

Jacques I. Pankove

**OPTICAL  
PROCESSES IN  
SEMICONDUCTORS**

---

# DOVER SCIENCE BOOKS

THE DEVELOPMENT OF MATHEMATICS, E. T. BELL. (0-486-27239-7)

507 MECHANICAL MOVEMENTS: MECHANISMS AND DEVICES, HENRY T. BROWN. (0-486-44360-4)

A REFRESHER COURSE IN MATHEMATICS, F. J. CAMM. (0-486-43225-4)

FLAWS AND FALLACIES IN STATISTICAL THINKING, STEPHEN K. CAMPBELL. (0-486-43598-9)

HARMONIC PROPORTION AND FORM IN NATURE, ART AND ARCHITECTURE, SAMUEL COLMAN. (0-486-42873-7)

THE CURVES OF LIFE, THEODORE A. COOK. (0-486-23701-X)

A SHORT HISTORY OF TECHNOLOGY: FROM THE EARLIEST TIMES TO A.D. 1900, T. K. DERRY AND TREVOR I. WILLIAMS. (0-486-27472-1)

MATHOGRAPHICS, ROBERT DIXON. (0-486-26639-7)

EINSTEIN'S ESSAYS IN SCIENCE, ALBERT EINSTEIN. (0-486-47011-3)

EXPERIMENTAL RESEARCHES IN ELECTRICITY, MICHAEL FARADAY. (0-486-43505-9)

THE GREAT PHYSICISTS FROM GALILEO TO EINSTEIN, GEORGE GAMOW. (0-486-25767-3)

THIRTY YEARS THAT SHOOK PHYSICS: THE STORY OF QUANTUM THEORY, GEORGE GAMOW. (0-486-24895-X)

ONE TWO THREE ... INFINITY: FACTS AND SPECULATIONS OF SCIENCE, GEORGE GAMOW (0-486-25664-2)

GRAVITY, GEORGE GAMOW. (0-486-42563-0)

FADS AND FALLACIES IN THE NAME OF SCIENCE, MARTIN GARDNER (0-486-20394-8)

RELATIVITY SIMPLY EXPLAINED, MARTIN GARDNER (0-486-29315-7)

THE GEOMETRY OF ART AND LIFE, MATILA GHYKA. (0-486-23542-4)

UNDERSTANDING EINSTEIN'S THEORIES OF RELATIVITY: MAN'S NEW PERSPECTIVE ON THE COSMOS, STAN GIBILISCO. (0-486-26659-1)

FROM GALILEO TO NEWTON, A. RUPERT HALL. (0-486-24227-7)

MECHANICAL APPLIANCES, MECHANICAL MOVEMENTS AND NOVELTIES OF CONSTRUCTION, GARDNER D. HISCOX. (0-486-46886-0)

1800 MECHANICAL MOVEMENTS, DEVICES AND APPLIANCES, GARDNER D. HISCOX. (0-486-

---

MAKERS OF MATHEMATICS, STUART HOLLINGDALE. (0-486-45007-4)

THE DIVINE PROPORTION, H. E. HUNTLEY. (0-486-22254-3)

ENGINEERING AND TECHNOLOGY, 1650-1750: ILLUSTRATIONS AND TEXTS FROM ORIGINAL SOURCES, MARTIN JENSEN. (0-486-42232-1)

SHORT-CUT MATH, GERARD W. KELLY. (0-486-24611-6)

MATHEMATICS FOR THE NONMATHEMATICIAN, MORRIS KLINE. (0-486-24823-2)

THE FOURTH DIMENSION SIMPLY EXPLAINED, HENRY P. MANNING. (0-486-43889-9)

VIOLENT PHENOMENA IN THE UNIVERSE, JAYANT V. NARLIKAR (0-486-45797-4)

BASIC MACHINES AND HOW THEY WORK, NAVAL EDUCATION. (0-486-21709-4)

EXCURSIONS IN GEOMETRY, C. STANLEY OGILVY. (0-486-26530-7)

MUSIC, PHYSICS AND ENGINEERING, HARRY F. OLSON. (0-486-21769-8)

COMPUTERS, PATTERN, CHAOS AND BEAUTY, CLIFFORD A. PICKOVER (0-486-41709-3)

AN INTRODUCTION TO INFORMATION THEORY, JOHN R. PIERCE. (0-486-24061-4)

INTRODUCTION TO MATHEMATICAL PHILOSOPHY, BERTRAND RUSSELL. (0-486-27724-0)

HELLENISTIC SCIENCE AND CULTURE IN THE LAST THREE CENTURIES B.C., GEORGE SARTON. (0-486-27740-2)

MATHEMATICIAN'S DELIGHT, W. W. SAWYER (0486-46240-4)

EINSTEIN'S LEGACY: THE UNITY OF SPACE AND TIME, JULIAN SCHWINGER. (0-486-41974-6)

THE UNITY OF THE UNIVERSE, D. W. SCIAMA. (0-486-47205-1)

FROM FALLING BODIES TO RADIO WAVES: CLASSICAL PHYSICISTS AND THEIR DISCOVERIES, EMILIO SEGRÈ. (0-486-45808-3)

FROM X-RAYS TO QUARKS: MODERN PHYSICISTS AND THEIR DISCOVERIES, EMILIO SEGRÈ. (0-486-45783-4)

GREAT EXPERIMENTS IN PHYSICS: FIRSTHAND ACCOUNTS FROM GALILEO TO EINSTEIN MORRIS H. SHAMOS. (0-486-25346-5)

SATAN, CANTOR AND INFINITY: MIND-BOGGLING PUZZLES, RAYMOND M. SMULLYAN. (0-486-47036-9)

THE LADY OR THE TIGER?: AND OTHER LOGIC PUZZLES, RAYMOND M. SMULLYAN. (0-486-47027-X)

HOW TO CALCULATE QUICKLY: FULL COURSE IN SPEED ARITHMETIC, HENRY STICKER (0-486-20295-X)

