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5th EDITION

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Charles Kittel

INTRODUCTION TO

SOLID STATE PHYSICS

FIFTH EDITION





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About the Author

CHARLES KITTEL has taught solid state physics at the University of California at Berkeley since 1951, having previously been at the Bell Laboratories. His undergraduate work in physics was done at M.I.T. and at the Cavendish Laboratory of Cambridge University. His Ph.D. research was in theoretical nuclear physics with Professor Gregory Breit at the University of Wisconsin. He has been awarded three Guggenheim fellowships, the Oliver Buckley Prize for Solid State Physics, and the Distinguished Teaching Award at Berkeley. He is a member of the National Academy of Science and of the American Academy of Arts and Sciences. The first edition of *ISSP* appeared in 1953 as the first textbook to integrate the elementary parts of solid state physics for use by seniors and beginning graduate students; now in the fifth edition, *ISSP* is one of the most widely translated science textbooks. His recent research is in the field of electronhole condensation in semiconductors.

This is an elementary textbook on solid state physics and materials science for senior undergraduate and beginning graduate students of science and engineering. Solid state physics is largely concerned with the remarkable properties exhibited by atoms and molecules because of their regular arrangement in crystals. The properties include electron energy bands and the elementary excitations of solids: phonons, plasmons, polarons, excitons, magnons, and polaritons. This book tells how they can be understood in terms of simple models. Real solids may be more complicated, but the power and utility of the elementary models cannot be overestimated.

The first edition appeared in 1953, five years after the publication of the discovery of the transistor. Today the solid state revolution is in full development. Because of the profitable interplay of experiment and theory, there is intellectual excitement in solid state physics—as witnessed by the Nobel Prize awards during the past decade. Throughout the world, more physicists are usefully employed in solid state physics than in any other field.

In this edition a new effort has been made to help undergraduates: the first half of the book now provides students with an elementary one-quarter or one-semester introduction to solid state physics through the physics of semiconductors in Chapter 8. This part makes only modest demands on the reader's background in electricity and magnetism. A short course might be completed by parts or all of Chapters 12 through 15. The second half of the book applies the material in the beginning chapters to well-defined areas. It contains matter that makes a frank appeal to electromagnetism at the intermediate level: plasmons, optical properties, superconductivity, ferroelectrics, and magnetism.

The discussion of superconductors is improved: simple estimates are given for the upper and lower critical fields, the Josephson-Anderson derivation of the London equation is adopted, and the lifetime of persistent currents is calculated to exceed the age of the universe. The most common and most serious defect in solid state textbooks is an inadequate derivation of the properties of holes, as in semiconductors; in this edition their properties are clearly and extensively argued. Among the new topics in this edition are the Peierls instability, magnetic bubbles, Gunn oscillators, solar cells, Alfvén waves, electron-hole drops, and thermoelectric effects. Many of the 54 tables have been revised; there are some 50 new drawings and numerous new problems.

Some instructors prefer to start their lectures with the Drude model of the free electron gas. To do this, start with the chapter sequence 6, 7, 2, 8, 9.

The selection of subjects should not be seen as a measure of the importance of various areas, any more than the selection of references measures individual contributions. A single textbook cannot represent the range of current activity. Reviews in the Seitz-Turnbull-Ehrenreich and other series may be consulted for subjects not treated here and for detailed bibliographies. There are in the literature perhaps 20,000 articles of high quality that could usefully be cited. I have tried to give a helpful, but small, sample of those most accessible in English. The translations of this book into French, German, Spanish, Italian, Japanese, Russian, Polish, Roumanian, Hungarian, Chinese, and Arabic often give further references in these languages; there is a good student's workbook in Swedish.

Important equations are repeated in SI and CGS-Gaussian units, where these differ. Exceptions to this rule are the figure captions, 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 translate from CGS to SI.

Tables are in conventional units. The contents pages of several chapters discuss conventions that were adopted to make parallel usage simple and natural. The symbol e denotes the charge on the proton and is positive. The notation (18) refers to Equation 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 over a vector, as in $\hat{\mathbf{k}}$, denotes a unit vector. Problems of appreciable length or difficulty are preceded by an asterisk; I like to assign them for extra credit. For production reasons the format of the book has been changed from recent editions. The present page is longer and the line is longer. Appendices in the last edition have either been incorporated into the chapters or, where rarely taught, they have been dropped.

