Springer Series in
Solid-State Sciences 75

M. L. Cohen
J. R. Chelikowsky

# Electronic Structure and Optical Properties of Semiconductors

Springer-Verlag

Marvin L. Cohen
James R. Chelikowsky

# Electronic Structure and Optical Properties of Semiconductors

With 161 Figures

Springer-Verlag Berlin Heidelberg New York
London Paris Tokyo

Professor Marvin L. Cohen, PhD

Department of Physics, University of California,
and Materials and Chemical Sciences Division,
Lawrence Berkeley Laboratory, Berkeley, CA 94720, USA

Professor James R. Chelikowsky, PhD

Department of Chemical Engineering and Materials Science,
University of Minnesota, Minneapolis, MN 55455, USA



ISBN 3-540-18818-5 Springer-Verlag Berlin Heidelberg New York
ISBN 0-387-18818-5 Springer-Verlag New York Berlin Heidelberg

Library of Congress Cataloging-in-Publication Data.
Cohen, Marvin L.
Electronic structure and optical properties of semiconductors /
Marvin L. Cohen, James R. Chelikowsky.
p. cm.–(Springer series in solid-state science ; 75)
Bibliography: p.
Includes index.
1. Semiconductors–Optical properties. 2. Electronic structure.
3. Energy-band theory of solids. I. Chelikowsky, James R.
II. Title. III. Series.
QC611.6.06C63 1988 537.6'22–dc 19 88-1964


Printed in Germany



Printing: Druckhaus Beltz, 6944 Hemsbach/Bergstr.
Binding: J. Schäffer GmbH & Co. KG., 6718 Grünstadt
2154/3150-543210

75 Springer Series in Solid-State Sciences

Edited by M. Cardona

# Springer Series in Solid-State Sciences

Editors: M. Cardona P. Fulde K. von Klitzing H.-J. Queisser

Volumes 1–49 are listed on the back inside cover

50 **Multiple Diffraction of X-Rays in Crystals**
By Shih-Lin Chang

51 **Phonon Scattering in Condensed Matter**
Editors: W. Eisenmenger, K. Laßmann, and S. Döttinger

52 **Superconductivity in Magnetic and Exotic Materials**
Editors: T. Matsubara and A. Kotani

53 **Two-Dimensional Systems, Heterostructures, and Superlattices**
Editors: G. Bauer, F. Kuchar, and H. Heinrich

54 **Magnetic Excitations and Fluctuations**
Editors: S. Lovesey, U. Balucani, F. Borsa, and V. Tognetti

55 **The Theory of Magnetism II**
Thermodynamics and Statistical Mechanics
By D.C. Mattis

56 **Spin Fluctuations in Itinerant Electron Magnetism** By T. Moriya

57 **Polycrystalline Semiconductors,**
Physical Properties and Applications
Editor: G. Harbeke

58 **The Recursion Method and Its Applications**
Editors: D. Pettifor and D. Weaire

59 **Dynamical Processes and Ordering on Solid Surfaces**
Editors: A. Yoshimori and M. Tsukada

60 **Excitonic Processes in Solids**
By M. Ueta, H. Kanzaki, K. Kobayashi, Y. Toyozawa, and E. Hanamura

61 **Localization, Interaction, and Transport Phenomena**
Editors: B. Kramer, G. Bergmann, and Y. Bruynseraede

62 **Theory of Heavy Fermions and Valence Fluctuations**
Editors: T. Kasuya and T. Saso

63 **Electronic Properties of Polymers and Related Compounds**
Editors: H. Kuzmany, M. Mehring, and S. Roth

64 **Symmetries in Physics** Group Theory Applied to Physical Problems
By W. Ludwig and C. Falter

65 **Phonons: Theory and Experiments II**
Experiments and Interpretation of Experimental Results By P. Brüesch

66 **Phonons: Theory and Experiments III**
Phenomena Related to Phonons
By P. Brüesch

67 **Two-Dimensional Systems: Physics and New Devices**
Editors: G. Bauer, F. Kuchar, and H. Heinrich

68 **Phonon Scattering in Condensed Matter V**
Editors: A.C. Anderson and J.P. Wolfe

69 **Nonlinearity in Condensed Matter**
Editors: A.R. Bishop, D.K. Campbell, P. Kumar and S.E. Trullinger

70 **From Hamiltonians to Phase Diagrams**
The Electronic and Statistical-Mechanical Theory of sp-Bonded Metals and Alloys
By J. Hafner

71 **High Magnetic Fields in Semiconductor Physics**
Editor: G. Landwehr

72 **One-Dimensional Conductors**
By S. Kagoshima, H. Nagasawa, and T. Sambongi

73 **Quantum Solid-State Physics**
Editors: S.V. Vonsovsky and M.I. Katsnelson

74 **Quantum Monte Carlo Methods** in Equilibrium and Nonequilibrium Systems
Editor: M. Suzuki

