where ΔG_M is the difference between the effective groups of the cations in the two compounds according to the Periodic Table, ΔP_M is the difference between the periods of the cations, ΔP_X is the difference between the periods of the anions, and ΔG_X is the difference between the groups of the anions. Explain the reason for this approximate rule. Use the rule to separate the II–VI and III–V compounds (ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe, AlP, AlAs, AlSb, GaP, GaAs, GaSb, InP, InAs, InSb) into groups with the same bandgap and order these groups according to decreasing bandgap. Check the results with experimentally reported values of bandgap for these materials.

Chapter 7

Carrier Transport

The application of an electric or magnetic field or of a thermal gradient to a crystal results in a variety of carrier transport phenomena. These phenomena are associated with the motion of electrons and holes in conduction or valence bands. In this chapter we consider some of the general properties of transport in crystals, with particular application to electrical and thermal conductivity. In Chapter 10 we consider additional processes associated with the presence of a magnetic field.

The description of the motion of an electron (or hole) in terms of a *wave packet* permits an equation of motion that has the same form as the classical treatment of the electron as a particle, provided that the expectation values of acceleration and force for the packet are used. This possibility permits a simplification in the whole area of carrier transport. A wave-packet constructed of Bloch waves has a velocity given by the group velocity associated with the waves used to construct the packet.

The governing equation for the description of transport is the *Boltzmann equation*. This equation describes the total rate of change of the occupancy of allowed states as a result of external fields, carrier diffusion, and carrier scattering. Many different types of scattering process are possible in a crystal and these are discussed in more detail in Chapter 8. If the change in energy of a carrier upon scattering is less than kT, it becomes appropriate to treat the solution of the Boltzmann equation in the *relaxation-time approximation*. For some scattering processes, however, the change in energy of the carrier upon scattering is greater than kT and a more general solution of the Boltzmann equation must be sought.

In those cases where it is applicable, the relaxation time for scattering is a useful parameter in describing transport. The relaxation time is defined as the average time that a carrier moves freely between collisions or scattering events. If the specific scattering mechanism is known, then detailed calculations may be made to calculate the relaxation time from fairly basic considerations. For most scattering processes, the relaxation time is a function of the energy of the carrier. In a real situation there is a distribution of such energies and hence an average relaxation time over energy must be calculated to compare with experimental values, the appropriate averaging process being determined by the Boltzmann equation. The particular dependence of relaxation time on carrier energy, which is characteristic of a given scattering process, is manifest also as a characteristic temperature dependence of the *mobility*, defined as the velocity of the carrier in the direction of the electric field per unit field.

General expressions for electrical conductivity, thermal conductivity, and the thermoelectric effect are derivable which are applicable to transport processes in both metals and semiconductors.

7.1 Wave Packets

According to wave mechanics, a free particle moving along the x axis is described by the Schroedinger equation,

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} = i\hbar \frac{\partial \Psi}{\partial t} \tag{7.1}$$

with the solution in the form of a plane wave,

$$\Psi_k(x, t) = e^{i(kx-\omega t)} \tag{7.2}$$

Since for a free electron k may take on all values, the general solution of Eq. (7.1) is

$$\Psi(x, t) = \int_{-\infty}^{+\infty} A(k)\, e^{i(kx-\omega t)}\, dk \tag{7.3}$$

where $A(k)$ is an arbitary function of k as long as the integral of Eq. (7.3) does not diverge, and the function $\Psi(x, t)$ is normalizable.

The general solution given in Eq. (7.3), known as a *wave packet*, provides a way to draw a correlation between the *particle* with a position x and a momentum mv, and the wave formulation in terms of a wavelength $\lambda = 2\pi/k$ and a frequency $\omega = E/\hbar$. By restricting the values of $A(k)$ to be large only

over a limited range of values of k, it becomes possible to represent the particle as a superposition of plane waves; the location of the maximum of the wave packet can be related to the particle position x, and the velocity of the wave packet can be related to the particle velocity v. Thus the wave packet becomes a kind of extended particle with properties that are in accord with the Schroedinger wave picture but which can be treated in terms of classical laws of motion, i.e., the *mean* values of acceleration and force for a wave packet can be shown to satisfy the classical equation of motion for a particle.

One of the most useful forms for $A(k)$ is that of a Gaussian distribution,

$$A(k) = C\, e^{-a^2(k-K)^2} \tag{7.4}$$

In this form $A(k)$ has its maximum value at $k = K$, and falls off to $1/e$ of its maximum value for $(k - K) = \pm 1/a$, as indicated in Fig. 7.1a. The corresponding wave packet is

$$\Psi(x, t) = C \int_{-\infty}^{+\infty} \exp\left\{-a^2(k-K)^2 + i\left[kx - \frac{\hbar^2 k^2}{2m}t\right]\right\} dk \tag{7.5}$$