SPEED MATHEMATICS SIMPLIFIED, EDWARD STODDARD. (0-486-27887-5)

A SCIENTIST AT THE SEASHORE, JAMES S. TREFIL. (0-486-44564-X)

INTRODUCTION TO MATHEMATICAL THINKING: THE FORMATION OF CONCEPTS IN

MODERN MATHEMATICS, FRIEDRICH WAISMANN. (0-486-42804-4)

SUNDIALS: THEIR THEORY AND CONSTRUCTION, ALBERT E. WAUGH. (0-486-22947-5)

HOW TO SOLVE MATHEMATICAL PROBLEMS, WAYNE A. WICKELGREN. (0-486-28433-6)

THE TRIUMPH OF THE EMBRYO, LEWIS WOLPERT. (0-486-46929-8)

SEE EVERY DOVER BOOK IN PRINT AT

[WWW.DOVERPUBLICATIONS.COM](http://WWW.DOVERPUBLICATIONS.COM)

---

# **OPTICAL PROCESSES IN SEMICONDUCTORS**

**Jacques I. Pankove**

Department of Electrical and Computer Engineering  
Optoelectronic Computing Systems Center  
University of Colorado

National Renewable Energy Laboratory  
Golden, Colorado

**Dover Publications, Inc.  
New York**

---

Copyright © 1971 by Jacques I. Pankove.

---

All rights reserved.

This Dover edition, first published in 1975, is an unabridged republication, with slight corrections, of the work originally published by Prentice-Hall, Inc., Englewood Cliffs, New Jersey, in 1971.

9780486138701

*Library of Congress Catalog Card Number: 75-16756*

Manufactured in the United States by Courier Corporation

60275313

[www.doverpublications.com](http://www.doverpublications.com)

*to Ethel*  
*and to Martin and Simon*

---

---

# PREFACE

This text has been the basis for a series of lectures presented at the University of California in Berkeley during the 1968–69 academic year. It grew out of a realization that in order to become familiar with all the phenomena involving light in semiconductors, one must consult a great variety of sources, search many journals, and then one finds that the material is packaged for the specialist. I have already done this task to nourish many years of experimental research. Hence it seemed desirable to weave together all this information into a coherent form, adding new concepts collected from the current literature and from recent conferences. In the process of writing this book, new insights evolved which are published here for the first time.

This book deals with the interactions among photons, electrons and atoms in semiconductor crystals. These interactions comprise the absorption, transformation, modulation and generation of light. In the range of phenomenological complexity, one always associates the most intricate processes with biological effects, whereas the physics of solids appears relatively simple. In fact, what could be simpler than a perfect crystal at low temperature where everything is still? One soon discovers excitons, complexes of excitons, polaritons. . . . Then, imperfections and impurities, which are unavoidable, produce new states. Thus, the diversity of possible interactions among electrons in the various levels, photons and phonons increases. The application of external influences such as pressure, temperature, electric and magnetic fields creates further perturbations of an already complex microcosm.

Spectroscopic data reveals a wealth of information about physical processes involving radiation. The position of an emission or absorption peak indicates the energy separating levels between which a strong interaction occurs. The lowest photon energy at which a spectral structure begins marks the threshold for a class of transitions, while the shape of the spectrum is a measure of the transition probability or of the distribution of states. Absorption links all the states which are empty and thus covers a broad spectrum. Emission, on the other hand, results from a nonequilibrium situation and since carriers relax to the lowest available states, such as a band edge, the emission spectrum covers a narrow range. When traps are involved, slow temperature-dependent effects are observed. Nonradiative recombination also often exhibits a temperature dependence. Light can excite electrons to a sufficiently high energy for them to overcome barriers and to be emitted into vacuum. Electron emission allows a study of states far from the band edges. Reflectance modulation is another technique for probing the distribution of states and for assigning definitive values to critical points in the band structure. Light can stimulate the absorption or desorption of atoms on the surface of semiconductors and engender other photochemical reactions. With the availability of lasers, it is possible to explore the scattering of intense monochromatic radiation by internal oscillators, thus shifting the characteristic frequency of these oscillations to a more convenient spectral range and gaining additional information about selection rules in the process. The practical applications of optical processes in semiconductors are too numerous for a detailed treatment in this text; however, the underlying principles have been covered. Electroluminescence and lasing are practical sources of



radiation. The absorption of light is used in a variety of photodetectors, photoconductors, photovoltaic cells and photoemitters.

---

My purpose is to give the student an insight into the relevant phenomena already uncovered and to present them in a form that couples readily to physical intuition. Many references have been included so that the reader, fascinated by some of these effects, can be guided to greater depths and to a more rigorous treatment of the subject. Problems have been devised to help the student firmly grasp the material by having an active interaction with the concepts. Although this book is primarily a text for graduate students, I hope it will be useful also to the seasoned researcher who is curious about optical phenomena in semiconductors.

I am grateful to the Department of Electrical Engineering and Computer Sciences of the University of California in Berkeley and to its Chairman, Professor Kuh, for inviting me to this, my first teaching experience. The management of the RCA Laboratories has kindly made this undertaking possible. I acknowledge that I have benefited from "Student Power" which has requested my teaching this course two terms instead of one. The students' attentive interest was a strong encouragement to complete my writing. Technical discussions with Professors L. Falicov, and S. Wang have been most helpful. I am also grateful to C. Bulucea, and P. Hoff for a critical reading of the manuscript, and to Mrs. I. Brown, Miss B. Bulivent, and Miss K. Shields for painstakingly transcribing from my manuscript.

Four of the chapters were completed after my return to the RCA Laboratories. For a thorough revision of the first draft, I drew upon the diverse expertise of many colleagues: W. Burke, N. Byer, I. Faughnan, A. Firester, W. Fonger, B. Goldstein, W. F. Kosonocky, H. Kressel, J. D. Levine, A. Miller, A. R. Moore, D. Redfield, R. E. Simon, R. W. Smith, and B. F. Williams. It is a pleasure to acknowledge their kind help. I am also thankful to A. Bahraman for assistance in designing some of the problems.