75 **Electronic Structure and Optical Properties of Semiconductors**
By M.L. Cohen and J.R. Chelikowsky

76 **Electronic Properties of Conjugated Polymers**
Editors: H. Kuzmany, M. Mehring, and S. Roth

77 **Fermi Surface Effects**
Editors: J. Kondo and A. Yoshimori

78 **Group Theory and Its Applications in Physics**
By T. Inui, Y. Tanabe and Y. Onodera

79 **Elementary Excitations in Quantum Fluids**
Editors: K. Ohbayashi and M. Watabe

80 **Monte-Carlo Simulation in Statistical Physics Introduction**
By K. Binder and D.W. Heermann

81 **Core-Level Spectroscopy in Condensed Systems**
Editors: J. Kanamori and A. Kotani

82 **Introduction to Photoemission Spectroscopy**
By S. Hüfner

83 **Physics and Technology of Submicrometer Structures**
Editors: G. Bauer, F. Kuchar and H. Heinrich

84 **Beyond the Crystalline State An Emerging Perspective**
By G. Venkataraman, D. Sahoo and V. Balakrishnan

85 **The Fractional Quantum Hall Effect Properties of an Incompressible Quantum Fluid**
By T. Chakraborty and P. Pietiläinen

*to Merrill,*
*Mark and Susan,*
*and Mitzy,*
*Bryan, Matthew and Todd*

# Preface

We began planning and writing this book in the late 1970s at the suggestion of Manuel Cardona and Helmut Lotsch. We also received considerable encouragement and stimulation from colleagues. Some said there was a need for instructional material in this area while others emphasized the utility of a research text. We tried to strike a compromise. The figures, tables, and references are included to enable researchers to obtain quickly essential information in this area of semiconductor research. For instructors and students, we attempt to cover some basic ideas about electronic structure and semiconductor physics with applications to real, rather than model, solids.

We wish to thank our colleagues and collaborators whose research results and ideas are presented here. Special thanks are due to Jim Phillips who influenced us both during our formative years and afterwards. We are grateful to Sari Yamagishi for her patience and skill with the typing and production of the manuscript. Finally, we acknowledge the great patience of Helmut Lotsch and Manuel Cardona.

Berkeley, CA
Minneapolis, MN,
March 1988

*M.L. Cohen*
*J.R. Chelikowsky*

# Contents

# 1. Introduction

Semiconductors have played a major role in the current technological revolution. The enormous advances in electronics and computer science were made possible by a better understanding of the properties of semiconductors, and it is likely that the revolution has only just begun.

From the point of view of basic science and solid state physics in particular, semiconductors have been central and fundamental. Research on the properties of semiconductors has led not only to the transistor (Nobel Prize, 1956) but also to new insights into properties of matter such as tunneling (Nobel Prize, 1973 and 1986), disorder (Nobel Prize, 1977), and new quantum effects (Nobel Prize, 1985). In addition, studies of semiconductor band structures have had a vast impact on our understanding of the fundamental electronic structure of solids. Although most device applications focus on the minimum semiconductor band gap, which is generally around 1 eV, solid state physicists have been interested in a wider range of energy $\sim 1$ Ry. Research on electronic structure in this range has led to tests of the theories of quantum mechanics, optics, and electromagnetism.

For the past 50 to 60 years, a major aspiration of condensed matter physics has been to explain and predict the properties of solids knowing only the identities of the constituent atoms. Recently, this goal has been realized for many semiconductor properties. The successes are best illustrated by the progress made in understanding the electronic and optical properties of semiconductors. Recently, even crystal structures have been determined using accurate electronic calculations, but this area is in its infancy relative to the vast amount of experimental and theoretical work on optical properties.

The use of optical measurements to study a physical system is not a departure from traditional physics since it is probably true that more physics has been learned using photons as probes than by any other means. For example, the great advances of Heisenberg and Pauli were based on spectroscopic data. For many years, the major tests of quantum mechanics were almost synonymous with optical measurements in atoms (i.e., gases). However, in most areas, the transition from studying atoms to studying solids using optical probes came slowly. The standard argument was that the band spectra of solids were too broad to give useful detailed electronic structure data. It was obvious that the sharp, narrow line spectra associated with atoms lend themselves readily to interpretation in terms of electron transi-

tions between narrow energy levels, but the band spectra of solids, although they also contain definitive structure capable of being interpreted, received far less attention. For solids, the experiments and theories require more sophistication, but the data are rich with clues, and a quantum mechanical theory can be constructed to unravel the mysteries.