Let $\Delta_{kK} = (k - K)$. Then the integrand of Eq. (7.5) becomes

$$\exp\left\{-a^2 \Delta_{kK}^2 + ix(K + \Delta_{kK}) - \frac{i\hbar t}{2m}(K + \Delta_{kK})^2\right\} \tag{7.6}$$
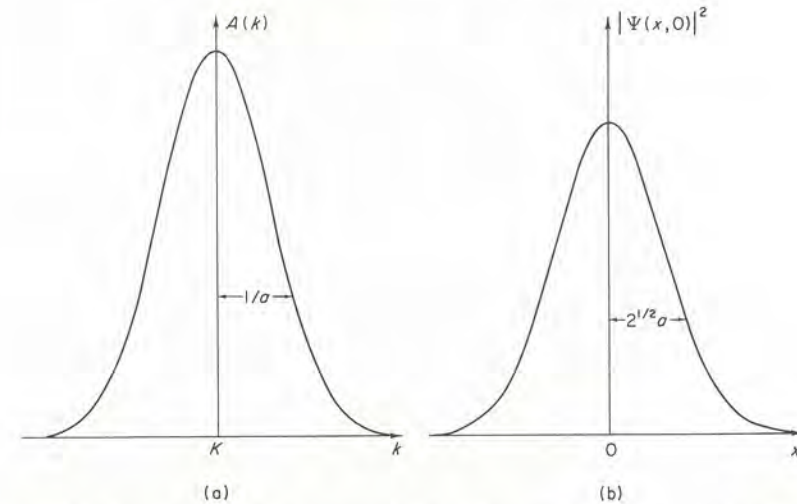

Fig. 7.1 A comparison of the square of the amplitude of the wavefunction for a wave packet at $t = 0$, $|\Psi(x, 0)|^2$, and a Gaussian form of the coefficient modulating factor, $A(k)$: (a) is Eq. (7.4); (b) is Eq. (7.14).

which we can write as

$$\exp\{-\alpha\Delta_{kK}^2 - 2\beta\Delta_{kK} - \gamma\} \tag{7.7}$$

if we define

$$\alpha \equiv a^2 + \frac{i\hbar t}{2m} \tag{7.8}$$

$$\beta \equiv \frac{i}{2}\left(-x + \frac{\hbar t K}{2m}\right) \tag{7.9}$$

$$\gamma \equiv iK\left(-x + \frac{\hbar t K}{2m}\right) \tag{7.10}$$

With these substitutions, Eq. (7.5) becomes

$$\Psi(x, t) = C \int_{-\infty}^{+\infty} \exp(-\alpha\Delta_{kK}^2 - 2\beta\Delta_{kK} - \gamma)\, d\Delta_{kK}$$

$$= C \exp\left[\frac{\beta^2}{\alpha} - \gamma\right] \int_{-\infty}^{+\infty} \exp\left[-\alpha\left(\Delta_{kK} + \frac{\beta}{\alpha}\right)^2\right] d\Delta_{kK} \tag{7.11}$$

The integrand can be written as $e^{-\alpha u^2}$ with $u \equiv [\Delta_{kK} + (\beta/\alpha)]$, giving for the result

$$\Psi(x, t) = C\left(\frac{\pi}{\alpha}\right)^{1/2} \exp\left(\frac{\beta^2}{\alpha} - \gamma\right) \tag{7.12}$$

or, in terms of the original variables,

$$\Psi(x, t) = \frac{C\pi^{1/2}}{(a^2 + i\hbar t/2m)^{1/2}} \exp\left[-\frac{(x - \hbar t K/m)^2}{4[a^2 + (i\hbar t/2m)]} + iK\left(x - \frac{\hbar t K}{2m}\right)\right] \tag{7.13}$$

In order to interpret $\Psi(x, t)$ as representing the motion of a particle, we must investigate the value of the probability $|\Psi(x, 0)|^2$ at $t = 0$, and compare it with the value of the probability $|\Psi(x, t)|^2$ at some later time. From Eq. (7.13) it follows that

$$|\Psi(x, 0)|^2 = \frac{|C|^2\pi}{a^2} e^{-x^2/2a^2} \tag{7.14}$$

and that

$$|\Psi(x, t)|^2 = \frac{|C|^2\pi}{[a^4 + (\hbar^2 t^2/4m^2)]^{1/2}} \exp\left[-\frac{a^2(x - \hbar t K/m)^2}{2[a^4 + (\hbar^2 t^2/4m^2)]}\right] \tag{7.15}$$

The wavefunction $\Psi(x, 0)$ represents a wave characterized by the wave vector K, and with amplitude modulated by $e^{-x^2/4a^2}$. Figure 7.1b shows a plot of Eq. (7.14) for $|\Psi(x, 0)|^2$ for comparison with $A(k)$. $|\Psi(x, 0)|^2$ gives the probability of finding the particle in a range dx at x at $t = 0$. The constant C must be chosen so that the total area under the $|\Psi(x, 0)|^2$ curve is unity. The probability falls to $1/e$ of its maximum value for $x = \pm(2a^2)^{1/2}$.

