

INTRODUCTION TO SOLID STATE PHYSICS

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Foreword

Brought about largely through the application of quantum mechanics, kinetic theory, and the theory of defect structures, great strides have been made recently in our understanding of the structure, properties, and behavior of materials. Scientists and engineers now use the tools of solid state physics and modern chemistry to investigate, develop, and apply metals, ceramics, glass, semiconductors, and polymers. In addition, but perhaps less obviously, research in atomic energy and electronics has catalyzed advances in the technology of these same materials. Developments in these fields have been stimulated by the demand for new materials with improved properties and for new properties in old materials.

The general plan of this series of books is to present the science and technology underlying the behavior and the manufacture and the technical use of all important solid materials. Serious overlapping will be avoided by having available to all authors the current state of development of the whole series so that each book can be better integrated with others related to it. The series is designed so that the books will meet the needs of university students, younger scientists and engineers, as well as the more experienced people who may not have had the benefit of the formal courses now coming into university curricula. It is proposed, furthermore, to serve these needs by presenting the material from a fundamental point of view so that the books will have lasting interest and importance.

In several volumes of the series the physics and chemistry of solids will be described. Other books will be concerned with the behavior of metals, ceramics, glass, semiconductors, and polymers. It is hoped that the series will be an extensive one, fully describing the science, technology, and engineering of materials. The scientific description of the behavior of these materials is the physics of solids. Dr. Kittel's

first edition of this book is an admirable introduction and review of this subject. The new edition, with its critical revision and new material, not only is the keystone of the series but also initiates it with a thoroughness and stature which the editor hopes to maintain.

JOHN H. HOLLOMON

Preface to the Second Edition

This volume is intended as an introductory textbook in solid state physics for students of physics, chemistry, and engineering. My object has been to write an elementary and short account of representative aspects of the physics of solids. The level of presentation supposes that the reader will have a good general familiarity with modern atomic physics to the extent of the undergraduate courses offered under this title in many universities. A course in quantum mechanics is not prerequisite to understanding most of the book, but the reader should be familiar with the Planck radiation law, the de Broglie relation, the Bohr theory of the hydrogen atom, the Zeeman effect, and the wave equation for free particles. Several advanced topics requiring a formal background of quantum mechanics are developed in appendices.

Solid state physics is a very wide field. It is concerned with the physical properties of solids, particularly the special properties exhibited by atoms and molecules because of their association and regular periodic arrangement in crystals. The existence of powerful theoretical methods and concepts applicable to a wide range of problems has been an important unifying influence in the field. It is quite natural therefore that an introductory textbook should emphasize the elementary theory of simple models of solids. In the selection of material I have frankly favored those areas which may be discussed in terms of simple, concrete, and well-developed models. One should remember, however, that real solids are almost always more complicated than the models we invent.

The second edition is longer than the first edition by about 200 pages. Half of the increase in length is brought about by fuller explanations of the basic concepts, particularly in the areas of crystal symmetry and energy band theory. The other half represents the addition of new material on alloys, semiconductors, photoconductivity,

luminescence, and imperfections in solids. I have been assisted in the preparation of the second edition by the responses made to a survey by the publishers among teachers using the earlier edition as a textbook; it is a pleasure to thank collectively the many persons who thus gave me the benefit of their experience.

This book is not intended to be a general reference book. Several active and important branches of solid state physics have not been mentioned at all. Among the topics omitted are internal friction, thermoelectric effects, phase transformations, oxide cathodes, surface physics, piezoelectricity, liquid and solid helium, plastics, and molecular crystals. As nearly every chapter is the subject of separate monographs by other authors, it is inevitable that the treatment of the subjects which have been included should be incomplete. In all chapters the references to the literature are intended only to be representative of some of the reviews and the classical papers, along with enough of a selection from recent work to enable the reader to get an impression of the nature of the current activity. The selection of citations from such a wealth of excellent work is more random than calculated. I extend apologies for those omitted through the action of the laws of chance.

Problem sets are included at the end of every chapter, with problems of considerable length or difficulty marked by an asterisk. A very brief summary of relevant parts of thermodynamics and statistical mechanics is given in Appendix R. Gaussian cgs units are used except where otherwise noted. The value of e , the charge on the electron, is taken as negative in sign: $e = -4.80 \times 10^{-10}$ esu for the electron.