Dozens of crystals have been analyzed, and the extent of the collaborative effort between experimentalists and theorists in this area has few parallels. The result is a detailed picture of the underlying mechanisms associated with optical processes. Some of the achievements are: accurate determinations of the electronic energy levels, wavefunctions for electrons in specific materials, interpretation of optical spectra in terms of electronic transitions between energy levels, theories giving gross trends for a wide variety of materials, and a variety of calculations related to properties not directly associated with optical probes. The approaches and techniques have allowed critical tests of the theory of electronic structure. These studies have resulted in the development of new approaches for electronic structure calculations, response theory, and so on.

The purpose of this volume is to review some of the highlights associated with the above studies and to provide information concerning the theoretical and experimental techniques. Another important objective is to supply some of the useful information which has been gathered in these studies. Sometimes references to the literature will be given in lieu of results.

Although some general aspects of electronic structure calculations will be reviewed, the focus will on the pseudopotential approach. On the experimental side, emphasis will be on techniques which investigate band structure. In particular, those measurements which give information about the electronic structure over a large energy range ($\sim 1\,\mathrm{Ry}$) will be discussed in detail. The primary particle probe will be photons; reflectivity and photoemission measurements will be featured.

Our hope is that this volume can serve both as a coherent source for the underlying ideas relating electronic structure and optical properties and as a source of factual information about semiconductors. Because of the latter goal, we have included other relevant information about semiconductor properties which is not directly connected with the studies discussed, that is, lattice constants, effective masses, minimum band gaps, etc., and an attempt was made to include the most accurate and most current values. Hence, this volume is intended to lie somewhere between a textbook and a reference book. Numerous references to the literature are made, and it is hoped that these will serve as bridges to material beyond the scope of this book.

In most cases when discussing results, we have relied on a prototypical crystal. Having presented the general ideas and results for the prototype, extensions to other materials in the same class are described. Following this,

other related classes of materials are discussed. For example, silicon will be used as one prototype. The band structure, optical response curves, density of states, and other properties will be described. Results for other diamond structure materials will then be given, and only those properties which differ from silicon will be discussed in any detail. The extensions to zinc-blende and other crystal types will then be made.

# 2. Theoretical Concepts and Methods

Of the many options for broadly classifying solids, electrical resistivity has proved to be the most useful. The grouping of materials into insulators, semiconductors, semimetals, and metals involves a parameter with a range of order $10^{30}$. The resistivity boundaries between the classifications are not very sharp, but they are sharp enough to make the separation for most practical purposes. For the semiconductor regime, the resistivity is betwen $10^{9}$ and $10^{-3}$ ohm-cm, but we will also discuss insulators with resistivities above $10^{9}$ ohm-cm and doped semiconductors and semimetals with resistivities below $10^{-3}$ ohm-cm. The distinction at the boundary between semiconductors and insulators will be made on the basis of the size of the fundamental (minimum) band gap. Semiconductors are assumed to have band gaps from 0 to $\sim 4\,\mathrm{eV}$, insulators $> 4\,\mathrm{eV}$, and semimetals $\leq 0$. Gray Sn ($\alpha$-Sn) is an example of a borderline material which has zero band gap. It has been called a zero-gap semiconductor; it has also been called in ideal semimetal.

The wide range of resistivities of crystalline solids can be explained using band theory, which is one of the major successes of condensed matter theory. The existence of bands, gaps, overlap of bands, and the other important properties of band theory will be discussed later. These concepts and properties are the direct consequences of the model used to describe a solid. There are two conceptual models commonly used by theorists which are both useful and lead to a wealth of practical calculations.

The two popular models of solids are the interacting atoms model and the elementary excitation model. Since a solid is clearly a set of interacting atoms, the former model implies that the atoms retain their character and that perturbation theory on atomic properties will lead to a convenient description of solids. Only partial success has been achieved when this approach is taken too literally. The interacting atoms model has therefore evolved from describing a collection of individual atoms to a model of a solid composed of cores and valence electrons (Fig. 2.1). A core is composed of a nucleus and core electrons. In the frozen-core approximation, which is fundamental to the pseudopotential approach, the cores are taken to be inert with respect to the formation of the solid. Therefore, cores in solids are the same as the cores in isolated atoms, and only the valence electrons readjust when the solid is formed. For silicon, this implies that the electronic structure of the core is $(1s)^2(2s)^2(2p)^6$. Thus sodium, magnesium, and alu-

