CHARLES KITTEL

Introduction to Solid State Physics

FOURTH EDITION

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Preface to the Fourth Edition

This volume gives an elementary account of central aspects of the physics of solids. The volume was written as a textbook in solid state physics and materials science for senior undergraduate and beginning graduate students of science and engineering. The necessary background is a course in modern atomic physics.

Solid state physics is largely concerned with the remarkable properties exhibited by atoms and molecules because of their association and regular periodic arrangements in crystals. These properties may be understood in terms of simple models of solids. Real solids and amorphous solids are more complicated, but the power and utility of the simple models can hardly be overestimated.

About one-half of the third edition was rewritten to produce the fourth edition, and one hundred forty new illustrations were added. The major changes are:

1. The International System of Units (SI) is introduced in parallel with the CGS-Gaussian System of Units, and the text proper, originally written in the CGS-Gaussian system, is largely bilingual in both systems. The limitations are discussed below. The International System is essentially the same as the MKSA System.

2. New topics, some brief or in problems, include solid state lasers, Josephson junctions, flux quantization, the Mott transition, the Fermi liquid, Zener tunneling, the Kondo effect, helicons, and applications of magnetic resonance. The dielectric function is introduced as a unifying theme in the treatment of electromagnetic propagation, optical modes, plasmons, screening, and polaritons.

3. The chapters on crystal diffraction, energy bands, superconductivity, and magnetic resonance were largely rewritten. A continuous effort was made to produce a clear, intelligible, and well-illustrated text directed to students' needs. I tried to act on any difficulty that any student brought to me.

4. The tables of values of solid state data were considerably expanded and revised. Forty tables of wide application are listed separately in the contents.

The great advances in energy band studies, superconductivity, magnetic resonance, and neutron scattering methods are reflected in the text, as they were in the third edition. Emphasis is given to elementary excitations: phonons, plasmons, polarons, magnons, and excitons.

Nearly every important equation is repeated in SI and in CGS-Gaussian units, wherever these differ. Exceptions to this rule are the figure legends, the Advanced Topics, the chapter summaries, and any long section of text where a single indicated substitution (as of 1 for c or $1/4\pi\epsilon_0$ for 1) will suffice to translate from CGS to SI. Tables are given in conventional units. The contents pages of several chapters include remarks on conventions adopted to make parallel usage simple and natural. Problems should be solved in whichever system is desired by the reader or the teacher.

I have added a few more elements of history, because solid state physics offers the most direct and successful applications of quantum theory to the natural world around us. But aware of the fragmentary record, I thought often of the lines of Jorge Luis Borges: "What is good no longer belongs to anyone . . . but to the language or to tradition."

The sequence of chapters makes it easy to select material for a one semester course. This might include much of the material in Chapters 1 to 11, with additional topics from the later chapters or elsewhere. The selection of subjects for the later chapters should not be seen as an attempt to weigh the importance of the areas of current activity. A single textbook cannot represent the range of current creative activity. The articles in the excellent Seitz-Turnbull-Ehrenreich series should be consulted for subjects not treated in this book and for detailed bibliographies. There are in the literature perhaps ten thousand articles of high quality that usefully could be cited. I have tried to give a helpful, but small, sample of the ones most accessible in English. The translations of earlier editions of this book in French, German, Spanish, Japanese, Russian, Polish, Hungarian, and Arabic often give further references in these languages.

Problems of appreciable length or difficulty are marked by an asterisk. The symbol e denotes the charge on the proton: $e = +4.80 \times 10^{-10}$ esu $= 1.60 \times 10^{-19}$ C. The notation (18) refers to equation number 18 of the current chapter, but (3.18) refers to equation 18 of Chapter 3; figures are referred to in the same way. A caret or "hat" over a vector, as in $\hat{\mathbf{k}}$, denotes a unit vector.

The preparation of this edition was made possible by the cooperation of many colleagues and friends. I would like to mention some of the contributors; there is not space to list all. My new debts include those to T. Nagamiya, V. Heine, D. F. Holcomb, C. H. Townes, A. R. Verma, U. Essmann, H. Träuble, P. W. Montgomery, K. Gschneidner, Jr., H. P. R. Frederikse, W. Känzig, F. A. E. Engel, C. Quate, C. Y. Fong, P. G. Angott, G. Thomas, R. W. De Blois, H. E. Stanley, S. Geller, R. Cahn, R. Gray, P. Richards, and L. Falicov. Parts of the manuscript were reviewed by W. L. McLean and Margaret Geller, and the whole manuscript was reviewed by Robert Kleinberg. I am not certain if Mrs. Madeline Moore could have written this edition without me, but I could not have written it without her. Robert Goff is responsible for the effective and attractive design of the book. I am grateful for the constant cooperation and advice of Donald Deneck and Gerhard Brahms.