At $t = 0$, the probability is quite high that the particle will lie within a distance $(2a^2)^{1/2}$ of the origin. If we take the uncertainty in the location of the particle, Δx, to be $(2a^2)^{1/2}$ at $t = 0$, therefore, then we can check the Heisenberg uncertainty relationship if we obtain a related value for Δp_x. From Eq. (7.4) we note that $A(k)$ falls to $1/e$ of its maximum value for $\Delta_{kK} = 1/a$. The quantity Δ_{kK} is really Δk, and since $p_x = \hbar k$, $\Delta p_x = \hbar/a$. At $t = 0$, then, we have

$$\Delta p_x \cdot \Delta x = 2^{1/2}\hbar \tag{7.16}$$

The fact that $\Delta p_x \cdot \Delta x$ for the Gaussian form of the wave packet is larger than the minimum value required by the Heisenberg relationship shows that a somewhat sharper distribution than the Gaussian can be used to define the wave packet and still maintain consistency with the uncertainty requirements.

Another form of the Heisenberg uncertainty relation can be derived by considering the uncertainty in time at which a particle, described by a wave packet, passes a given point on the x axis,

$$\Delta t = \frac{\Delta x}{v_g} = \frac{\hbar\, \Delta x}{\partial E/\partial k} \tag{7.17}$$

For small Δk, we may write

$$\Delta E = \frac{\partial E}{\partial k}\, \Delta k$$

and therefore

$$\Delta t \cdot \Delta E = \hbar\, \Delta x \cdot \Delta k = \Delta x \cdot \Delta p_x \tag{7.18}$$

Thus the indeterminacy relationship between the complementary quantities, time and energy, is directly connected with the relationship between the complementary quantities, position and momentum.

The behavior of the wave packet as a function of time for $t > 0$ is described by Eq. (7.15). The maximum value of $|\Psi(x, t)|^2$ occurs for

$x = \hbar t K/m$ at time t. This means that the maximum of the wave packet travels in the x direction with a velocity

$$v_g = \frac{\hbar}{m} K = \left(\frac{\partial \omega}{\partial k}\right)_{k=K} \tag{7.19}$$

since $\omega = \hbar k^2/2m$. Thus the maximum of the wave packet moves with the average velocity of the particle. Inspection of Eq. (7.15) also shows that the maximum value of $|\Psi(x, t)|^2$ decreases and that the $1/e$ width of $|\Psi(x, t)|^2$ increases with time. Thus the passage of time sees the wave packet moving in the x direction, but with decreasing maximum amplitude and with increasing spread away from the maximum, as indicated in Fig. 7.2. Of course the area under the various curves of Fig. 7.2 must remain constant, but information on the probable location of the particle is lost with increasing time. For very large values of t (i.e., $t \gg 2ma^2/\hbar$), the maximum value is given by

$$|\Psi(x, t)|^2_{\max} = \frac{2m |C|^2 \pi}{\hbar t} \tag{7.20}$$

and the $1/e$ width is given by

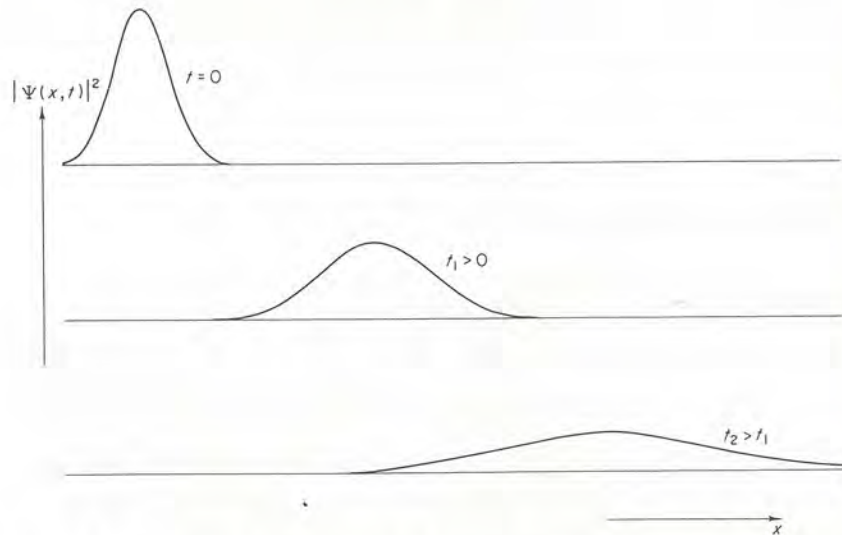$$\text{Width} = \frac{\hbar}{2^{1/2}ma} t \tag{7.21}$$

Fig. 7.2 Behavior of the square of the amplitude of the wavefunction for a wave packet $|\Psi(x, t)|^2$ with the passage of time, according to Eq. (7.15).

BLOCH-FUNCTION WAVE PACKETS

If we construct a wave packet from Bloch waves, we can show directly the relationship between velocity and the gradient of $E(\mathbf{k})$.