Jacques I. Pankov

*Princeton, N. J.*

---

# Table of Contents

DOVER SCIENCE BOOKS

Title Page

Copyright Page

Dedication

PREFACE

OPTICAL PROCESSES IN SEMICONDUCTORS

ENERGY STATES IN SEMICONDUCTORS - 1

PERTURBATION OF SEMICONDUCTORS BY EXTERNAL PARAMETERS - 2

ABSORPTION - 3

RELATIONSHIPS BETWEEN OPTICAL CONSTANTS - 4

ABSORPTION SPECTROSCOPY - 5

RADIATIVE TRANSITIONS - 6

NONRADIATIVE RECOMBINATION - 7

PROCESSES IN p-n JUNCTIONS - 8

STIMULATED EMISSION - 9

SEMICONDUCTOR LASERS - 10

EXCITATION OF LUMINESCENCE AND LASING IN SEMICONDUCTORS - 11

PROCESSES INVOLVING COHERENT RADIATION - 12

PHOTOELECTRIC EMISSION - 13

PHOTOVOLTAIC EFFECTS - 14

POLARIZATION EFFECTS - 15

PHOTOCHEMICAL EFFECTS - 16

EFFECT OF TRAPS ON LUMINESCENCE - 17

REFLECTANCE MODULATION - 18

APPENDIX

INDEX

---

# OPTICAL PROCESSES IN SEMICONDUCTORS

---

# ENERGY STATES IN SEMICONDUCTORS

## 1

In this chapter we shall sketch how the assemblage of similar atoms into an array leads to the formation of bands of allowed states separated by an energy gap. Then we shall show that the energy gap can be filled with a great variety of allowed states, some localized due to impurities and others permeating the crystal (excitons). We shall also describe how the various particles can interact to form complexes.

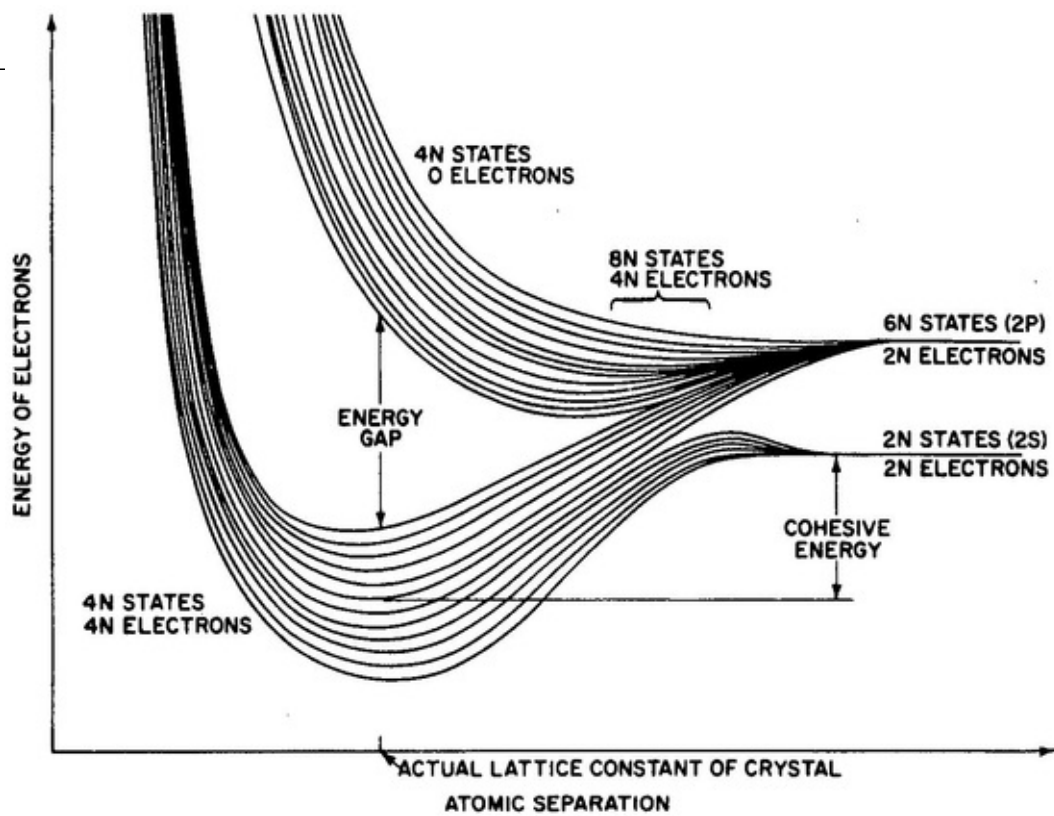
The relevance of these levels to the optical properties of the semiconductors lies in the fact that optical effects deal with transitions between various states and, therefore, it is well to review these first and to see how they come about.

### 1-A Band Structure

#### 1-A-1 BANDING OF ATOMIC LEVELS

To understand the nature of semiconductors one must consider what happens when similar atoms are brought together to form a solid such as a crystal. As two similar atoms approach each other the wave functions of their electrons begin to overlap. To satisfy Pauli's exclusion principle, the states of all spin-paired electrons acquire energies which are slightly different from their values in the isolated atom. Thus if  $N$  atoms are packed within a range of interaction,  $2N$  electrons of the same orbital can occupy  $2N$  different states, forming a band of states instead of a discrete level as in the isolated atom.

The energy distribution of the states depends strongly on the interatomic distance. This is illustrated in Fig. 1-1 for an assemblage of carbon atoms. The lowest-energy states are depressed to a minimum value when the diamond crystal is formed. The average amount by which the potential energy has dropped is related to the cohesive energy of the crystal. Notice that some of the higher-energy states ( $2P$ ) merge with the band of  $2S$  states. As a result of this mixing of states, the lower band contains as many states as electrons. This band is called the valence band and is characterized by the fact that it is completely filled with electrons. Such a filled band cannot carry a current. The upper band of states, which contains no electron, is called the conduction band. If an electron were placed in this band, it could acquire a net drift under the influence of an electric field.