The preparation of this edition was made possible by the cooperation of many colleagues and friends. M. L. Cohen and L. M. Falicov kindly reviewed several new chapters. Among my new debts are those to: D. Gugan, D. Penn, C. D. Jeffries, A. M. Portis, M. J. Buerger, Leo Brewer, F. L. Richards, F. C. Brown, A. Maradudin, B. T. Matthias, R. Dalven, W. M. Star, C. P. Slichter, J. A. Wilson, J. C. Hensel, and R. T. Schumacher. I am again grateful to the more than 150 people who contributed to the earlier editions. I thank Felix Cooper, who did the artwork, and Carol Tung for the preparation of the manuscript. Richard Robinson and Frank Velek of our Physics Library have been generous with their interest and their time.

C. Kittel

BERKELEY, CALIFORNIA

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, New York 10016.

Some General References

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Guides to the literature

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*, *Springer tracts in modern physics*, Reviews of Modern Physics, Soviet Physics (Uspekhi), and Advances in Physics. The *Solid state physics literature guides* (Plenum) are valuable aids.

SOLID STATE PHYSICS

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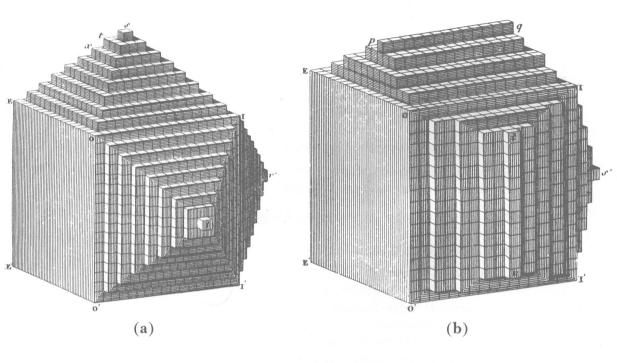
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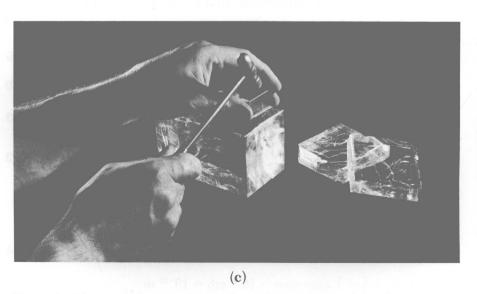


Figure 1 Relation of the external form of crystals to the form of the elementary building blocks. The building blocks are identical in (a) and (b), but different crystal faces are developed. (c) Cleaving a crystal of rocksalt.

Solid state physics is devoted largely to the study of crystals and electrons in crystals. The study of solid state physics as an extension of atomic physics began in the early years of this century following the discovery of x-ray diffraction and the publication of a series of simple and successful

calculations and predictions of crystalline properties.

The regularity of the external form of crystals disposed early observers to the belief that crystals are formed by the regular repetition of identical building blocks (Fig. 1). When a crystal grows in a constant environment, the shape remains unchanged during growth, as if identical building blocks are added continuously. The building blocks are atoms or groups of atoms: a crystal is a three-dimensional periodic array of atoms. This was known in the 18th century when mineralogists discovered that the index numbers of the directions of all faces of a crystal are exact integers. Haüy¹ showed that the arrangement of identical particles in a three-dimensional periodic array could account for a law of rational or integral indices.

On June 8, 1912, a paper entitled "Interference effects with Röntgen rays" was presented to the Bavarian Academy of Sciences in Munich. In the first part of the paper, Laue developed an elementary theory of diffraction of x-rays by a periodic array of atoms. In the second part, Friedrich and Knipping reported the first experimental observations of x-ray diffraction by crystals. The work proved decisively that crystals are composed of a periodic array of atoms2 and marked the beginning of the field of solid state physics. With an established atomic model of a crystal, physicists could think much further.