A wave packet constructed from time-dependent Bloch waves has the form

$$\Psi(\mathbf{r}, t) = \int A(\mathbf{k}') u_{\mathbf{k}'}(\mathbf{r}) \exp\left[i\left(\mathbf{k}' \cdot \mathbf{r} - \frac{E(\mathbf{k}') t}{\hbar}\right)\right] d\mathbf{k}' \tag{7.22}$$

The wave packet is constructed from Bloch waves corresponding to wave vectors $\mathbf{k}'$ in the vicinity of $\mathbf{k}$. The function $A(\mathbf{k}')$ is chosen to have a sharp maximum magnitude at $\mathbf{k}' = \mathbf{k}$, and to fall off rapidly for $\mathbf{k}'$ different from $\mathbf{k}$.

Because of this property of the $A(\mathbf{k}')$ function, we can expand $E(\mathbf{k}')$ about $\mathbf{k}$ in a Taylor series and retain only the first two terms,

$$E(\mathbf{k}') = E(\mathbf{k}) + (\mathbf{k}' - \mathbf{k}) \cdot \nabla_{\mathbf{k}} E(\mathbf{k}) \tag{7.23}$$

Using this expansion, $\Psi(\mathbf{r}, t)$ given in Eq. (7.22) becomes

$$\Psi(\mathbf{r}, t) = \exp\left[i\left(\mathbf{k} \cdot \mathbf{r} - \frac{E(\mathbf{k}) t}{\hbar}\right)\right] \int A(\mathbf{k}') u_{\mathbf{k}'}(\mathbf{r})$$
$$\times \exp\left\{i\left[(\mathbf{k}' - \mathbf{k}) \cdot \left(\mathbf{r} - \frac{t\nabla_{\mathbf{k}}E}{\hbar}\right)\right]\right\} d\mathbf{k}' \tag{7.24}$$

If we assume that $u_{\mathbf{k}}(\mathbf{r})$ does not change appreciably over the effective range of the integral, we may set $u_{\mathbf{k}'}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})$ and remove it from the integrand of Eq. (7.24). Then the result is

$$\Psi(\mathbf{r}, t) = \Psi_{\mathbf{k}}(\mathbf{r}, t) \int A(\mathbf{k}') \exp\left\{i\left[(\mathbf{k}' - \mathbf{k}) \cdot \left(\mathbf{r} - \frac{t\nabla_{\mathbf{k}}E}{\hbar}\right)\right]\right\} d\mathbf{k}' \tag{7.25}$$

which corresponds to a wave packet moving with velocity $\mathbf{v} = (1/\hbar) \nabla_{\mathbf{k}} E$.

7.2   Description of Particle Motion Using Wave Packets

In this section we desire to demonstrate the following basic result. If a particle is represented by a wave packet, its motion under the action of an external force satisfies the classical equation of motion, i.e., $\mathbf{F} = m\mathbf{a}$, provided that the expectation values of acceleration and force defined in terms of the wave packet are used.

Restating this in more quantitative terms, we desire to show that

$$F = -\frac{\partial V}{\partial x} = ma = m\frac{d^2 x}{dt^2}$$

is still valid for the particle in the wave-packet treatment if we replace x by its expectation value $\langle x \rangle$, and if we replace $-\partial V/\partial x$ by its expectation value $\langle -\partial V/\partial x \rangle$. Our approach is to calculate $d^2\langle x\rangle/dt^2$, and show that it is indeed equal to $\langle -\partial V/\partial x\rangle/m$.

The expectation value of x is given by

$$\langle x \rangle = \int_{-\infty}^{+\infty} \Psi^*(x, t)\, x\Psi(x, t)\, dx \qquad (7.26)$$

where

$$\Psi(x, t) = \int A(k)\, \psi_k(x)\, e^{-iEt/\hbar}\, dk \qquad (7.27)$$

is a suitable wave-packet general solution of

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} + V(x)\,\Psi = i\hbar\frac{\partial \Psi}{\partial t} \qquad (7.28)$$

The velocity is given by

$$v = \frac{d\langle x \rangle}{dt} = \int_{-\infty}^{+\infty}\left[x\Psi^*\frac{\partial \Psi}{\partial t} + x\Psi\frac{\partial \Psi^*}{\partial t}\right] dx \qquad (7.29)$$

Since x is an operator in Eq. (7.29), its time derivative does not enter. The time derivatives of Eq. (7.29) can be transformed into x derivatives by using the Schroedinger equation. We multiply Eq. (7.28), written for the complex conjugate wavefunction Ψ^*, by $x\Psi$, and subtract from Eq. (7.28) multiplied by $x\Psi^*$. Integrate the difference over all x, and obtain

$$-\frac{\hbar^2}{2m}\int_{-\infty}^{+\infty}\left[x\Psi^*\frac{\partial^2 \Psi}{\partial x^2} - x\Psi\frac{\partial^2 \Psi^*}{\partial x^2}\right] dx$$

$$= i\hbar\int_{-\infty}^{+\infty}\left[x\Psi^*\frac{\partial \Psi}{\partial t} + x\Psi\frac{\partial \Psi^*}{\partial t}\right] dx$$