*Fig. 1-1 Energy banding of allowed levels in diamond as a function of spacing between atoms.<sup>1</sup>*

Clearly, since in the energy gap there are no allowed states, one would not expect to find an electron within that range of energies.

It is the extent of the energy gap and the relative availability of electrons that determine whether a solid is a metal, a semiconductor, or an insulator. In a semiconductor the energy gap usually extends over less than about three electron-volts and the density of electrons in the upper band (or of holes in the lower band) is usually less than  $10^{20} \text{ cm}^{-3}$ . By contrast, in a metal the upper band is populated with electrons far above the energy gap and the electron concentration is of the order of  $10^{23} \text{ cm}^{-3}$ . Insulators, on the other hand, have a large energy gap—usually greater than 3 eV—and have a negligible electron concentration in the upper band (and practically no holes in the lower band).

Since the interatomic distance in a crystal is not isotropic but rather varies with the crystallographic direction, one would expect this directional variation to affect the banding of states. Thus, although the energy gap which characterizes a semiconductor has the same minimum value in each unit cell, its topography within each unit cell can be extremely complex.

## 1-A-2 DISTRIBUTION IN MOMENTUM SPACE

We have just seen that allowed states have definite energy assignments. Now we must consider how the allowed states are distributed in momentum space. The importance of this consideration will be evident later when we find that in optical transitions we must conserve both energy and momentum.

The kinetic energy of an electron is related to its momentum  $p$  by the classical relation:

$$E = \frac{p^2}{2m^*}$$

where  $m^*$  is the electron effective mass (which may be different from the value in vacuum). From quantum mechanics we have the following expression :

$$p = k\hbar$$

(1-2)

where  $\hbar$  is Dirac's constant =  $h/2\pi$ ,  $h$  being Planck's constant; and  $k$  is the wave vector. Because of the relation (1-2), and to better couple to classical intuition, we shall call  $k$  the "momentum vector." If we conceive of the crystal as a square well potential with an infinite barrier and a bottom of width  $L$ , we shall find that  $k$  can have the discrete values  $k = n(\pi/L)$ , where  $n$  is any nonzero integer. Note that  $L$  is an integral number  $N$  of unit lattice cells having a periodicity,  $a$ . Therefore,  $a$  is the smallest potential well one could construct. Hence, when  $n = N$ ,  $k = \pi/a$  is the maximum significant value of  $k$ . This maximum value occurs at the edge of the Brillouin zone. A Brillouin zone is the volume of  $k$ -space containing all the values of  $k$  up to  $\pi/a$ , where  $a$  varies with direction. Larger values of the momentum vector  $k'$  just move the system in to the next Brillouin zone, which is identical to the first zone and, therefore, the system can be treated as having a momentum-vector  $k = k' - \pi/a$ . The kinetic energy of the electron can be expressed as

$$E = \frac{k^2\hbar^2}{2m^*}$$

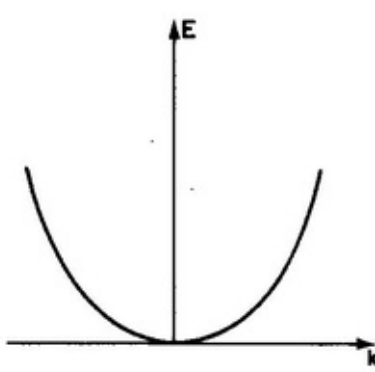
(1-3)

If the whole crystal, a cube whose sides have a length  $L$ , is the potential well, the allowed energies are

$$E = \frac{h^2}{2m^*L^2}(n_x^2 + n_y^2 + n_z^2)$$

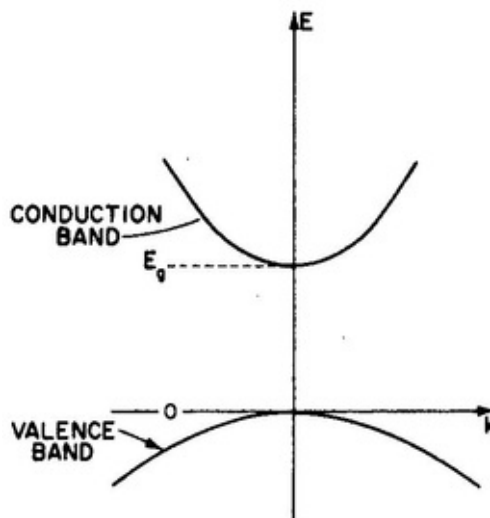
(1-4)

Although  $E$  varies in discrete steps, since the quantum numbers  $n$  are integers, the steps are so small ( $\sim 10^{-18}$  eV for a  $1\text{-cm}^3$  crystal) that  $E$  appears as a quasi-continuum.



*Fig. 1-2 Parabolic dependence of energy vs. momentum.*

Let us first consider how the energy varies with momentum along one direction of momentum space. [Figure 1-2](#) illustrates the parabolic dependence of  $E$  on  $k$ . Hence such a distribution of states is called a parabolic valley—the pictorial impact is even more pronounced in a three-dimensional representation of  $E$  vs.  $k_x$  and  $k_y$ . In a three-dimensional momentum space, a constant-energy surface forms a closed shell and, with every increment in momentum, the energy of successive shells increases quadratically. One often takes the top of the valence bands as the reference level. Then the bottom of the conduction band is located at a higher potential corresponding to the energy gap ([Fig. 1-3](#)). The significance of the downward curvature of the valence band is that if electrons could have a net motion in the valence band (if it were not completely filled), the electrons would be accelerated in the direction opposite to that in which they would move if they were in the conduction band, as if they had negative mass.