R. J. Hauy, Essai d'une théorie sur la structure des cristaux, Paris, 1784; Traité de cristallographie, Paris, 1801.

²For 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.

PERIODIC ARRAYS OF ATOMS

An ideal crystal is constructed by the infinite repetition in space of identical structural units. In the simplest crystals such as copper, silver, iron, aluminum, and the alkali metals, the structural unit is a single atom. Often the structural unit is several atoms or molecules, up to perhaps 100 in inorganic crystals³ and 10,000 in protein crystals. The structure of all crystals is described in terms of a lattice with a group of atoms attached to each lattice point. The group is called the **basis**; it is repeated in space to form the crystal structure. We now make these definitions more precise.

Lattice Translation Vectors and Lattices

An ideal crystal is composed of atoms arranged on a lattice defined by three fundamental translation vectors \mathbf{a} , \mathbf{b} , \mathbf{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

$$\mathbf{r}' = \mathbf{r} + u\mathbf{a} + v\mathbf{b} + w\mathbf{c} , \qquad (1)$$

where u, v, w are arbitrary integers. The set of points \mathbf{r}' specified by (1) for all values of the integers u, v, w defines a lattice. A lattice 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

The lattice and the translation vectors \mathbf{a} , \mathbf{b} , \mathbf{c} are said to be **primitive** if any two points \mathbf{r} , \mathbf{r}' from which the atomic arrangement looks the same always satisfy (1) with a suitable choice of the integers u, v, w. This definition of the primitive translation vectors guarantees that there is no cell of smaller volume that could serve as a building block for the structure. We often use primitive translation vectors to define the crystal axes, although nonprimitive crystal axes may be used when they are simpler. The crystal axes \mathbf{a} , \mathbf{b} , \mathbf{c} form three adjacent edges of a parallelepided. If there are lattice points only at the corners of the parallelepiped, then it is a primitive parallelepiped. A lattice translation operation is defined as the displacement of a crystal parallel to itself by a crystal translation vector

$$\mathbf{T} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c} . \tag{2}$$

Any two lattice points are connected by a vector of this form.

³The intermetallic compound NaCd₂ has a cubic cell of 1192 atoms as its smallest structural unit; S. Samson, Nature **195**, 259 (1962).

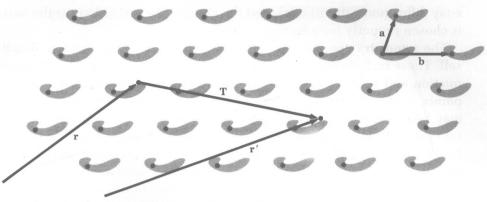


Figure 2 Portion of a crystal of an imaginary protein molecule, in a two-dimensional world. (We picked a protein molecule because it is not likely to have a special symmetry of its own.) The atomic arrangement in the crystal looks exactly the same to an observer at \mathbf{r}' as to an observer at \mathbf{r} , provided that the vector \mathbf{T} which connects \mathbf{r}' and \mathbf{r} may be expressed as an integral multiple of the vectors \mathbf{a} and \mathbf{b} . In this illustration, $\mathbf{T} = -\mathbf{a} + 3\mathbf{b}$. The vectors \mathbf{a} and \mathbf{b} are primitive translation vectors of the two-dimensional lattice.

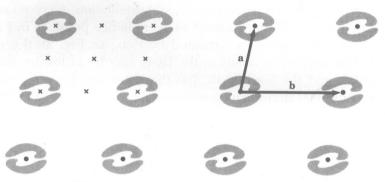


Figure 3 Similar to Fig. 2, but with protein molecules associated in pairs. The crystal translation vectors are ${\bf a}$ and ${\bf b}$. A rotation of π radians about any point marked \times will carry the crystal into itself. This occurs also for equivalent points in other cells, but we have marked the points \times only within one cell.

Symmetry Operations

In describing a crystal structure, there are three important questions to answer: What is the lattice? What crystal axes a, b, c do we wish to use to describe the lattice? What is the basis? More than one lattice is always possible for a given structure and more than one set of crystal axes is always possible for a given lattice. We cannot pick the basis until we have selected the lattice and the axes we wish to use. Everything (such as the