$$= i\hbar\frac{d\langle x \rangle}{dt} \qquad (7.30)$$

Integrating by parts,

$$\int_{-\infty}^{+\infty}x\Psi^*\frac{\partial^2 \Psi}{\partial x^2}\, dx = x\Psi^*\frac{\partial \Psi}{\partial x}\Big|_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty}\frac{\partial \Psi}{\partial x}\left(x\frac{\partial \Psi^*}{\partial x} + \Psi^*\right) dx \qquad (7.31)$$

with a similar expression for $\int_{-\infty}^{+\infty}x\Psi(\partial^2\Psi^*/\partial x^2)\, dx$. The first term on the right of Eq. (7.31) is equal to zero since the wavefunction goes to zero at infinity. The evaluation of Eq. (7.30) therefore leads to

$$i\hbar\frac{d\langle x \rangle}{dt} = \frac{\hbar^2}{2m}\int_{-\infty}^{+\infty}\left(\Psi^*\frac{\partial \Psi}{\partial x} - \Psi\frac{\partial \Psi^*}{\partial x}\right) dx \qquad (7.32)$$

Now

$$\int_{-\infty}^{+\infty}\Psi^*\frac{\partial \Psi}{\partial x}\, dx = \Psi^*\Psi\Big|_{-\infty}^{\infty} - \int_{-\infty}^{+\infty}\Psi\frac{\partial \Psi^*}{\partial x}\, dx \qquad (7.33)$$

so that Eq. (7.32) becomes

$$i\hbar\frac{d\langle x \rangle}{dt} = \frac{\hbar^2}{m}\int_{-\infty}^{+\infty}\Psi^*\frac{\partial \Psi}{\partial x}\, dx \qquad (7.34)$$

Now we can continue with our calculation of

$$m\frac{d^2\langle x \rangle}{dt^2} = -i\hbar\int_{-\infty}^{+\infty}\left(\frac{\partial \Psi^*}{\partial t}\frac{\partial \Psi}{\partial x} + \Psi^*\frac{\partial^2 \Psi}{\partial x\, \partial t}\right) dx \qquad (7.35)$$

The form of Eq. (7.35) can be made more symmetric by realizing that

$$\int_{-\infty}^{+\infty}\Psi^*\frac{\partial^2 \Psi}{\partial x\, \partial t}\, dx = \Psi^*\frac{\partial \Psi}{\partial t}\Big|_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty}\frac{\partial \Psi}{\partial t}\frac{\partial \Psi^*}{\partial x}\, dx \qquad (7.36)$$

so that

$$m\frac{d^2\langle x \rangle}{dt^2} = -i\hbar\int_{-\infty}^{+\infty}\left(\frac{\partial \Psi^*}{\partial t}\frac{\partial \Psi}{\partial x} - \frac{\partial \Psi}{\partial t}\frac{\partial \Psi^*}{\partial x}\right) dx \qquad (7.37)$$

In view of our initial goal, we need to introduce the potential energy $V(x)$ explicitly into the calculation. We can do this by substituting for the time derivatives of Ψ and Ψ^* from Eq. (7.28) and its complex conjugate. We obtain

$$m\frac{d^2\langle x \rangle}{dt^2} = -\frac{\hbar^2}{2m}\int_{-\infty}^{+\infty}\left(\frac{\partial^2 \Psi^*}{\partial x^2}\frac{\partial \Psi}{\partial x} + \frac{\partial^2 \Psi}{\partial x^2}\frac{\partial \Psi^*}{\partial x}\right) dx$$

$$+ \int_{-\infty}^{+\infty}V(x)\left(\Psi^*\frac{\partial \Psi}{\partial x} + \Psi\frac{\partial \Psi^*}{\partial x}\right) dx \qquad (7.38)$$

The first integral in Eq. (7.38) is zero since

$$\int_{-\infty}^{+\infty}\frac{\partial \Psi}{\partial x}\frac{\partial^2 \Psi^*}{\partial x^2}\, dx = \frac{\partial \Psi}{\partial x}\frac{\partial \Psi^*}{\partial x}\Big|_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty}\frac{\partial \Psi^*}{\partial x}\frac{\partial^2 \Psi}{\partial x^2}\, dx \qquad (7.39)$$

The second integral in Eq. (7.38) can be simplified since

$$\int_{-\infty}^{+\infty} V(x) \, \Psi^* \, \frac{\partial \Psi}{\partial x} \, dx = V(x) \, \Psi^* \Psi \Big|_{-\infty}^{+\infty}$$
$$- \int_{-\infty}^{+\infty} \Psi \left[V(x) \, \frac{\partial \Psi^*}{\partial x} + \Psi^* \, \frac{\partial V(x)}{\partial x} \right] dx \qquad (7.40)$$

