad

PREFACE

This volume is intended to serve as a general text in solid state physics for undergraduates in physics, applied physics, engineering, and other related scientific disciplines. I also hope that it will serve as a useful reference tool for the many workers engaged in one type of solid state research activity or another, who may be without formal training in the subject.

Since there are now many books on solid state physics available, some justification is needed for the introduction of yet another at this time. This I can perhaps do best by stating the goals I strove to achieve in the writing of it, and let the reader judge for himself how successful the effort may have been.

First, I have attempted to cover a wide range of topics, which is consistent with my purpose in writing a general and complete text which may also serve as an effective general reference work. The wide coverage also reflects the immensely wide scope of curent research in solid state physics. But despite this, I have made a determined effort to underline the close interrelationships between the disparate parts, and bring the unity and coherence of the whole subject into perspective.

Second, I have tried to present as many practical applications as possible within the limits of this single volume. In this not only have I taken into consideration those readers whose primary interest lies in the applications rather than in physics *per se*, but I have also encouraged prospective physics majors to think in terms of the practical implications of the physical results; this is particularly vital at the present time, when great emphasis is placed on the contribution of science and technology to the solution of social and economic problems.

Third, this book adheres to an interdisciplinary philosophy; thus, in addition to the areas covered in traditional solid state texts in the first ten chapters, the last three chapters introduce additional material to which solid state physicists have made many significant contributions. The subjects include metallurgy, defects in solids, new materials, and biophysics and are of great contemporary importance and practical interest.

Fourth, I have made every effort to produce a modern, up-to-date text. Solid state physics has progressed very rapidly in the past two or three decades, and yet many advances have thus far failed to make their way into elementary texts, and remain scattered haphazardly throughout many different sources in the literature. Yet it is clear that early and thorough assimilation of the concepts underlying these advances, particularly by the young student, is essential to the growth and development in this field which await us in the future.

Fifth, and of greatest importance, this book is elementary in nature, and I have made every effort to ensure that it is thoroughly understandable to the well-prepared undergraduate student. I have attempted to introduce new concepts gradually, and to supply the necessary mathematical details for the various steps along the way. I have then discussed the final results in terms of their physical meaning, and their relation to other more familiar situations whenever this seems helpful. The book is liberally illustrated with figures, and a fairly complete list of references is supplied for those readers interested in further pursuit of the subjects discussed here.

Chapter 1 covers the crystal structures of solids, and the interatomic forces responsible for these structures. Chapter 2 includes the various experimental techniques, such as x-ray diffraction, employed in structure analysis. Except at very low temperatures, however, the atoms in a solid are not at rest, but rather oscillate around their equilibrium positions; therefore, Chapter 3 covers the subject of lattice vibrations, together with their effects on thermal, acoustic, and optical properties. This is followed in Chapter 4 by a discussion of the free-electron model in metals, whereby the valence electrons are assumed to be free particles. A more realistic treatment of these electrons is given in Chapter 5, on energy bands in solids. Before beginning Chapter 5, the student should refresh his understanding of quantum mechanics by reference to the appendix. The brief treatment of this complex subject there is not intended to be a short course for the uninitiated, but rather a summary of its salient points to be employed in Chapter 5, on the energy bands in solids. This is, in fact, the central chapter of the book, and it is hoped that, despite its somewhat demanding nature, the reader will find it rewarding in terms of a deeper understanding of the electronic properties of crystalline solids.

Semiconductors are discussed in Chapter 6. The detailed coverage accorded these substances is warranted not only by their highly interesting and wide-ranging properties but also by the crucial role played by semiconductor devices in today's technology. These devices are discussed at length in Chapter 7. When an electric field, static or alternating, penetrates a solid, the field polarizes the positive and negative charges in the medium; the effects of polarization on the dielectric and optical properties of solids are the subject of Chapter 8. The magnetic properties of matter, including recent developments in magnetic resonances, are taken up in Chapter 9, and the fascinating phenomenon of superconductivity in Chapter 10.

Chapter 11 is devoted to some important topics in metallurgy and defects in solids, and Chapter 12 features some interesting and new substances such as amorphous semiconductors and liquid crystals, which are of great current interest; this chapter includes also applications of solid state techniques to chemical problems. Chapter 13 is an introduction to the field of molecular biology, presented in terms of the concepts and techniques familiar in solid state physics. This is a rapidly expanding and challenging field today, and one in which solid state physicists are making most useful contributions.

Each chapter concludes with a number of exercises. These consist of two types: *Questions*, which are rather short, and intended primarily to test conceptual understanding, and *Problems*, which are of medium difficulty and cover the entire chapter. Virtually all the problems are solvable on the basis of material presented in the chapter, and require no appeal to more advanced references. The exercises are an integral part of the text and the reader, particularly the student taking a solid state course for the first time, is urged to attempt most of them.

ACKNOWLEDGEMENTS
Several persons helped me directly or indirectly in this work. Professor Herbert Kroemer of the University of Colorado has given me the benefit of his insight and incisive opinion during the early stages of writing. Professor Masataka Mizushima, also of the University of Colorado, gave me unfailing encouragement and support over a number of years. Chapter 5 on band theory profited from lectures by Professor Henry Ehrenreich of Harvard University, and Chapter 9 on magnetism reflects helpful discussions with Professor Marcel W. Muller of Washington University. Professor J. H. Tripp of the University of Connecticut made several useful comments and pointed out some editorial errors in the manuscript.

Professor David Lazarus of the University of Illinois-Urbana read the entire manuscript with considerable care. His comments and suggestions, based on his wide experience in teaching and research, resulted in substantial improvement in the work and its usefulness as a textbook in solid state physics.