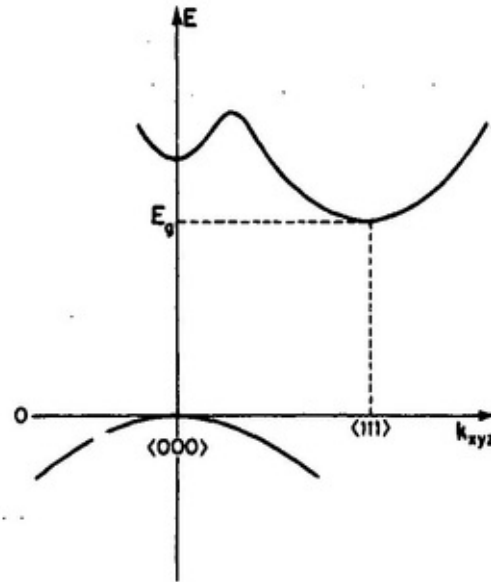


*Fig. 1-3 Energy vs. momentum in a direct-gap two-band system.*

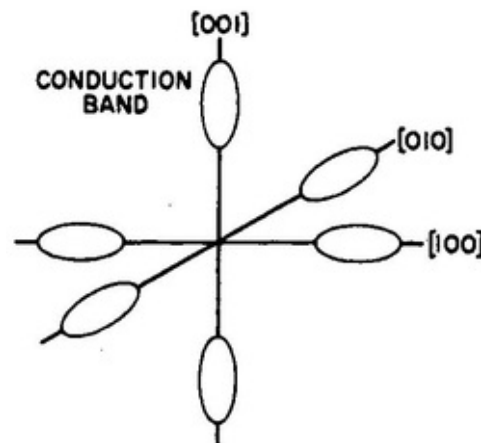
The separation between nearest atoms varies in different directions. Therefore, the shape of a constant-energy surface must deviate from that of a perfect sphere.<sup>2, 3</sup> Furthermore, because of the cumulative interactions from nearest neighbors, next-nearest neighbors, and all the higher-order neighbors, the minimum of the valley may occur not at  $k_x = k_y = k_z = 0$  but at some point defining a specific crystallographic direction such as [111] ([Fig. 1-4](#)). Because of crystal symmetry, the same distribution  $E(k_x, k_y, k_z)$  must be repeated at all equivalent directions. Thus there can be four or eight

$\langle 111 \rangle$  valleys and three or six  $\langle 100 \rangle$  valleys. The lower number is obtained when the valleys occur at the edges of the Brillouin zone (at  $k = \pi/a$ ,  $a$  is the lattice constant) and are shared by adjacent zones. For example, in germanium the four  $\langle 111 \rangle$  valleys consist of cigar-shaped ellipsoids (the parabolicity is not isotropic), and their longitudinal axis is oriented along the  $[111]$  directions. The higher number of valleys is obtained when the valleys are inside the Brillouin zone (for example, the  $\langle 100 \rangle$  valleys of silicon, as in Fig. 1-5).

**Fig. 1-4** Energy vs. momentum diagram for a semiconductor with conduction band valleys at  $k = \langle 000 \rangle$  and  $k = \langle 111 \rangle$ .



**Fig. 1-5** Constant-energy contours of valleys in the conduction band edge of silicon, forming six ellipsoidal valleys in the  $[100]$  directions.



### 1-A-3 DENSITY-OF-STATES DISTRIBUTION

In momentum space the density of allowed points is uniform. The surfaces of constant energy are, to first approximation, spherical (isotropic-medium); then the volume of  $k$ -space between spheres of energy  $E$  and  $E + dE$  is  $4\pi k^2 dk$ . Here  $E$  is measured with respect to the edge of the parabolic band.



Since a single state occupies in momentum space a volume  $8\pi^3/V$  ( $V$  is the actual volume of the crystal) and there are two states per level, one finds that the number of energy states in the interval  $E$  and  $E + dE$  is

$$N(E) dE = \frac{1}{2\pi^2\hbar^3} (2m^*)^{3/2} E^{1/2} dE$$

(1-5)

where  $m^*$  is the electron effective mass. For convenience,  $V$  is taken as a unit volume (e.g.,  $1 \text{ cm}^3$  in cgs units). The total density of states up to some energy  $E$  is

$$N = \frac{1}{3\pi^2} \frac{1}{\hbar^3} (2m^*E)^{3/2}$$

(1-6)

Since, in general, the valleys are rotational ellipsoids instead of spherical surfaces, the effective mass is not isotropic; then an average density of state effective mass is used:

$$m^* = (m_l^* m_{t_1}^* m_{t_2}^*)^{1/3}$$

(1-7)

where  $m_l^*$  is the longitudinal effective mass and  $m_{t_1}^*$  and  $m_{t_2}^*$  are the two transverse masses.

Each valley contributes its own set of states; therefore, each energy level may consist of states from several valleys. Hence to find the density of states one must add the contributions of all the valleys. Thus in a multivalley semiconductor the number of states between, say, the bottom of the conduction band and some energy  $E$  is

$$N = \frac{1}{3\pi^2\hbar^3} \sum_j g_j (2m_j^*)^{3/2} (E - E_j)^{3/2}$$

(1-8)

where  $g_j$  is the number of valleys of type  $j$ ,  $m_j^*$  is the average effective mass of a  $j$ -valley, and  $E_j$  is the energy at the bottom of the  $j$ -valley. A similar treatment applies to states in the valence band.

We have stated above that the effective mass is usually not perfectly isotropic. We shall now blur this picture somewhat further by pointing out that the valleys are parabolic in energy-momentum space only over a limited range near the bottom of the valley. This limitation could be expected, since the quasi-continuum of states makes a gradual connection between all the valleys (Fig. 1-4).

Furthermore, spin-orbit interactions induce a perturbation which results in subbands and in deviation from parabolicity at potentials away from the edge of the valley. However, the assumption of a parabolic band is usually a good first approximation, and we shall see later that in practice the subtleties of the theoretical model are obscured by the imperfections of nature.