Finally we obtain

$$m \, \frac{d^2 \langle x \rangle}{dt^2} = - \int_{-\infty}^{+\infty} \Psi^* \, \frac{\partial V(x)}{\partial x} \Psi \, dx$$
$$= \left\langle - \frac{\partial V(x)}{\partial x} \right\rangle \qquad (7.41)$$

Although this calculation has been carried out for the one-dimensional case, generalization of the result to three dimensions leads to the same conclusions. As long as the equation of motion is discussed in terms of the expectation values of acceleration and force, therefore, the wave-mechanical equation utilizing wave packets leads to the same results as classical physics for the equivalent particles. This result affords us the possibility of extensive simplification in the discussion of the motion of electrons in crystals. Instead of it being necessary for us constantly to revert to the solution of the entire Schroedinger equation, we can in many cases continue to treat the motion of electrons in crystals in a quasi-classical particle framework, remembering the wave-mechanical justification for this is the wave-packet context.

7.3   The Boltzmann Equation

What the Schroedinger equation is for describing energy levels in crystals, the Boltzmann equation is for describing carrier transport in crystals. The Boltzmann equation expresses the total time rate of change of the distribution function $f(\mathbf{k}, \mathbf{r}, t)$, which describes the occupancy of allowed energy states involved in transport processes:

$$\frac{df}{dt} = \frac{\partial f}{\partial t} \bigg]_{\text{external field}} + \frac{\partial f}{\partial t} \bigg]_{\text{diffusion}} + \frac{\partial f}{\partial t} + \frac{\partial f}{\partial t} \bigg]_{\text{scattering}} \qquad (7.42)$$

In steady state $df/dt = \partial f/\partial t = 0$. For a force F, we can write

$$\frac{\partial f}{\partial t} \bigg]_{\text{external field}} = - \frac{\partial \mathbf{k}}{\partial t} \cdot \nabla_{\mathbf{k}} f$$
$$= - \frac{1}{\hbar} \, \mathbf{F} \cdot \nabla_{\mathbf{k}} f \qquad (7.43)$$

in view of Eq. (6.26). Similarly we can write

$$\frac{\partial f}{\partial t} \bigg]_{\text{diffusion}} = - \frac{d\mathbf{r}}{dt} \cdot \nabla_{\mathbf{r}} f$$
$$= - \mathbf{v} \cdot \nabla_{\mathbf{r}} f \qquad (7.44)$$

The steady-state equation is therefore

$$\frac{1}{\hbar} \, \mathbf{F} \cdot \nabla_{\mathbf{k}} f + \mathbf{v} \cdot \nabla_{\mathbf{r}} f = \frac{\partial f}{\partial t} \bigg]_{\text{scattering}} \qquad (7.45)$$

The form of $(\partial f/\partial t)_{\text{scattering}}$ depends on the nature of the specific scattering process.

Consider the general situation where $P_{\mathbf{kk}'}$ is the probability per unit time for scattering from $\mathbf{k}$ to $\mathbf{k}'$. Then the formal relation holds,

$$\frac{\partial f}{\partial t} \bigg]_{\text{scattering}} = \int \{ P_{\mathbf{k}'\mathbf{k}} f(\mathbf{k}')[1 - f(\mathbf{k})] - P_{\mathbf{kk}'} f(\mathbf{k})[1 - f(\mathbf{k}')] \} \, d\mathbf{k}' \qquad (7.46)$$

At equilibrium the distribution function is given by its equilibrium value, which is a function only of the energy E,

$$f(\mathbf{k}, \mathbf{r}, t)_{\text{equil.}} = f_0(E) \qquad (7.47)$$

where $f_0(E)$ is given by Eq. (4.84). Since $(\partial f/\partial t)_{\text{scattering}} = 0$ at equilibrium,

$$P_{\mathbf{k}'\mathbf{k}} = P_{\mathbf{kk}'} \, \frac{f_0(E)[1 - f_0(E')]}{f_0(E')[1 - f_0(E)]} \qquad (7.48)$$

as long as $P_{\mathbf{kk}'}$ is not a function of $\mathbf{F}$, which we are assuming to be the case.

It is customary to express the departure of the distribution function from equilibrium as

$$f(\mathbf{k}, \mathbf{r}) = f_0(E) + f'(\mathbf{k}, \mathbf{r}) \qquad (7.49)$$

and to write in addition

$$f'(\mathbf{k}, \mathbf{r}) = -\phi(\mathbf{k}, \mathbf{r}) \, \frac{\partial f_0}{\partial E} \qquad (7.50)$$

If Eqs. (7.48) through (7.50) are substituted into Eq. (7.46), it becomes

$$\frac{\partial f}{\partial t} \bigg]_{\text{scattering}} = \frac{1}{kT} \int P_{\mathbf{kk}'} f_0(E)[1 - f_0(E')][\phi(\mathbf{k}') - \phi(\mathbf{k})] \, d\mathbf{k}' \qquad (7.51)$$

