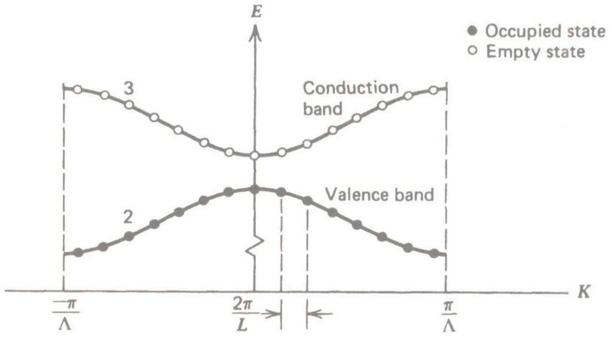

Figure 17.5 In an insulator (which includes the case of an intrinsic semiconductor at very low temperatures) all the quantum states in the valence band are occupied by electrons (black dots). All the energy bands lying above the valence band, of which only one (the conduction band) is shown, are empty.

the sum of the two velocities, hence the currents, cancel. The crystal is thus an insulator. This exact balancing on a one-to-one basis of electrons with positive K values by those with negative K numbers is disrupted by the application of an electric field to a crystal with a partially filled band, so that a net current flow results, that is, the crystal is metallic.

We thus find that the radically different conduction properties of crystals depend fundamentally on the crystal structure—that is, number of valence electrons per unit cell. As an example of metallic behavior we may take the case of sodium. The crystal is body centered cubic. Its Brillouin zone contains two states for each atom of the crystal. Each sodium atom, however, contributes but one 3*s* electron. The band is consequently only half full and the crystal is highly conductive.

Sodium chloride (NaC1) is a good example of an insulating crystal. The unit NaC1 associated with each unit cell has 28 electrons, which is an even number. It follows that the topmost occupied band is completely full.

In crystals with an even number of electrons per unit cell, one usually refers to the uppermost fully occupied band as the *valence band* and to the next higher band that is empty as the conduction band. The energy separating the extrema of these bands—that is, the smallest energy separation—is called the energy gap E_g.

Now our statement about the valence band being fully occupied while the conduction band is empty is strictly true only in the limit of zero temperature. At finite temperatures it follows from the Fermi–Dirac distribution law (16.6) that some electrons are to be found in the conduction band. Each such electron must leave an unoccupied state (*hole*) in the valence band. An application of an electric field will now cause a current flow, since the bands are not perfectly *full* or *empty*, so that crystals with sufficiently small values of E_g, where the excitation of carriers across the gap is appreciable, are called semiconductors. Some of the better known and widely used semiconductors are crystals of Si ($E_g = 1.1\,\mathrm{eV}$), and GaAs ($E_g = 1.45\,\mathrm{eV}$).

The conductivity of undoped semiconductors, unlike that of metals, depends on excitation of electrons across an energy gap and is thus a strong function of temperature, disappearing altogether at $T = 0$, since according to (16.6) at zero temperature the valance band is completely full.

As mentioned above, the application of an electric field to a semiconductor or a conductor causes a net flow of charge that is due to the unbalanced motion of the electrons in the conduction band, in the case of semiconductors, and valence bands. Since the number of occupied states in the valence band is typically many orders of magnitude larger than that of the vacant states, it is a convenient matter of bookkeeping to consider the valence band as completely full with electrons and to add to it a number of positive charges equal to the actual number of vacant states so as to preserve the actual total electronic charge in the valence band. Since the fully occupied valence band does not contribute to the current flow, we can attribute it *solely* to the fictitious positive charges called "holes."

In the case of a pure ("intrinsic") semiconductor, the number of conduction band electrons and holes is equal, since each conduction band electron leaves behind a vacancy in the valence band. This situation is depicted in Fig. 17.6. The incorporation of impurity atoms into the crystal can change this balance and leads to crystals whose conductivity is dominated by conduction band electrons; that is, the number of electrons far exceeds that of the holes (N-type semiconductor), or by valence band holes (P-type).

