

SEVENTH EDITION

Introduction to Solid State Physics

CHARLES KITTEL

About the Author

Charles Kittel taught solid state physics at Berkeley from 1951 to 1978; earlier he was a member of the solid state group at the Bell Laboratories. His undergraduate work was at M.I.T. and at Cambridge University, followed by graduate work at the University of Wisconsin. He is a member of the National Academy of Science and of the American Academy of Arts and Sciences.

His research in solids began with studies of ferromagnetic, antiferromagnetic, and paramagnetic resonance, along with work on magnetic domains, spin waves, and domain boundaries in ferromagnets and ferroelectrics. His work on the single domain structure of fine particles has had broad application in magnetic recording, geomagnetism, and biomagnetism. Along with collaborators at Berkeley he did the first work on cyclotron resonance in semiconductors, which led to the understanding of the band structure of silicon, germanium, and indium antimonide, together with the theory of their impurity states. He also worked on the interpretation of magnetoplasma resonance in semiconductors and of Alfvén resonance in electron-hole drops in germanium.

The first edition of *ISSP* integrated the elementary aspects of solid state physics for study by seniors and beginning graduate students. Now in its seventh edition, *ISSP* plays the same part for the current generation of students.

Copyright © 1953, 1956, 1966, 1971, 1976, 1986, 1996 by John Wiley & Sons, Inc.

All rights reserved. Published simultaneously in Canada.

No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning or otherwise, except as permitted under Sections 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, (978) 750-8400, fax (978) 750-4470. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008, E-Mail: PERMREQ@WILEY.COM.

To order books or for customer service please, call 1(800)-CALL-WILEY (225-5945).

Library of Congress Cataloging in Publication Data:

Charles Kittel.

Introduction to solid state physics / Charles Kittel. — 7th ed.

p. cm.

Includes index.

ISBN 0-471-11181-3 (cloth : alk. paper)

1. Solid state physics. I. Title.

QC176.K5 1996

530.4'1—dc20

95-18445

CIP

Printed in the United States of America

15 14 13

Contents

<i>Guide to Tables</i>	ix
<i>General References</i>	xi
1 CRYSTAL STRUCTURE	1
2 RECIPROCAL LATTICE	27
3 CRYSTAL BINDING AND ELASTIC CONSTANTS	53
4 PHONONS I. CRYSTAL VIBRATIONS	97
5 PHONONS II. THERMAL PROPERTIES	115
6 FREE ELECTRON FERMI GAS	141
7 ENERGY BANDS	173
8 SEMICONDUCTOR CRYSTALS	197
9 FERMI SURFACES AND METALS	233
10 PLASMONS, POLARITONS, AND POLARONS	269
11 OPTICAL PROCESSES AND EXCITONS	305
12 SUPERCONDUCTIVITY	333
13 DIELECTRICS AND FERROELECTRICS	379
14 DIAMAGNETISM AND PARAMAGNETISM	415
15 FERROMAGNETISM AND ANTIFERROMAGNETISM	441
16 MAGNETIC RESONANCE	485
17 NONCRYSTALLINE SOLIDS	519
18 POINT DEFECTS	539

19	SURFACE AND INTERFACE PHYSICS	553
20	DISLOCATIONS	585
21	ALLOYS	609

Appendix

A	TEMPERATURE DEPENDENCE OF THE REFLECTION LINES	631
B	EWALD CALCULATION OF LATTICE SUMS	634
C	QUANTIZATION OF ELASTIC WAVES: PHONONS	638
D	FERMI-DIRAC DISTRIBUTION FUNCTION	643
E	DERIVATION OF dk/dt EQUATION	646
F	BOLTZMANN TRANSPORT EQUATION	647
G	VECTOR POTENTIAL, FIELD MOMENTUM, AND GAUGE TRANSFORMATIONS	651
H	COOPER PAIRS	656
I	GINSBURG-LANDAU EQUATION	658
J	ELECTRON-PHONON COLLISIONS	662

Subject Index

Table of SI Prefixes

667
673

7

Energy Bands

NEARLY FREE ELECTRON MODEL	176
Origin of the energy gap	177
Magnitude of the energy gap	179
BLOCH FUNCTIONS	179
KRONIG-PENNEY MODEL	180
WAVE EQUATION OF ELECTRON IN A PERIODIC POTENTIAL	183
Restatement of the Bloch theorem	185
Crystal momentum of an electron	186
Solution of the central equation	186
Kronig-Penney model in reciprocal space	187
Empty lattice approximation	188
Approximate solution near a zone boundary	189
NUMBER OF ORBITALS IN A BAND	192
Metals and insulators	193
SUMMARY	195
PROBLEMS	195
1. Square lattice, free electron energies	195
2. Free electron energies in reduced zone	195
3. Kronig-Penney model	195
4. Potential energy in the diamond structure	195
5. Complex wavevectors in the energy gap	196
6. Square lattice	196
REFERENCES	196