The preface to the third edition included the following statement of acknowledgments.

"The entire manuscript was strongly influenced by detailed criticism by Marvin L. Cohen and Michael Millman; my debt to them is indeed great. Successive drafts were kindly read by Ching Yao Fong and Joseph Ryus, and the problems were checked by Leonard Sander. Individual chapters were reviewed by Adolf Pabst, Charles S. Smith, David Templeton, Raymond Bowers, Sidney Abrahams, Earl Parker, G. Thomas, and M. Tinkham. Walter Marshall very kindly prepared an extensive selection of neutron diffraction results. The preparation of the historical introduction was assisted by Adolf Pabst, P. P. Ewald, Elizabeth Huff, Muriel Kittel, Georgianne Titus, and the physics librarian of the Ecole Normale Supérieure. For their experienced advice in the selection of experimental data for tables of values I am grateful to Leo Brewer, R. M. Bozorth, Norman Phillips, Bernd Matthias, Vera Compton, M. Tinkham, Charles S. Smith, E. Burstein, F. P. Jona and S. Strässler. The illustrations were developed in their final form by Felix Cooper, with early help by Ellis Myers. Credits are given with the individual photographs and figures; exceptional help in their collection was given by Robert van Nordstrand, T. Geballe, W. Parrish, Betsy Burleson, I. M. Templeton, and G. Thomas; also by H. McSkimin, H. J. Williams, R. W. De Blois, E. L. Hahn, A. von Hippel, B. N. Brockhouse, R. C. Miller, R. C. Le Craw, E. W. Müller, P. R. Swann, G. E. Bacon, G. M. Gordon, and Alan Holden."

I am grateful to Yvonne Tsang, Thomas Bergstresser, and Philip Allen for their permission to use the photograph that appears on the jacket.

Berkeley, California *C. Kittel*

Note to the Reader

Chapters 1 and 2 on crystal structure analysis are fundamental. Every concept developed in Chapter 2 is exploited heavily in the chapters on energy bands and semiconductors; this is particularly true of the reciprocal lattice and of Brillouin zones. The general method developed in Advanced Topic A for x-ray diffraction is repeated in Chapter 9 as the basis of the theory of electron energy bands. Chapter 4 may be omitted on a first reading. Chapters 5 and 6 are concerned with the velocity, quantization, and interaction of elastic waves in crystals; among the topics used later are the enumeration of modes in a Brillouin zone and the number of modes per unit frequency range.

Chapters 7, 8, 9, and 10 are devoted to electrons in metals. Chapters 9 and 10 on energy bands are the most important chapters in the book; the line of development is somewhat new in a textbook, but reflects the attitude of current research in the field. The proof of the Bloch theorem is central for the understanding of the chapters. The properties of holes are discussed with particular care as preparation for Chapter 11 on semiconductors.

Chapter 12 on superconductivity gives the essential experimental facts as viewed in the light of the BCS theory, but at this level it is not possible to give a meaningful derivation of the theory; the author's *Quantum theory of solids* or the book by Ziman may be consulted. Chapters 13 to 17 are devoted to the dielectric and magnetic properties of solids. Chapter 18 is on excitons and optical properties; it contains a discussion of solid state lasers. The final two chapters (19, 20) are concerned largely with imperfections in solids and may be read at any convenient stage.

An instructor's manual is available to instructors who have adopted the text for classroom use. Requests may be directed to John Wiley & Sons, Inc., 605 Third Avenue, New York, N.Y. 10016.

Some General References

Atomic physics background

Max Born, *Atomic physics,* Hafner, New York, 7th ed., 1962.

R. L. Sproull, *Modern physics,* Wiley, 2nd ed., 1963.

Statistical physics background

C. Kittel, *Thermal physics,* Wiley, 1969. Cited as *TP.*

Crystallography

F. C. Phillips, *An introduction to crystallography,* Wiley, 3rd ed., 1963.

J. F. Nye, *Physical properties of crystals: their representation by tensors and matrices,* Oxford, 1957.

Problem collection

H. J. Goldsmid, ed., *Problems in solid state physics,* Academic Press, 1968.

Advanced series

F. Seitz, D. Turnbull and H. Ehrenreich, *Solid state physics, advances in research and applications,* Academic Press. Cited as *Solid state physics.*

Advanced texts

R. E. Peierls, *Quantum theory of solids,* Oxford, 1955.

C. Kittel, *Quantum theory of solids,* Wiley, 1963. Cited as *QTS.*

J. M. Ziman, *Principles of the theory of solids,* Cambridge, 1964.

Table of values

American Institute of Physics Handbook, McGraw-Hill, 3rd ed., 1971.