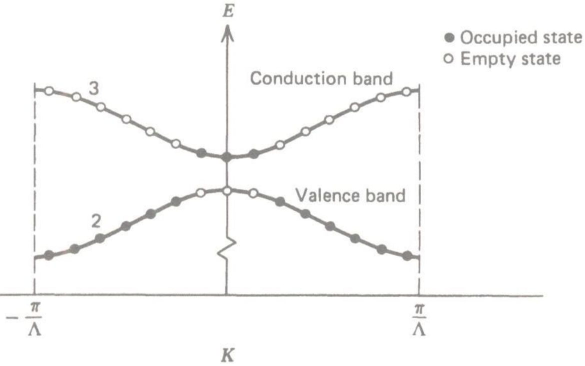

Figure 17.6 A semiconductor. The energy gap E_g is small enough so that thermal excitation elevates a sizeable number of electrons to the conduction band. Occupied states are shown as black dots, while empty ones are white. The conductivity is due to the electrons in the conduction band as well as to the missing electrons (holes) in the valence band.

The control of the conductivity type of a semiconductor (N or P) is the basis for the operation of the transistor, the semiconductor laser, and other devices currently changing the face of the electronic and optical fields. These topics are considered in Chapter 20.

17.3 THE MOTION OF ELECTRONS IN CRYSTALS

The classical motion of a pointlike electron is not directly compatible with the quantum mechanical behavior of an electron described by a Bloch eigenstate

$$\psi_K(x,t)=u_K(x)e^{i(Kx-E_Kt/\hbar)} \tag{17.35}$$

This is due to the fact that $\psi_K(t)$ is distributed over the whole volume of the crystal and is not localized. To pinpoint an electron we need to describe its wavefunction as a distribution of eigenstates $\psi_K(x,t)$.

Let the wavefunction at some time, which without loss of generality we take as $t=0$, be denoted by $\psi(x,0)$. Let $\psi(x,0)$ be limited (localized) to a characteristic distance δ as sketched in Fig. 17.7. Since the states $\psi_K(x,0)$ form a complete orthonormal set (see Section 2.6), we may expand $\psi(x,0)$ as

$$\psi(x,0)=\sum_K a_K u_K(x)e^{iKx} \tag{17.36}$$

$$a_K=\int_0^L \psi(x,0)u_K^*(x)e^{-iKx}\,dx \tag{17.37}$$

where L is the "crystal" length. The distribution of a_K is shown in Fig. 17.7*b*, and is centered about a mean value K_0. The wavefunction $\psi(x,t)$ $(t>t_0)$ must satisfy the time-dependent Schrödinger equation $\hat{\mathcal{H}}\psi=i\hbar(\partial\psi/\partial t)$ as well as the initial condition (17.36). This can be accomplished by taking

$$\psi(x,t>0)=\sum_K a_K u_K(x)e^{i(Kx-E_Kt/\hbar)} \tag{17.38}$$

Expanding E_K in the vicinity of K_0,

$$E_K\simeq E_{K_0}+\left.\frac{dE_K}{dK}\right|_{K_0}(K-K_0)$$

we rewrite (17.38) as

$$\begin{aligned}\psi(x,t)&=\sum_{\Delta K} a_{K_0+\Delta K}u_{K_0+\Delta K}(x)\\&\quad\times\exp\left\{i\left[(K_0+\Delta K)x-\frac{1}{\hbar}\left(E_{K_0}+\frac{dE_K}{dK}\Delta K\right)t\right]\right\}\\&=e^{i(K_0x-E_{K_0}t/\hbar)}\sum_{\Delta K}a_{K_0+\Delta K}u_{K_0+\Delta K}\\&\quad\times\exp\left[i\left(\Delta Kx-\frac{1}{\hbar}\frac{dE_K}{dK}\Delta Kt\right)\right]\end{aligned} \tag{17.39}$$

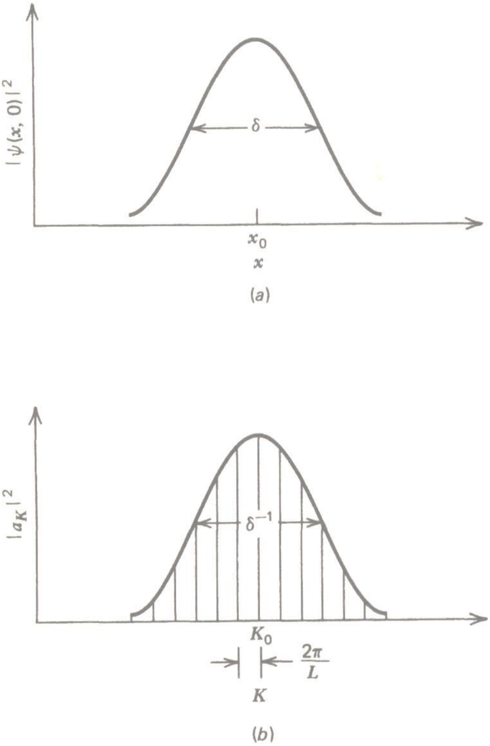

Figure 17.7 (*a*) The spatial probability distribution of a localized electron at $t=0$. (*b*) The corresponding "momentum" distribution function $|a_K|^2$.