The preface to the first edition included the following statement of acknowledgments: I am greatly indebted to my students who have checked over parts of the volume: E. Abrahams, M. Cohen, H. Kaplan, F. Keffer, J. Tessman, and Y. Yafet. I wish to thank J. Bardeen for reviewing the chapters on superconductivity and semiconductors, and F. Seitz for reviewing the chapters dealing with imperfections in solids; K. K. Darrow has kindly reviewed several chapters. It is a pleasure to thank R. T. Birge for assistance in connection with the values of fundamental physical constants; N. Bloembergen for the suggestion of a number of problems; Sir Lawrence Bragg and W. M. Lomer for a photograph of a dislocation model; A. von Hippel and P. W. Forsbergh, Jr., for a photograph of ferroelectric domains; H. F. Kay and B. J. Applebe for a photograph of crystal growth pattern; A. F. Kip and M. Tinkham for a hyperfine structure photograph; E. R. Parker for a photograph of a low angle grain boundary; H. J. Williams for a ferromagnetic domain photograph; and W. H. Zachariasen for

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C. KITTEL

Berkeley, California
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The Description of Crystal Structures

We are concerned first with the geometrical properties of perfect crystals. A perfect crystal is considered to be constructed by the infinite regular repetition in space of identical structural units or building blocks. We give in this chapter an introductory discussion of the essential symmetry properties of crystal structures. It is impossible to give a full discussion here; the interested reader is referred to the specialized textbooks listed at the end of the chapter. The properties of periodic arrangements of atoms are of central importance in solid state physics; in this chapter our task is to analyze and describe the geometrical properties of the possible periodic arrangements.

TRANSLATION GROUP

We define an ideal crystal as a body composed of atoms arranged in a lattice such that there exist three fundamental translation vectors \mathbf{a} , \mathbf{b} , \mathbf{c} , with the property that the atomic arrangement looks the same in every respect when viewed from any point \mathbf{r} as when viewed from the point

$$(1.1) \quad \mathbf{r}' = \mathbf{r} + n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c},$$

where n_1 , n_2 , n_3 are arbitrary integers. The fundamental translation vectors are *primitive* if any two points \mathbf{r} , \mathbf{r}' from which the atomic arrangement looks the same always satisfy (1.1) with a suitable choice of the integers n_1 , n_2 , n_3 . We shall consider frequently the primitive translation vectors as defining the *crystal axes* \mathbf{a} , \mathbf{b} , \mathbf{c} , although other (non-primitive) choices of crystal axes will be employed also.

The operation of displacing a crystal parallel to itself by

$$(1.2) \quad \mathbf{T} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$$

is called a *translation operation*. The totality of such operations, for all values of the integers n_1 , n_2 , n_3 , is known as the *translation group* of the crystal. The most important descriptive characteristics of crys-

tal structures are the symmetry operations¹ associated with the structure. The discussion of the symmetry of crystals in three dimensions can become rather tedious, and instead we shall treat fairly completely the theory of crystals in two dimensions, with a discussion of only a few important examples of structures in three dimensions.

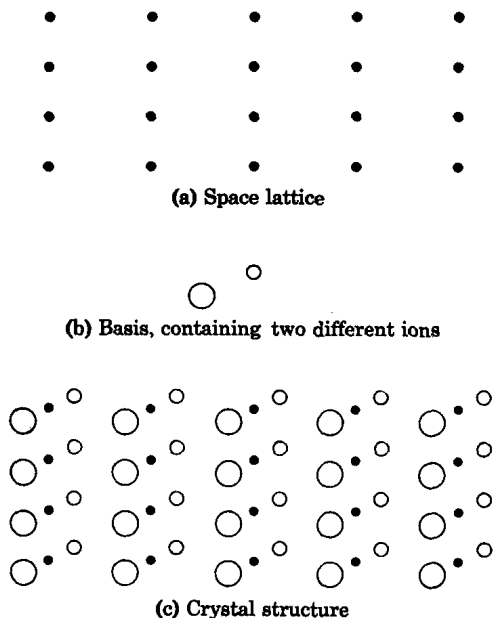


Fig. 1.1. The crystal structure (c) may be considered to be formed by the addition of the basis (b) to every lattice point of the space lattice (a).

A parallel net-like arrangement of points is by definition a *lattice*, provided the environment about any particular point is in every way the same as about any other point. It is essential to distinguish a lattice from a crystal structure: a crystal structure is formed by associating with every lattice point a unit assembly, or *basis*, of atoms identical in composition, arrangement, and orientation. The distinction is illustrated in Fig. 1.1. All lattice points are connected, as we would expect, by the translation operations \mathbf{T} defined by Eq. (1.2) above.

¹ The present discussion of crystal symmetry follows generally the treatment by F. Seitz, *Z. Krist.* **88**, 433 (1934); **90**, 289 (1935); **91**, 336 (1935); **94**, 100 (1936); and Vol. 1 of *International tables for x-ray crystallography*, Kynoch Press, Birmingham, 1952. A particularly readable discussion of space groups is given by F. C. Phillips, *An introduction to crystallography*, Longmans, London, 1946, pp. 221–272.