Guides to the literature

The original papers of the early workers in the field are most conveniently identified in the great scientific bibliographic series known as *Poggendorf;* this covers the last 100 years and more. The most valuable modern bibliographic aid is the *Scientific citation index.* For references to data on specific materials, consult the formula indices to *Chemical abstracts* and the subject indices to *Physics abstracts* and *Solid state abstracts.* Good bibliographies often accompany the review articles in *Reports on progress in physics, Critical reviews in solid state sciences, Solid state physics* (see above), *Springer tracts in modern physics,* Reviews of Modern Physics, Soviet Physics (Uspekhi), Comments on Solid State Physics, and Advances in Physics.

Contents

Advanced Topics

Guide to Major Tables

1

Crystal Structure

NOTATION: 1 Å = 1 angstrom = 10^{-8} cm = 10^{-10} m. Crystal lattice parameters are sometimes reported in kx-units, with 1.00208 kxu = 1 Å.

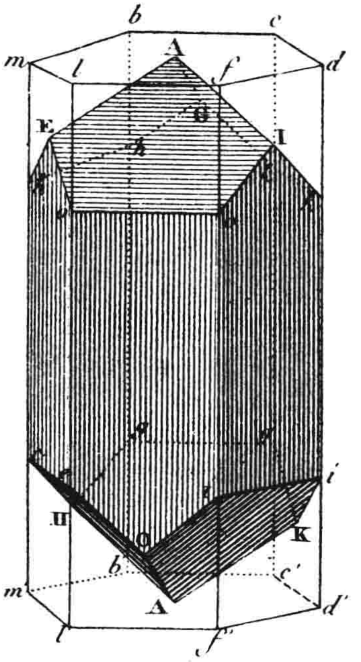

Figure 1 Sketch of a crystal, selected at random from an early mineralogy treatise. (Haüy.)