To these distinguished scholars my sincerest thanks. The responsibility for any remaining errors or shortcomings is, of course, mine.

Joyce Rey not only typed and edited the manuscript with admirable competence, but always went through the innumerable revisions with patience, care, and understanding. For her determined efforts to anglicize the style of the author (at times, perhaps, a little over-enthusiastically), and for keeping constant track of the activities of the main characters, those "beady-eyed" electrons, despite her frequent mystification with the "plot," I am most grateful to "Joycie."

In closing, the following quotation from Reif (*Fundamentals of Statistical and Thermal Physics*) seems most appropriate: "It has been said that 'an author never finishes a book, he merely abandons it.' I have come to appreciate vividly the truth of this statement and dread to see the day when, looking at the manuscript in print, I am sure to realize that many things could have been done better and explained more clearly. If I abandon the book nevertheless, it is in the modest hope that it may be useful to others despite its shortcomings."

Lowell, Massachusetts M. A. O.
July 1974

CONTENTS

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CHAPTER 1 CRYSTAL STRUCTURES AND INTERATOMIC FORCES

Good order is the foundation of all good things.

Edmund Burke

1.1 INTRODUCTION

To the naked eye, a solid appears as a *continuous* rigid body. Experiments have proved, however, that all solids are composed of *discrete* basic units—atoms. These atoms are not distributed randomly, but are arranged in a highly ordered manner relative to each other. Such a group of ordered atoms is referred to as a *crystal*. There are several types of crystalline structure, depending on the geometry of the atomic arrangement; a knowledge of these is important in solid-state physics because these structures usually influence the physical properties of solids. This statement will be amply illustrated in the following chapters.

In the first part of this chapter, we shall expand on the meaning of the crystalline structure, and introduce some of the basic mathematical definitions employed in describing it. We shall then enumerate the various structures possible, and introduce the concept of Miller indices. We shall also present a few examples.

The atoms in some solids appear to be randomly arranged, i.e., the crystalline structure is absent. Such noncrystalline—or *amorphous*—solids will also be described briefly.

The chapter closes with an account of the interatomic forces that cause bonding in crystals.

Chapter 2 will discuss the experimental determination of crystal structure by x-rays.

1.2 THE CRYSTALLINE STATE

A solid is said to be a *crystal* if the atoms are arranged in such a way that their positions are *exactly periodic*. Figure 1.1 illustrates the concept. The distance between any two nearest neighbors along the x direction is a, and along the y direction is b (the x and y axes are not necessarily orthogonal). A *perfect* crystal maintains this periodicity (or repetitivity) in both the x and y directions from $-\infty$ to ∞. It follows from the periodicity that the atoms A, B, C, etc., are *equivalent*. In other words, to an observer located at any of these atomic sites, the crystal appears exactly the same.

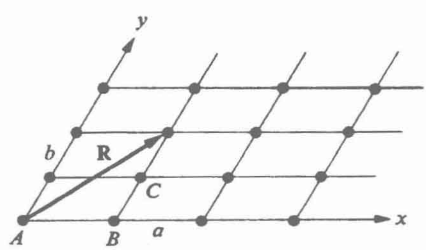

Fig. 1.1 A crystalline solid. All the atoms are arranged periodically.

The same idea is often expressed by saying that a crystal possesses a *translational symmetry*, meaning that if the crystal is translated by any vector joining two atoms, say **R** in Fig. 1.1, the crystal appears exactly the same as it did before the translation. In other words, the crystal remains *invariant* under any such translation. The consequences of this translational symmetry or invariance are many, and a great portion of this book will be concerned with them.

Strictly speaking, one cannot prepare a perfect crystal. For example, even the surface of a crystal is a kind of *imperfection* because the periodicity is interrupted there. The atoms near the surface see an environment different from the environment seen by atoms deep within the crystal, and as a result behave differently. Another example concerns the thermal vibrations of the atoms around their equilibrium positions for any temperature $T > 0°K$. Because of these vibrations, the crystal is always distorted, to a lesser or greater degree, depending on T. As a third example, note that an actual crystal always contains some foreign atoms, i.e., impurities. Even with the best crystal-growing techniques, some impurities ($\simeq 10^{12}\ cm^{-3}$) remain, which spoils the perfect crystal structure.

Notwithstanding these difficulties, one can prepare crystals such that the effects of imperfections on the phenomena being studied are extremely minor. For example, one can isolate a sodium crystal so large ($\simeq 1\ cm^3$) that the ratio of surface atoms to all atoms is small, and the crystal is pure enough so that impurities are negligible. At temperatures that are low enough, lattice vibrations are weak, so weak that the effects of all these imperfections on, say, the optical properties of the sodium sample are negligible. It is in this spirit that we speak of a "perfect" crystal.

Imperfections themselves are often the main object of interest. Thus thermal vibrations of the atoms are the main source of electrical resistivity in metals. When this is the case, one does not abandon the crystal concept entirely, but treats the imperfection(s) of interest as a small perturbation in the crystalline structure.

Many of the most interesting phenomena in solids are associated with imperfections. That is why we shall discuss them at some length in various sections of this book.

1.3 BASIC DEFINITIONS

In order to talk precisely about crystal structures, we must introduce here a few of the basic definitions which serve as a kind of crystallographic language. These definitions are such that they apply to one-, two-, or three-dimensional crystals. Although most of our illustrative examples will be two-dimensional, the results will be restated later for the 3-D case.

The crystal lattice

In crystallography, only the geometrical properties of the crystal are of interest, rather than those arising from the particular atoms constituting the crystal. Therefore one replaces each atom by a geometrical point located at the

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