#### 1-A-4 CARRIER CONCENTRATION

So far we have dealt with band states and their distribution in energy and momentum space. Now we must consider the occupancy of these states. When photons are interacting with electrons, the intensity of the interaction will depend on the number of electrons involved. The density of electrons is simply the product of the density of states and the Fermi-Dirac function (see Fig. 1-6):

$$f(E) = \frac{1}{\exp \frac{(E - E_F)}{kT} + 1}$$

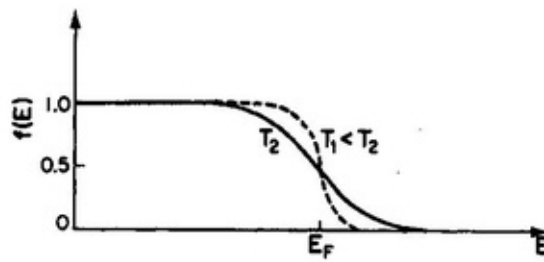
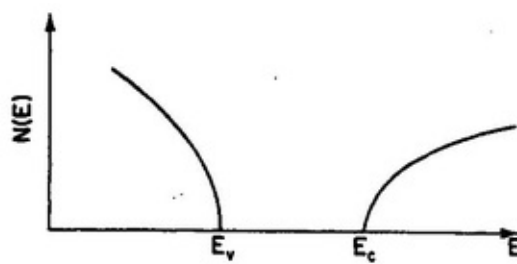
(1-9)

where  $k$  is Boltzmann's constant and  $T$  is the absolute temperature;  $E_F$ , the Fermi level, is the energy at which the expectation of finding a state occupied by an electron is  $\frac{1}{2}$ . Pauli's principle allows each state to be occupied by at most two electrons; however, a given energy level may consist of more than one state (in this case it is said to be degenerate). The density of holes is the product of the density of states and the probability of the state being empty. This probability is given by

$$1 - f(E) = \frac{1}{\exp \left( \frac{E_F - E}{kT} \right) + 1}$$

(1-10)

*Fig. 1-6 The upper diagram shows the variation of the density of states near the energy gap; the lower diagram shows the Fermi-Dirac function at two temperatures. The product of the two ordinates determines the electron concentration at various energies.*



## 1-B Impurity States

When an impurity atom is introduced in a lattice, it produces several types of interactions. If the impurity atom replaces one of the constituent atoms of the crystal and provides the crystal with one or more additional electrons than the atom it replaced, the impurity is a donor. Thus As on a Ge-site in a germanium crystal is a donor, and Te on an As-site in GaAs is a donor, as is Si on a Ga-site in GaAs. If the impurity atom provides less electrons than the atom it replaces, it forms an acceptor (e.g., Zn on a Ga-site in GaAs, or Si on an As-site in GaAs).

Instead of replacing an atom of the host crystal, the impurity may lodge itself in an interstitial position. Then its outer-shell electrons are available for conduction and the interstitial impurity is a donor.

A missing atom results in a vacancy and deprives the crystal of one electron per broken bond. This makes the vacancy an acceptor. Vacancies and interstitial impurities often combine to form a molecular impurity which may be either a donor or an acceptor.

In compound semiconductors a deviation from stoichiometry generates donors or acceptors depending on whether it is the cation or the anion which is in excess. However, it has been shown that in PbTe it is not the excess ion but rather the vacancy which determines whether the material is *n*-type or *p*-type.<sup>4</sup> Accordingly, a Pb-vacancy in the Te-rich PbTe transfers two states from the valence band to the conduction band; since 4 electrons are associated with each Pb atom, the Pb-vacancy leaves two holes in the valence band, which makes the semiconductor *p*-type. On the other hand, a Te-vacancy in Pb-rich material transfers 8 levels from the valence to the conduction band and removes the 6 Te-electrons. Hence the two electrons which no longer can be accommodated in the valence band occupy the lowest two states of the conduction band, making the Pb-rich PbTe *n*-type.

The extra electron of the donor is attracted most strongly to the positive charge of the impurity nucleus. Thus it acts as the electron of a hydrogen atom immersed in the high dielectric constant  $\epsilon$  of the crystal. This enables us to calculate the energy binding the electron to the impurity, i.e., its ionization energy:

$$E_i = \frac{m^* q^4}{2h^2 \epsilon^2 n^2} = \frac{m^*}{m \epsilon^2 n^2} 13.6 \text{ eV}$$

(1-11)

where  $q$  is the electron charge,  $m$  is the mass of the electron in vacuum, and  $n$  is a quantum number  $\geq 1$ . Ionization from successively higher quantum states requires rapidly decreasing increments in energy. The ionization energy from the ground state to the conduction band is obtained by making  $n = 1$  in Eq. (1-11). Since  $\epsilon$  is of the order of 10 and the effective-mass ratio is less than 1, the ionization energy is usually less than 0.1 eV. When the electron of the donor is in the conduction band, it is essentially free; therefore, its ground state, the donor level, is one ionization energy below the conduction band. Similarly, the acceptor level is one binding or ionization energy above the valence band. Note that since the effective masses of electrons and holes are usually different, the donor and acceptor binding energies can be different. It should be pointed out that the hydrogenic model is a very crude approximation because the effective mass varies considerably around the impurity atom.

Along with the reduced binding energy of a hydrogen-like impurity imbedded in a high dielectric medium, one finds that the electron orbit around the impurity atom becomes very large. If one makes the analogy with a hydrogen-like atom, the radius of the first Bohr orbit is

$$a = \frac{\hbar^2 \epsilon}{q^2 m^*} = \frac{\epsilon}{m^*/m} a_0$$

(1-12)

where  $a_0$  is the radius of the first Bohr orbit of hydrogen (equal to  $0.53 \times 10^{-8}$  cm). Hence the electron bound to the donor is not localized at the donor but rather travels through many lattice sites in the neighborhood of the impurity.

As the impurity concentration is increased, the electron wave functions at the impurity level begin to overlap. This obviously happens at a concentration of the order of  $1/a^3$  (i.e.,  $10^{20}$  cm<sup>-3</sup>). In practice the wave-function overlap occurs already at impurity concentrations as low as  $10^{16}$  cm<sup>-3</sup>. An overlap of wave functions is an interaction which changes slightly the potential of each level, resulting in the formation of a band of states in the region of overlap.<sup>5</sup> As the impurity concentration is increased further, the impurity band broadens and eventually merges with the nearest intrinsic band.