Finally, by setting $\mathbf{F}$ in Eq. (7.45) explicitly equal to the Lorentz force for a carrier with charge e,

$$\mathbf{F} = e\left(\mathscr{E} + \frac{1}{c}\,\mathbf{v}\times\mathbf{B}\right) = e\left(\mathscr{E} + \frac{1}{c\hbar}\,\nabla_{\mathbf{k}}\,E(\mathbf{k})\times\mathbf{B}\right) \qquad (7.52)$$

and using $\mathbf{v} = (1/\hbar)\,\nabla_{\mathbf{k}}\,E(\mathbf{k})$ in the second term of Eq. (7.45), we convert Eq. (7.45) with Eq. (7.51) into the Bloch equation,

$$e\left(\mathscr{E} + \frac{1}{c\hbar}\,\nabla_{\mathbf{k}}\,E(\mathbf{k})\times\mathbf{B}\right)\cdot\frac{1}{\hbar}\,\nabla_{\mathbf{k}}f(\mathbf{k},\mathbf{r}) + \frac{1}{\hbar}\,\nabla_{\mathbf{k}}\,E(\mathbf{k})\cdot\nabla_{\mathbf{r}}\,f(\mathbf{k},\mathbf{r})$$

$$= \frac{1}{kT}\int P_{\mathbf{kk}'}f_0(E)[1 - f_0(E')][\phi(\mathbf{k}') - \phi(\mathbf{k})]\,d\mathbf{k}' \qquad (7.53)$$

7.4   Solution of the Boltzmann Equation

A particularly simple solution of the Boltzmann equation becomes possible in those particular cases where the effects of scattering can be described in terms of a relaxation time τ.

$$\left.\frac{\partial f}{\partial t}\right]_{\text{scattering}} = -\frac{f(\mathbf{k},\mathbf{r}) - f_0(E)}{\tau} = -\frac{f'(\mathbf{k},\mathbf{r})}{\tau} \qquad (7.54)$$

We consider the solution of the Boltzmann equation in the relaxation time approximation in the following section. Here we consider briefly the criterion for using the relaxation-time approximation justifiably.

A formal relaxation time $\tau(\mathbf{k})$ can always be defined,

$$\tau(\mathbf{k}) \equiv \phi(\mathbf{k})\frac{(\partial f_0/\partial E)}{(\partial f/\partial t)_{\text{scattering}}} \qquad (7.55)$$

following Eq. (7.54). Using Eq. (7.51) this becomes

$$\frac{1}{\tau(\mathbf{k})} = \frac{1}{\phi(\mathbf{k})}\,\frac{1}{(\partial f_0/\partial E)}\,\frac{1}{kT}\int P_{\mathbf{kk}'}f_0(E)[1 - f_0(E')][\phi(\mathbf{k}') - \phi(\mathbf{k})]\,d\mathbf{k}'$$

$$= \int P_{\mathbf{kk}'}\left[\frac{1 - f_0(E')}{1 - f_0(E)}\right]\left[1 - \frac{\phi(\mathbf{k}')}{\phi(\mathbf{k})}\right]d\mathbf{k}' \qquad (7.56)$$

since $(\partial f_0/\partial E) = -f_0(E)[1 - f_0(E)]/kT$.

The relaxation time $\tau(\mathbf{k})$ is a meaningful quantity provided that it is independent of the strength and type of the perturbation causing f to depart from f_0. If the relaxation time is a function of the type of perturbation

(for example, electric field, thermal gradient), then it is not a physically useful quantity.

Equation (7.56) shows that two conditions are imposed on the particular process in order for the relaxation-time approximation to be justified. (1) $f_0(E') = f_0(E)$. This means that $E(\mathbf{k}') = E(\mathbf{k})$, or that the scattering process is *elastic*, i.e., involves no energy change, or at least in practical considerations an energy change much less than the average carrier energy of kT. (2) $[\phi(\mathbf{k}')/\phi(\mathbf{k})]$ must be independent of the type of perturbation. This condition can be checked for particular types of perturbation, as is demonstrated in the following section.

In those cases where the relaxation-time approximation is not justified, e.g., for inelastic scattering, another method must be used for the solution of the Boltzmann equation. A variational calculation is used based on the principle that, for a particular perturbation, the steady-state distribution achieved is such that, were the perturbation removed suddenly, the return to equilibrium would be the most rapid for a particular relaxation mechanism. This corresponds physically to maximizing the time rate of change of entropy production associated with the scattering processes. We will not pursue the details of this process further here, but will cite some of its results where applicable in later sections.