TWO-DIMENSIONAL CRYSTALS

The general two-dimensional lattice shown in Fig. 1.2 is an infinite array of points. The points obey the lattice condition that every point should have the same environment in the same orientation. It is apparent that \mathbf{a} , \mathbf{b} indicated in the figure are a possible choice for the primitive translation vectors of the lattice. The general parallelogram defined by primitive \mathbf{a} , \mathbf{b} forms a *primitive cell*, which is a type of *unit cell*. We shall later discuss unit cells in detail, but it will suffice now to state that the crystal translation operations applied to a unit cell will cover all points of the plane. A unit cell which contains lattice points at corners only is called a *primitive cell*.

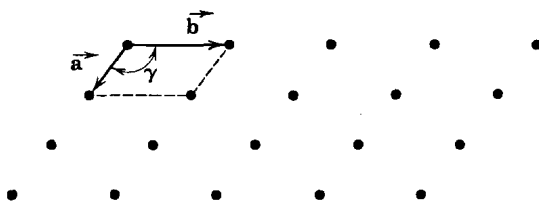


Fig. 1.2. General oblique lattice in two dimensions, showing a choice of the fundamental translation vectors \mathbf{a} , \mathbf{b} and a unit cell.

It is useful to introduce special relations connecting the primitive vectors \mathbf{a} , \mathbf{b} . The relations will define four special lattices with symmetry properties not present in the general oblique lattice, Fig. 1.2. To understand the special lattices, we must first discuss the symmetry operations associated with two-dimensional point groups.

TWO-DIMENSIONAL POINT GROUPS

A point group is a collection of symmetry operations applied about a point which leave the body invariant. The body may be, for example, a molecule, a group of atoms, a lattice, or a crystal structure. The symmetry operations in the two-dimensional crystallographic point groups are the one-, two-, three-, four-, and six-fold rotations about a point and mirror reflection across a line. The rotations are denoted by number, and the mirror reflection by the symbol m . For a planar molecule, any rotation $2\pi/n$, where n is an integer, may in principle be a symmetry operation. For a lattice, we shall now show that only values $n = 1, 2, 3, 4,$ and 6 are compatible with the translational symmetry requirement, Eq. (1.1).

An example of an excluded rotation is $2\pi/5$. A lattice does not exist which can be brought into coincidence with itself by a rotation of $2\pi/5$ about an axis through a lattice point. The proof of this partic-

ular statement is left as Problem 1.1, although the general result derived immediately below is sufficient to exclude such a rotation.

RESTRICTION OF POINT GROUPS BY TRANSLATIONAL SYMMETRY REQUIREMENT

We have seen that the lattice is invariant under the translations

$$(1.3) \quad \mathbf{T} = n_1\mathbf{a} + n_2\mathbf{b},$$

in two dimensions. As we shall see, this requirement puts restrictions on the allowed rotations and on the translations compatible with a given rotation. We also wish to study lattices which are invariant under more general conditions: under a rotation about a lattice point combined with a translation.

Referred to a fixed Cartesian coordinate system, the rotation of a point x, y through an angle ϕ (about the origin) to the point x', y' is represented by the equations

$$x' = x \cos \phi - y \sin \phi;$$

$$y' = x \sin \phi + y \cos \phi.$$

We assume that \mathbf{a} is the shortest non-vanishing translation in the translation group. We choose coordinate axes so that \mathbf{a} is parallel to the x axis. If now we rotate \mathbf{a} by an angle ϕ , we get a new vector \mathbf{a}' with components

$$a_{x'} = a \cos \phi;$$

$$a_{y'} = a \sin \phi.$$

If the lattice is invariant under the rotation ϕ , the vector $\mathbf{a}' - \mathbf{a}$ must be of the form \mathbf{T} , as in Eq. (1.3). The vector $\mathbf{a}' - \mathbf{a}$ has the components

$$a_{x'} - a_x = a(\cos \phi - 1);$$

$$a_{y'} - a_y = a \sin \phi;$$

and so

$$(1.4) \quad |\mathbf{a}' - \mathbf{a}|^2 = a^2(2 - 2 \cos \phi).$$

Now we must have $|\mathbf{a}' - \mathbf{a}|^2 \geq a^2$, because $\mathbf{a}' - \mathbf{a}$ is a vector \mathbf{T} , and \mathbf{a} is the shortest vector of this type. Thus, from (1.4), $2 - 2 \cos \phi \geq 1$, or $\cos \phi \leq \frac{1}{2}$, so that

$$(1.5) \quad \frac{\pi}{3} \leq \phi \leq \frac{5\pi}{3}.$$