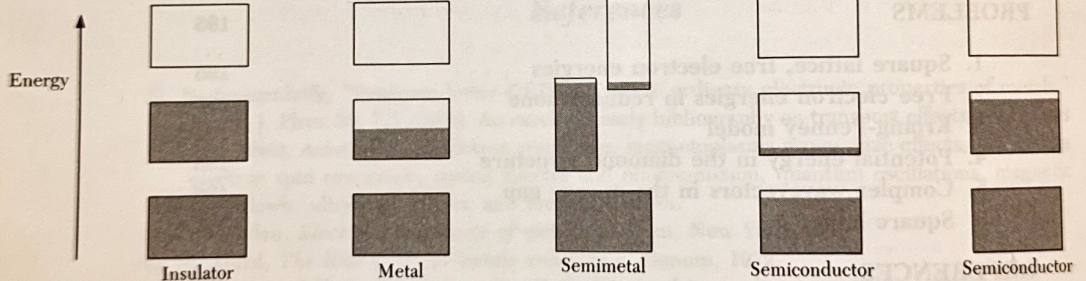


Figure 1 Schematic electron occupancy of allowed energy bands for an insulator, metal, semimetal, and semiconductor. The vertical extent of the boxes indicates the allowed energy regions; the shaded areas indicate the regions filled with electrons. In a **semimetal** (such as bismuth) one band is almost filled and another band is nearly empty at absolute zero, but a pure **semiconductor** (such as silicon) becomes an insulator at absolute zero. The left of the two semiconductors shown is at a finite temperature, with carriers excited thermally. The other semiconductor is electron-deficient because of impurities.

CHAPTER 7: ENERGY BANDS

When I started to think about it, I felt that the main problem was to explain how the electrons could sneak by all the ions in a metal. . . . By straight Fourier analysis I found to my delight that the wave differed from the plane wave of free electrons only by a periodic modulation.

F. Bloch

The free electron model of metals gives us good insight into the heat capacity, thermal conductivity, electrical conductivity, magnetic susceptibility, and electrodynamics of metals. But the model fails to help us with other large questions: the distinction between metals, semimetals, semiconductors, and insulators; the occurrence of positive values of the Hall coefficient; the relation of conduction electrons in the metal to the valence electrons of free atoms; and many transport properties, particularly magnetotransport. We need a less naïve theory, and fortunately it turns out that almost any simple attempt to improve upon the free electron model is enormously profitable.

The difference between a good conductor and a good insulator is striking. The electrical resistivity of a pure metal may be as low as 10^{-10} ohm-cm at a temperature of 1 K, apart from the possibility of superconductivity. The resistivity of a good insulator may be as high as 10^{22} ohm-cm. This range of 10^{32} may be the widest of any common physical property of solids.

Every solid contains electrons. The important question for electrical conductivity is how the electrons respond to an applied electric field. We shall see that electrons in crystals are arranged in **energy bands** (Fig. 1) separated by regions in energy for which no wavelike electron orbitals exist. Such forbidden regions are called **energy gaps** or **band gaps**, and result from the interaction of the conduction electron waves with the ion cores of the crystal.

The crystal behaves as an insulator if the allowed energy bands are either filled or empty, for then no electrons can move in an electric field. The crystal behaves as a metal if one or more bands are partly filled, say between 10 and 90 percent filled. The crystal is a semiconductor or a semimetal if one or two bands are slightly filled or slightly empty.

To understand the difference between insulators and conductors, we must extend the free electron model to take account of the periodic lattice of the solid. The possibility of a band gap is the most important new property that emerges.

We shall encounter other quite remarkable properties of electrons in crystals. For example, they respond to applied electric or magnetic fields as if the electrons were endowed with an effective mass m^* , which may be larger or smaller than the free electron mass, or may even be negative. Electrons in crystals respond to applied fields as if endowed with negative or positive

charges, $-e$ or $+e$, and herein lies the explanation of the negative and positive values of the Hall coefficient.

NEARLY FREE ELECTRON MODEL

On the free electron model the allowed energy values are distributed essentially continuously from zero to infinity. We saw in Chapter 6 that

$$\epsilon_{\mathbf{k}} = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2), \quad (1)$$

where, for periodic boundary conditions over a cube of side L ,

$$k_x, k_y, k_z = 0; \pm \frac{2\pi}{L}; \pm \frac{4\pi}{L}; \dots \quad (2)$$

The free electron wavefunctions are of the form

$$\psi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}); \quad (3)$$

they represent running waves and carry momentum $\mathbf{p} = \hbar\mathbf{k}$.

The band structure of a crystal can often be explained by the nearly free electron model for which the band electrons are treated as perturbed only weakly by the periodic potential of the ion cores. This model answers almost all the qualitative questions about the behavior of electrons in metals.

We know that Bragg reflection is a characteristic feature of wave propagation in crystals. Bragg reflection of electron waves in crystals is the cause of energy gaps. (At Bragg reflection wavelike solutions of the Schrödinger equation do not exist, as in Fig. 2.) These energy gaps are of decisive significance in determining whether a solid is an insulator or a conductor.

We explain physically the origin of energy gaps in the simple problem of a linear solid of lattice constant a . The low energy portions of the band structure are shown qualitatively in Fig. 2, in (a) for entirely free electrons and in (b) for electrons that are nearly free, but with an energy gap at $k = \pm \pi/a$. The Bragg condition $(\mathbf{k} + \mathbf{G})^2 = k^2$ for diffraction of a wave of wavevector $\mathbf{k}$ becomes in one dimension

$$k = \pm \frac{1}{2}G = \pm n\pi/a, \quad (4)$$

where $G = 2\pi n/a$ is a reciprocal lattice vector and n is an integer. The first reflections and the first energy gap occur at $k = \pm \pi/a$. The region in k space between $-\pi/a$ and π/a is the **first Brillouin zone** of this lattice. Other energy gaps occur for other values of the integer n .

The wavefunctions at $k = \pm \pi/a$ are not the traveling waves $\exp(i\pi x/a)$ or $\exp(-i\pi x/a)$ of free electrons. At these special values of k the wavefunctions are