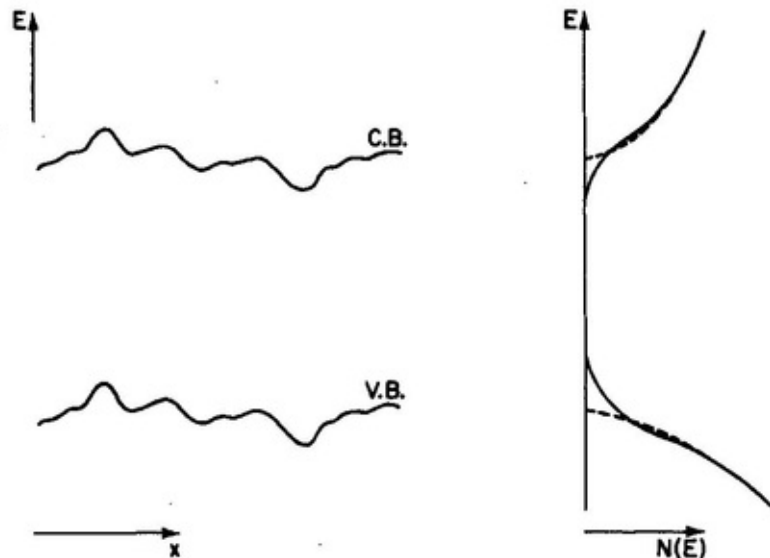
When the impurity atom can contribute more than one extra carrier (electron or hole), it is called a multiple donor or a multiple acceptor. The multiple impurity has a state for each carrier it can contribute. Obviously, when the multiple donor has released one electron it is singly ionized. When it is doubly ionized, the donor is doubly charged and, therefore, the corresponding binding energy is much greater than for the singly ionized state. Hence as the degree of ionization increases, the various donor levels go deeper below the conduction-band edges.

Some impurities do not agree, by far, with the simple hydrogen model, and form levels which may lie deep in the energy gap. All the transition elements seem to form deep levels. The reasons for which certain impurities form a deep level are not yet completely understood.

## 1-C Band Tailing

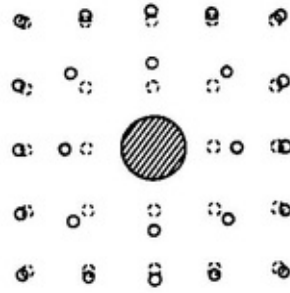
While impurity-band formation is an obvious consequence of increased impurity concentration, another important effect occurs: a perturbation of the bands by the formation of tails of states extending the bands into the energy gap. The problem of band tailing has received much theoretical attention.<sup>6, 7, 8, 9, 10, 11, 12, 13</sup> An ionized donor exerts an attractive force on the conduction electrons and a repulsive force on the valence holes (acceptors act conversely). Since impurities are distributed randomly in the host crystal, the local interaction will be more or less strong depending on the local crowding of impurities (Fig. 1-7). It should be noted that the local energy gap—the separation between the top of the valence band and the bottom of the conduction band—is everywhere maintained constant. But the density-of-states distribution which integrates the number of states at each energy inside the whole volume shows that there are conduction-band states at relatively low potentials and valence-band states in high-potential regions. It must be remembered that, in this model, the states of each tail are spatially separated, as is evident on the left side of Fig. 1-7.

Deep impurity states move up and down with the potential of the associated band edge (e.g., acceptors move with the valence band edge). Hence at high concentrations, the impurity states form a band whose distribution tails into the energy gap like the associated band edge.<sup>14</sup>



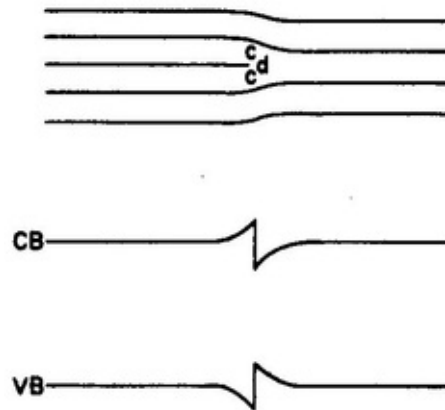
**Fig. 1-7** The left diagram shows the perturbation of the band edges by Coulomb interaction with inhomogeneously distributed impurities. This leads to the formation of tails of states shown on the right side. The dashed lines show the distribution of states in the unperturbed case.

There is still another type of interaction between impurities and the surrounding crystal: the deformation potential.<sup>15</sup> Since the impurity is usually either larger or smaller than an atom of the host lattice, a local mechanical strain is obtained (a compression as in Fig. 1-8, or a dilation). As is evident from Fig. 1-1, in some materials compression will increase the energy gap and dilation will reduce it. This type of interaction will, therefore, also perturb the band edges. An interstitial atom evidently induces a deformation potential corresponding to compressional strain, whereas a vacancy will have the opposite effect, since it produces dilational strain. Usually, both interstitials and vacancies are present in addition to substitutional impurities.



Dislocations are also usually present in crystals. They occur at the edge of an extra plane of atoms. The misfit of such an extra plane results in compressional and dilational strains, with the consequent onset of both lowering and raising of the potentials in the neighborhood of the dislocation (Fig. 1-9).

Hence we can say that impurities will induce tails in the density states by perturbing the band edge via deformation potential, via coulomb interaction, and by forming a band of impurity states.



**Fig. 1-9** An edge dislocation produces both compressional strains (c) and dilational strain (d) which result in the deformation potential shown in the lower diagram.