where $\Delta K \equiv K - K_0$. An observer moving in such a way that the exponent

$$(\Delta K)x - \frac{1}{\hbar}\frac{dE_K}{dK}\Delta K t \tag{17.40}$$

of eq. (17.39) remains a constant will "see" the same value of $|\psi(x,t)|$. This observer will have to travel at a velocity

$$\frac{dx}{dt} = \frac{1}{\hbar}\frac{dE_K}{dK} \equiv v_g \tag{17.41}$$

The quantity v_g is called the *group velocity* of the electron wave packet. It represents the velocity of the envelope $|\psi(x,t)|^2$ of Fig. 17.7*a*. For most practical purposes, *when one talks about the velocity of an electron in a crystal, one talks about* v_g.

Another important relation results from equating the work $-e\mathcal{E}v_g\,dt$, done on an electron in a time dt by an externally applied electric field $\mathcal{E}$, to the change in electron energy dE_K (we use the definition $e \equiv |e|$):

$$\begin{aligned} -e\mathcal{E} v_g\, dt &= dE_K \\ &= \frac{dE_K}{dK} dK \end{aligned} \tag{17.42}$$

Using $v_g = \hbar^{-1} dE_k / dK$ leads to

$$\frac{dK}{dt} = -\frac{e\mathcal{E}}{\hbar} \tag{17.43}$$

or, in general,

$$\frac{d}{dt}(\hbar K) = \text{External Force} \tag{17.44}$$

We thus find that as far as external forces are concerned the electron (i.e., the electron wave packet) behaves as if it possesses a momentum $\hbar K$. The quantity $\hbar K$ is called the *crystal momentum*. The acceleration of the electron wave packet in response to an external force is

$$\begin{aligned} \frac{dv_g}{dt} &= \frac{1}{\hbar} \frac{d}{dt}\left(\frac{dE_K}{dK} \right) \\ &= \frac{1}{\hbar} \frac{d^2 E_K}{dK^2} \frac{dK}{dt} \end{aligned} \tag{17.45}$$

and using (17.43),

$$\begin{aligned} \frac{dv_g}{dt} &= -e\mathcal{E}\left(\frac{1}{\hbar^2} \frac{d^2 E_K}{dK^2} \right) \\ &= \text{Force/Effective Mass} \end{aligned} \tag{17.46}$$

so that

$$\begin{aligned} m_e &= \text{Effective Mass} \\ &= \left(\frac{1}{\hbar^2} \frac{d^2 E_K}{dK^2} \right)^{-1} \end{aligned} \tag{17.47}$$

The motion of an electron in a crystal in response to an external force is governed by an effective mass that is inversely proportional to the curvature of the dispersion (E_K vs. K) graph. The effective masses of carriers in some commonly used electronic semiconductor crystals are given in Table 19.1.

17.4 THE CONTROL OF CONDUCTIVITY OF SEMICONDUCTORS BY IMPURITIES

The occupation of electronic states in a semiconductor can be affected by the introduction of foreign atoms—a process referred to as impurity "doping." The impurity atoms often enter the lattice by displacing an original atom. In the process of bonding to the surrounding atoms the impurity atoms lose or gain electrons so as to end up with a number of valence electrons equal to that of the majority atoms. If, as an example, pentavalent arsenic is used to dope a crystal of Si (valence $=4$), then the extra, fifth electron is given up. Since all the states in the valence band of silicon are filled (see Fig. 17.5), the extra electron must be accommodated in the conduction band. This type of doping is called *N* (for negative) type.

If the impurity atom possesses fewer valence electrons, then the host atom—Zn in Si as an example—can complete its chemical bonding by removing an electron from the valence band. The vacancy left behind is called a "hole" and it takes part in the current transport, as discussed below. This type of doping is called *P* (for positive) type.