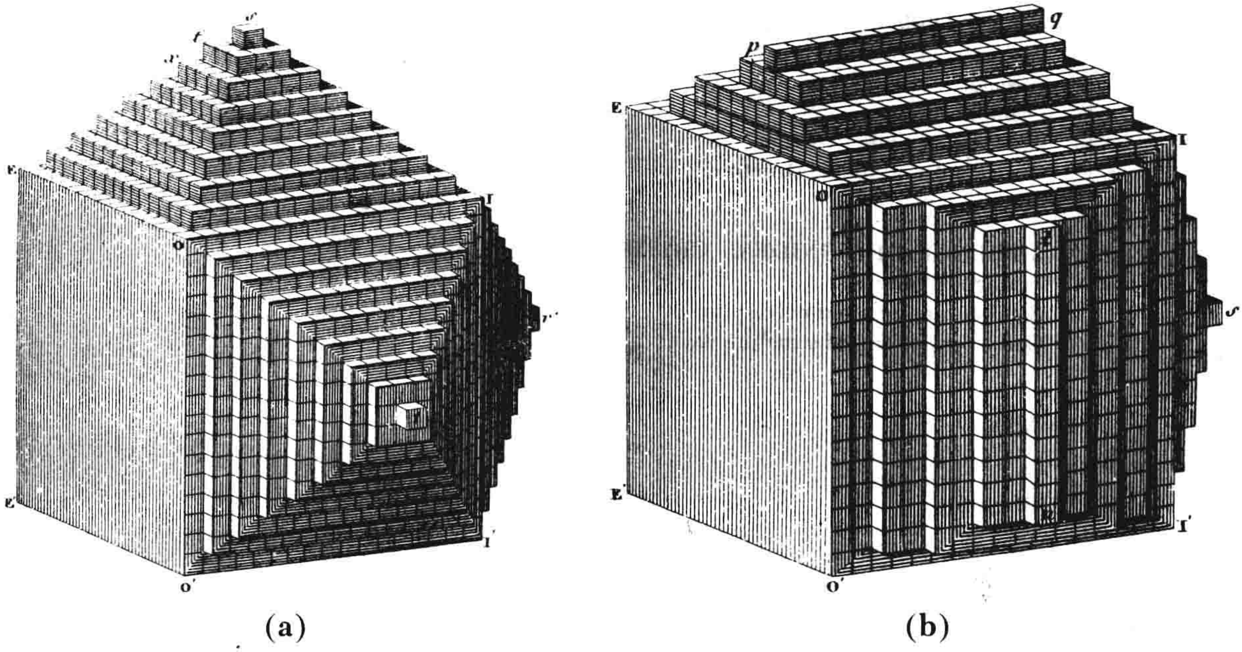

Figure 2 Relation of the external form of crystals to the form of the elementary building blocks. The building blocks are identical in (a) and (b), but different crystal faces are developed. (Haüy, from the atlas to the 1822 edition of his *Traité de cristallographie.*)

The study of the physical properties of the solid state, viewed as a branch of atomic physics, began in the early years of this century. Solid state physics is largely devoted to the study of crystals and of electrons in crystals. A century ago the study of crystals was concerned only with their external form and with symmetry relationships among the various coefficients that describe the physical properties. After 1910 physicists became deeply concerned with atomic models of crystals, following the discovery of x-ray diffraction and the publication of a series of simple and reasonably successful calculations and predictions of crystalline properties.

Many crystalline minerals and gems have been known and described for several thousand years. One of the earliest drawings of a crystal appears in a Chinese pharmacopeia of the eleventh century A.D. Quartz crystals from crowns have been preserved since 768 A.D. in the Shōsōin, the storehouse of the emperors of Japan in Nara. The word crystal referred first only to ice and then to quartz until the late middle ages when the word acquired a more general meaning.

The regularity of the appearance and of the external form of the crystals found in nature (Fig. 1) or grown in the laboratory disposed observers since the seventeenth century to the belief that crystals are formed by a regular repetition of identical building blocks (Fig. 2). When a crystal grows in a constant environment the shape remains unchanged during growth, as if identical elementary building blocks are added continuously to the crystal. We now know the elementary building blocks are atoms or groups of atoms: crystals are a three-dimensional periodic array of atoms.

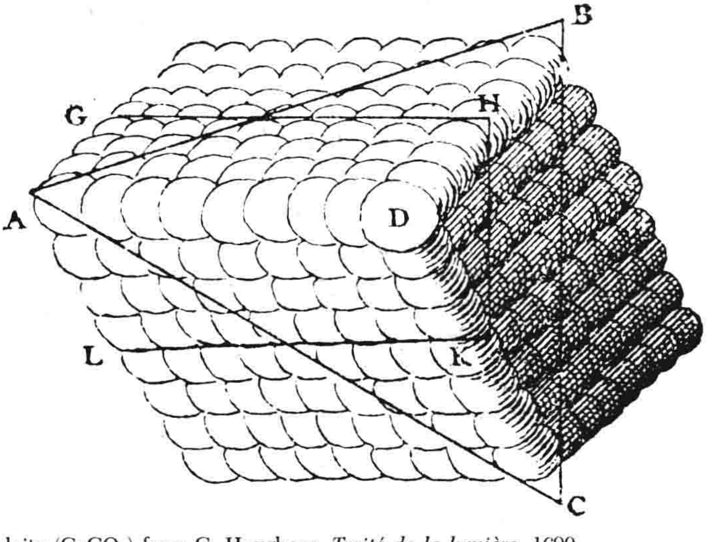

Figure 3 Model of calcite ($CaCO_3$) from C. Huyghens, *Traité de la lumière*, 1690.

In the eighteenth century mineralogists made the important discovery that the index numbers (on a certain scheme of indexing to be described later) of the directions of all faces of a crystal are exact integers. Haüy[1] showed that the arrangement of identical particles in a three-dimensional periodic array could account for this law of rational indices. A. L. Seeber[2] of Freiburg suggested in 1824 that the elementary building blocks of crystals were small spheres, and he proposed an empirical law of interatomic force with both attractive and repulsive regions as needed to cause a lattice array to be the stable equilibrium state of a system of identical atoms.

Probably the most important date in the history of the physics of solids is June 8, 1912, when a paper[3] entitled "Interference effects with Röntgen rays" was laid before the Bavarian Academy of Sciences in Munich. In the first part of the paper Laue develops an elementary theory of diffraction of x-rays by a periodic array of atoms. In the second part Friedrich and Knipping report the first experimental observations of x-ray diffraction by crystals.