## 1-D Excitons<sup>16</sup>

### 1-D-1 FREE EXCITONS

A free hole and a free electron as a pair of opposite charges experience a coulomb attraction. Hence the electron can orbit about the hole as if this were a hydrogen-like atom. The ionization energy for such a system is then

$$E_x = \frac{-m_r^* q^4}{2h^2 \epsilon^2} \frac{1}{n^2}$$

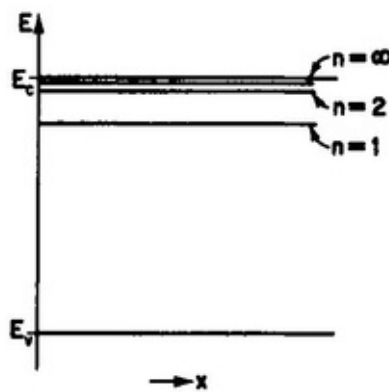
where  $n$  is an integer  $\geq 1$  indicating the various exciton states and  $m_r^*$  is the reduced mass:

$$\frac{1}{m_r^*} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$$

$m_e^*$  and  $m_h^*$  being the electron and hole effective masses, respectively. In an impurity atom—say, a donor—or in the hydrogen atom, the effective mass of the nucleus is very large and, therefore, the reduced mass is equal to that of the electron. But in an exciton the reduced mass is lower than the effective mass of the electron because  $m_e^*$  and  $m_h^*$  are more nearly of the same order of magnitude. Hence we should expect the exciton binding energy to be lower than either the donor or the acceptor binding energies.

The exciton can wander through the crystal (the electron and the hole are now only relatively free because they are associated as a mobile pair). Because of this mobility, the exciton is not a set of spatially localized states. Furthermore, the exciton states do not have a well-defined potential in the semiconductor's energy diagram. However, it is customary to use the conduction-band edge as a reference level and to make this edge the continuum state ( $n = \infty$ ). Then the various states of the exciton are represented as shown in Fig. 1-10.

**Fig. 1-10** Energy level diagram for the exciton and its excited states, exciton energy being referred to the edge of the conduction band.



Note that when a free electron and a free hole have the same momentum  $k$ , in general they move with different velocities:  $h(dE_c/dk)$  for the electron and  $h(dE_v/dk)$  for the hole ( $E_c$  referring to the conduction band and  $E_v$  to the valence band). Since the electron and the hole of an exciton must move together through the crystal, their translational velocities must be identical. This condition places a restriction on the regions in  $(E - k)$ -space where excitons can be found, namely at the “critical points”:

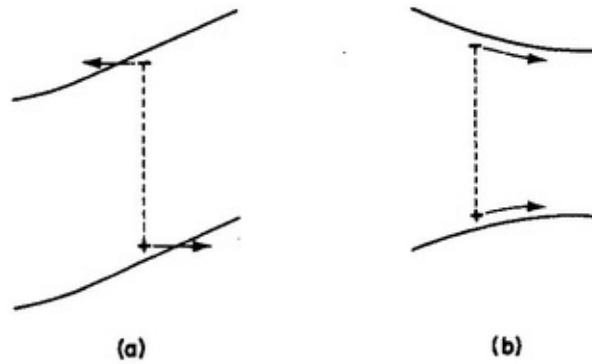
$$\left[ \frac{dE}{dk} \right]_{\text{electron}} = \left[ \frac{dE}{dk} \right]_{\text{hole}}$$

Since the effective mass of the hole is many orders of magnitude smaller than that of the proton, the analogy to the hydrogen atom must be modified: the center of gravity of the exciton may be located many lattice spaces away from the hole. The moving exciton has a kinetic energy

$$\frac{\hbar^2 K^2}{2(m_e^* + m_h^*)}$$

where  $K$  is the momentum vector associated with the motion of the center of gravity. The addition of the kinetic energy means that exciton levels are slightly broadened into bands.

At high electron and hole concentrations, electron-electron and hole-hole coulombic repulsion tend to reduce the range over which the attractive coulomb interaction can occur (screened coulomb interaction), but pairing still can occur.<sup>17</sup> However, at high doping, the potential fluctuations of the band edges generate internal fields. Local fields in the semiconductor exert a force on the electron and the hole separately. These forces can act in opposite directions for the electron and the hole as shown in Fig. 1-11(a). When the intensity of the local field exceeds the coulomb field inside the exciton, the exciton dissociates.



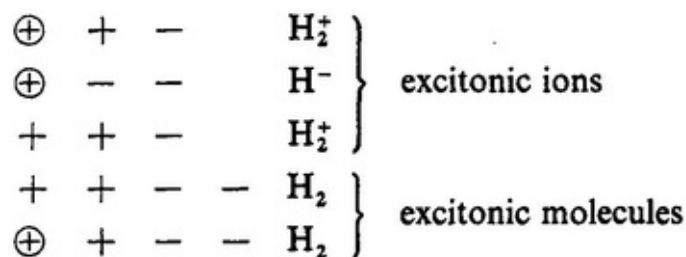
**Fig. 1-11** Exciton in a region of perturbed band potentials: (a) strong local field; (b) deformation potential.

However, when the local field is due to a deformation potential [Fig. 1-11(b)], the forces act on the electron and the hole in the same direction. These forces cause the exciton to drift to the region of minimum-energy gap without breaking up.

Note that when the exciton dissociates, it creates a free electron and a free hole. When the lifetime of an exciton is very short, the energies of the exciton states are broadened via the uncertainty principle.

## 1-D-2 EXCITONIC COMPLEXES

It is conceivable that three or more particles combine to form ion-like or molecule-like complexes.<sup>18</sup> The simplest set of possible complexes is reproduced below:





- [\*\*read online Life: The Science of Biology \(7th Edition\) for free\*\*](#)
- [read online The Marriage Bargain pdf, azw \(kindle\), epub, doc, mobi](#)
- [\*\*read No Enemy But Time for free\*\*](#)
- [\*\*click The Three-Arched Bridge\*\*](#)
  
- <http://hasanetmekci.com/ebooks/Life--The-Science-of-Biology--7th-Edition-.pdf>
- <http://interactmg.com/ebooks/The-Marriage-Bargain.pdf>
- <http://tuscalaural.com/library/No-Enemy-But-Time.pdf>
- <http://crackingscience.org/?library/The-Three-Arched-Bridge.pdf>