The main difference between this extrinsic conductivity and the intrinsic conductivity discussed earlier, which is due to excitation of electrons from the valence band to the conduction band in a pure (undoped) crystal, is that in the extrinsic case the number of holes and electrons is not equal. A more quantitative discussion of this case is given in Chapter 19.

Current Flow in Semiconductors

The process of current flow in an N doped semiconductor is illustrated in Fig. 17.8. The occupancy of the electron states in K space before the application of an electric field is shown in Fig. 17.8*a*. The physical location at $t=0$ of the single conduction band electron is shown in 17.8*b*. The application at $t=0$ of an electric field causes, according to (17.43), the K value of each electron to increase at a rate

$$\frac{dK}{dt} = -\frac{e\mathcal{E}}{\hbar}$$

The resulting distribution in K space after a time Δt is shown in Fig. 17.8*c*.

Since the valence band is full, it does not contribute to the current flow. This is due to the fact that for each electron with a positive group velocity $(1/\hbar)(dE/dK)$ there exists an electron (at $-K$) with an equal but oppositely directed group velocity. The net current is thus due to the conduction band electrons only. Since the single conduction electron of Fig. 17.8*a* moves in the positive K direction, it has a positive group velocity and its physical translation is to the right, as shown in 17.8*d*. The electron is thus accelerated in the direction of the force, indicating a positive mass. This is consistent with Eq. (17.47),

$$m_e = \left(\frac{1}{\hbar^2}\frac{d^2E}{dK^2}\right)^{-1}$$

which relates the effective electron mass to the curvature of the energy band $E(K)$ in K space.

The situation in a *P*-type semiconductor is depicted in Fig. 17.9. In our example a single state on top of the valence band is shown as unoccupied at

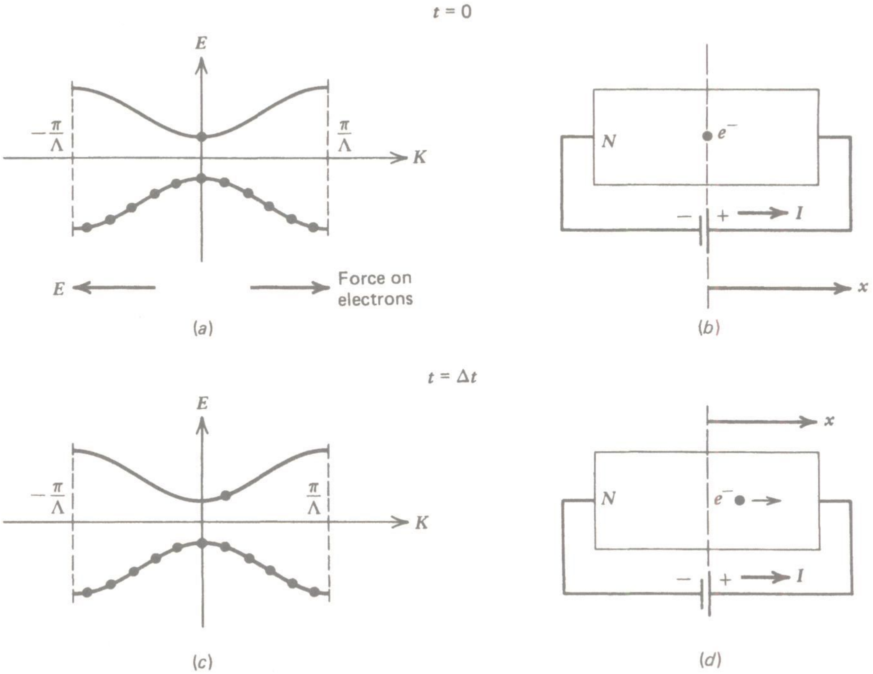

Figure 17.8 Current flow in an N-type semiconductor. At $t=0$: (a) the electron shown at the bottom ($K=0$) of the conduction band; (b) the electron is shown at $t=0$ as localized at $x=0$. At $t=\Delta t$: (c) the electron has moved in "K" space to the region of positive slope; hence, since $v_g=(1/\hbar)\, dE_K/dK>0$, it moved in physical space to the right. This corresponds to a positive effective electron mass ($m_e>0$).

$t=0$ (17.9a). The spatial and temporal bookkeeping of the electronic distribution will be unaltered if we fill the vacancy with an electron, thereby filling the valence band, provided we attach to the electron a positive charge that follows it everywhere, in *real space* as well as in *K space*. Since the full valence band does not contribute to the current flow, the latter can be accounted for completely by the motion of the fictitious positive charge—the "hole."