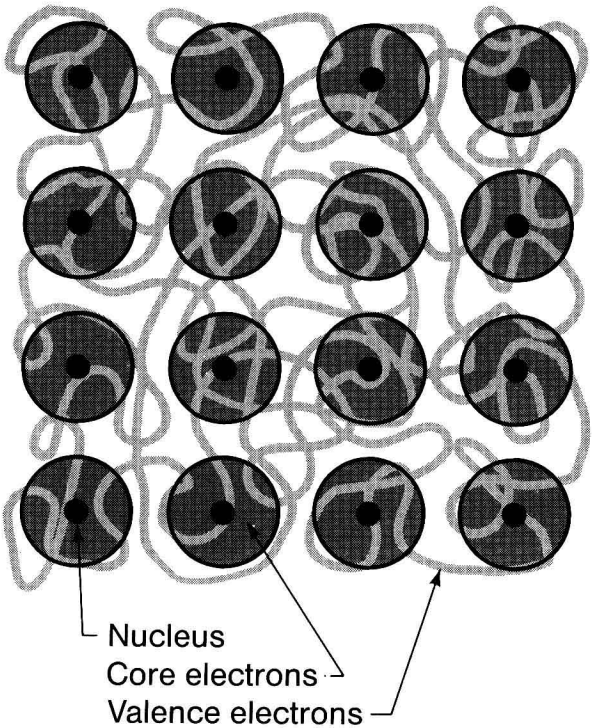


**Fig. 2.1.** Model of a solid with cores and valence electrons

minum all have the same core electrons as silicon, but the core charges, because of the nuclei involved, are +1 for sodium, +2 for magnesium, +3 for aluminum, and +4 for silicon. The valence electrons are $(3s)^1$, $(3s)^2$, $(3s)^2(3p)^1$, and $(3s)^2(3p)^2$ respectively for these elements.

The interacting atoms model for silicon consists of cores with charge +4 arranged in a regular array with the four valence electrons per core moving more or less freely through the core lattice. Interactions exist between the cores, between the cores and valence electrons, and between the valence electrons themselves. The Coulomb interaction dominates, and the many-body problem involving around $10^{23}$ particles per $cm^3$ can, in principle, be solved using quantum mechanics.

For the elementary excitation model, the excitations of the solid are considered to be decomposed into normal modes, and the responses of the solid to external probes are described in terms of these modes or collective excitations. A similar approach is used for describing electromagnetic radiation in terms of photons using the formalism of quantum electrodynamics. An example of an analogous description for solids would be the concept of phonons. We begin with a description of the vibrations of atomic cores. The simplest models involve masses connected by springs [2.1]. The dispersion curve, i.e., the wavevector dependent frequency, $\omega(q)$, describes

the motion of the cores in real space. The next step uses the language of quantum electrodynamics to describe the energy in the vibrational mode using the harmonic oscillator energy levels $E_n = (n + 1/2)\hbar\omega(q)$. A sound mode can be viewed as $n$ quanta or phonons excited above the ground state. The phonons are a particular type of elementary excitation. They are collective excitations which do not resemble the constituent particles which are atomic cores and valence electrons holding the core together. Other examples of collective excitations are plasmons and magnons which result from collective motions of electrons or spins. Collective excitations are usually bosons.

There is another class of elementary excitation which consists of quasi-particles. Quasi-particles are fermions which resemble their constituent particles. Electrons excited by an external probe in a solid are quasi-particles. An electron or quasi-electron in a solid is strongly coupled to other electrons and to the lattice of atomic cores. When an electron is probed with an electromagnetic field, it does not usually respond as an individual particle. The interactions can manifest themselves in a number of ways.

One way of including these interactions is by associating an effective mass, $m^*$, with the electron. This concept is common in solid state physics, and it represents a convenient way of describing an interacting fermion. If the effective mass correction arises primarily from the interaction between an electron and the periodic core potential, the resulting effective mass is usually called the band mass. If the mass correction arises from electron-electron or electron-phonon interactions, then the effective mass correction is considered to be a many-body correlation correction. An example of the former is the small conduction band effective mass of InSb which arises from the interaction of electrons in the conduction band with the periodic potential. This is a band structure effect, and it will be discussed later. An example of the latter is the polaron in an ionic crystals. In this case, the electron polarizes the ionic lattice and carries a strain field with it as it moves through the crystal. The combined electron plus strain field or optical phonon cloud is a quasi-particle, a polaron, which behaves like an electron with an increased mass.

The elementary excitation picture describes a solid as a gas or liquid of excitations which can be created by external probes. The collective excitations are bosons, and they can interact with each other. An important component of this approach is based on the Landau theory of Fermi liquids. This theory demonstrates that there is a one-to-one correspondence between the excitations of a strongly coupled electron system (electron liquid) and single particles states, that is, quasi-electrons. For many applications, this important approach allows one to view the interacting electron system in terms of single particle excitations.

To make contact with experimental measurements, the concepts embodied in the interacting atoms or elementary excitation models need to