The work demonstrated that x-rays are waves, because they can be diffracted. The work also proved decisively that crystals are composed of a periodic array of atoms. This experimental proof marks the beginning of the field of solid state physics as we know it today. With an established atomic model of a crystal, physicists could think or calculate further. Much important pioneer work in physics of solids was done in the years immediately following 1912. The first determinations of crystal structures by x-ray diffraction analysis were reported by W. L. Bragg in 1913: the structures of KCl, NaCl, KBr and KI are given by him in Proc. Roy. Soc. (London) **A89**, 248 (1913).

PERIODIC ARRAYS OF ATOMS

A symbolic language has been built up to describe crystal structures. A person who has learned the language of crystallography can reconstruct a crystal structure from a few printed symbols. We give here several elemen-

[1] R. J. Haüy, *Essai d'une théorie sur la structure des cristaux,* Paris, 1784; *Traité de cristallographie,* Paris, 1801.

[2] A. L. Seeber, "Versuch einer Erklärung des inneren Baues der festen Körper," Annalen der Physik (Gilbert) **76**, 229–248, 349–372 (1824).

[3] "Interferenz-Erscheinungen bei Roentgenstrahlen," W. Friedrich, P. Knipping, and M. Laue, Sitzungsberichte der Bayerischen Akademie de Wissenschaften, Math.-phys. Klasse, pp. 303–322, 1912. This paper, together with several others from the group around Laue, is reprinted with valuable annotations in Vol. 204 of Ostwald's *Klassiker der exakten Wissenschaften,* Akad. Verlag, Leipzig, 1923; the historical excerpts from Laue's Nobel prize lecture are of special interest. For personal accounts of the early years of x-ray diffraction studies of crystals, see P. P. Ewald, ed., *Fifty years of x-ray diffraction,* A. Oosthoek's Uitgeversmij., Utrecht, 1962. Shrewd guesses about the structures of a number of crystals had been made much earlier by W. Barlow, Nature **29**, 186, 205, 404 (1883); he argued from considerations of symmetry and packing (the filling of space).

tary ideas about the language, sufficient to describe the geometry of simple crystal structures.

An ideal crystal is constructed by the infinite regular repetition in space of identical structural units. In the simplest crystals such as copper, silver, gold, and the alkali metals the structural unit contains a single atom. More generally the structural unit contains several atoms or molecules, up to perhaps 100 in inorganic crystals[4] and 10^4 in protein crystals. A crystal may be composed of more than one chemical element (as in NaCl) or it may contain associated groups of identical atoms (as in H_2). We describe the structure of all crystals in terms of a single periodic lattice, but with a group of atoms attached to each lattice point or situated in each elementary parallelepiped. This group of atoms is called the **basis**; the basis is repeated in space to form the crystal. We now make these definitions more precise.

Crystal Translation Vectors and Lattices

An ideal crystal is composed of atoms arranged on a lattice defined by three **fundamental translation vectors a, b, c** such that the atomic arrangement looks the same in every respect when viewed from any point $\mathbf{r}$ as when viewed from the point

$$\mathbf{r}' = \mathbf{r} + n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c} \ , \qquad (1)$$

where n_1, n_2, n_3 are arbitrary integers (Fig. 4). Crystallographers may use $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ to denote the fundamental translation vectors.

The set of points $\mathbf{r}'$ specified by (1) for all values of the integers n_1, n_2, n_3 defines a **lattice.** A lattice[5] is a regular periodic arrangement of points in space. A lattice is a mathematical abstraction: the crystal structure is formed only when a basis of atoms is attached identically to each lattice point. The logical relation is

lattice + basis = crystal structure.

The lattice and the translation vectors **a, b, c** are said to be **primitive** if *any* two points $\mathbf{r}$, $\mathbf{r}'$ from which the atomic arrangement looks the same[6] always satisfy (1) with a suitable choice of the integers n_1, n_2, n_3.

[4] The intermetallic compound $NaCd_2$ has a cubic cell of 1192 atoms as its smallest structural unit; see S. Samson, Nature **195**, 259 (1962).

[5] We use the words *lattice* and *lattice points* interchangeably. Bravais noted that the lattice points are the roots of the equation

$$\sin^2(\pi\xi/a) + \sin^2(\pi\eta/b) + \sin^2(\pi\zeta/c) = 0,$$

where ξ, η, ζ are spatial coordinates referred to a system of three coordinate axes, in general oblique. The unit vectors of the coordinate system are denoted by $\hat{\mathbf{a}}$, $\hat{\mathbf{b}}$, $\hat{\mathbf{c}}$.

[6] This definition may sound clumsy, but it guarantees that there is no cell of smaller volume which could serve as a building block for the structure.