The motion of the hole in K space under the influence of an electronic field is shown in Fig. 17.9c. The added electron and its shadowing hole move according to (17.43) in the $+K$ direction. Since the slope dE/dK and hence the electron group velocity v_g is negative, the physical translation of the hole (which must accompany the electron) is to the left, in the direction of the electric field. Since the hole has positive charge, its acceleration is in the direction of the force $e\mathcal{E}$ so that its mass is positive. The mass of a hole is thus the negative of its associated electron, that is,

$$m_h = -\left(\frac{1}{\hbar^2}\frac{d^2E_K}{dK^2}\right)^{-1} \tag{17.48}$$

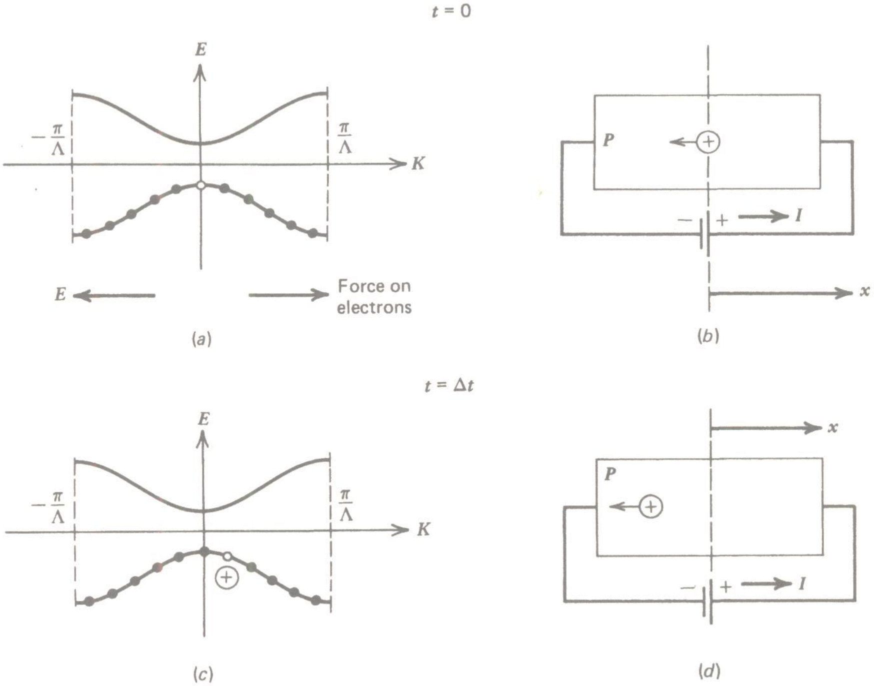

Figure 17.9 A P-doped semiconductor. (a) One electron state in the valence band is unoccupied at $t=0$. The corresponding excess mobile positive charge ("hole") is shown at $x=0$ [see (b)]. (c) Under the influence of the applied electric field the electron distribution moves to the right in K space, where $dE/dK \propto v_g < 0$. Since $v_g < 0$, the corresponding physical motion is to the left. This can be represented by the motion of a positive charge carrier ("hole") with a positive effective mass

$$m^* = \left(\frac{1}{\hbar^2} \frac{d^2E}{dK^2} \right)^{-1}$$

which both in K space and in real space is at the location of the electron vacancy.

The control of current flow in semiconductor crystals, which are doped selectively with N- and P-type impurities, is the basic principle behind the operation of transistors and of the technology of integrated electronics. This topic is discussed in some detail in Chapter 19.

PROBLEMS

1. Derive the expressions for the matrix elements A, B, C, D of (17.22).
2. Prove Eq. (17.33).
3. (Requires numerical analysis sophistication.) Solve numerically for the eigenvalues and eigenfunctions of an electron in a periodic Kronig–Penney

potential with $s = t = 4$ Å, $V_0 = 5$ volts. Assume a value of $E = \hbar^2 k_2^2/2m$, then solve for the corresponding value of K from (17.30) and the eigenvector (a_0, b_0) as given by (17.27). Repeat for values of K spanning the interval 0 to π/Λ ($\Lambda = s + t = 8$ Å).

4. If the electron momentum in a crystal is taken as $\hbar k_i$ show that the classical expression Power $=$ Force $\times$ Velocity is still valid provided the electron velocity is taken as the group velocity.