7.5   Relaxation-Time Solution of the Boltzmann Equation

In the relaxation-time approximation, the Bloch equation of Eq. (7.53) can be written

$$e\left[\mathscr{E} + \frac{1}{c}\,\mathbf{v}\times\mathbf{B}\right]\cdot\frac{1}{\hbar}\,\nabla_{\mathbf{k}}f + \mathbf{v}\cdot\nabla_{\mathbf{r}}f = -\frac{f'}{\tau}$$

$$= \frac{\phi}{\tau}\,\frac{\partial f_0}{\partial E} \qquad (7.57)$$

We have the following relationships:

$$\nabla_{\mathbf{r}}f \approx \nabla_{\mathbf{r}}f_0 = \frac{\partial f_0}{\partial T}\,\nabla_{\mathbf{r}}T \qquad (7.58)$$

$$\frac{\partial f_0}{\partial T} = -\frac{E - E_{\mathrm{F}}}{T}\,\frac{\partial f_0}{\partial E} - \frac{\partial E_{\mathrm{F}}}{\partial T}\,\frac{\partial f_0}{\partial E} \qquad (7.59)$$

so that

$$\nabla f \approx -\left[\frac{E - E_{\mathrm{F}}}{T}\,\nabla T + \nabla E_{\mathrm{F}}\right]\frac{\partial f_0}{\partial E} \qquad (7.60)$$

where, in keeping with ordinary practice, we have set $\nabla_{\mathbf{r}} \equiv \nabla$. In the processes of this section, we are discussing steady-state conditions, and we may therefore drop the term in Eq. (7.60) involving ∇E_F. In a later discussion of thermal conductivity, the term involving ∇E_F must be included. We also have that

$$\nabla_{\mathbf{k}} f = \frac{\partial f_0}{\partial E} \nabla_{\mathbf{k}} E + \nabla_{\mathbf{k}} f' \tag{7.61}$$

where we neglect the second term on the right as long as the first term does not make an identically zero contribution. With the substitution of the results of Eqs. (7.58) through (7.61) into Eq. (7.57), we obtain

$$e\mathscr{E} \cdot \mathbf{v} \frac{\partial f_0}{\partial E} + \frac{e}{c} [\mathbf{v} \times \mathbf{B}] \cdot \mathbf{v} \frac{\partial f_0}{\partial E} + \frac{e}{c\hbar} [\mathbf{v} \times \mathbf{B}] \cdot \nabla_{\mathbf{k}} f'$$

$$- (E - E_F) \frac{\partial f_0}{\partial E} \mathbf{v} \cdot \nabla \ln T = \frac{\phi}{\tau} \frac{\partial f_0}{\partial E} \tag{7.62}$$

The second term in this equation is identically zero, and hence we retain the term involving f'. Collecting terms,

$$[e\mathscr{E} - (E - E_F) \nabla \ln T] \cdot \mathbf{v} \frac{\partial f_0}{\partial E} + \frac{e}{c\hbar} [\mathbf{v} \times \mathbf{B}] \cdot \nabla_{\mathbf{k}} f' = \frac{\phi}{\tau} \frac{\partial f_0}{\partial E} \tag{7.63}$$

In view of Eq. (7.50),

$$\frac{e}{c\hbar} [\mathbf{v} \times \mathbf{B}] \cdot \nabla_{\mathbf{k}} f' = \frac{e}{c\hbar} \mathbf{B} \cdot [\nabla_{\mathbf{k}} f' \times \mathbf{v}]$$

$$= -\frac{e}{c\hbar^2} \mathbf{B} \cdot [\nabla_{\mathbf{k}} E \times \nabla_{\mathbf{k}} f']$$

$$= \frac{e}{c\hbar^2} \mathbf{B} \cdot [\nabla_{\mathbf{k}} E \times \nabla_{\mathbf{k}} \phi] \frac{\partial f_0}{\partial E} \tag{7.64}$$

Substitution of Eq. (7.64) into Eq. (7.63) permits the solution for ϕ,

$$\phi = \tau [e\mathscr{E} - (E - E_F) \nabla \ln T] \cdot \mathbf{v} + \frac{e\tau}{c\hbar^2} \mathbf{B} \cdot [\nabla_{\mathbf{k}} E \times \nabla_{\mathbf{k}} \phi] \tag{7.65}$$

This is the basic equation for the treatment of transport problems involving steady state and a meaningful relaxation time.

ELECTRIC FIELD ONLY

For an electric field only, $\mathbf{B} = 0$ and $\nabla T = 0$. From Eq. (7.65),

$$\phi = \tau e \mathscr{E} \cdot \mathbf{v} \tag{7.66}$$

and

$$f = f_0 - \tau e \mathscr{E} \cdot \mathbf{v} \frac{\partial f_0}{\partial E} \tag{7.67}$$

If the electric field is applied in the x direction, i.e., $\mathscr{E} = \mathscr{E}_x$,

$$f = f_0 - \frac{e\tau\mathscr{E}_x}{\hbar} \frac{\partial E}{\partial k_x} \frac{\partial f_0}{\partial E}$$

$$= f_0 - \frac{e\tau\mathscr{E}_x}{\hbar} \frac{\partial f_0}{\partial k_x} \tag{7.68}$$

and the total distribution function is expressible as

$$f(k_x, k_y, k_z) = f\left[k_x - \frac{e\mathscr{E}_x \tau}{\hbar}, k_y, k_z\right] \tag{7.69}$$

The displacement of the Fermi sphere in $\mathbf{k}$ space and of the distribution function as it depends on k_x, with respect to the equilibrium positions, are shown in Fig. 7.3. All points on these surfaces undergo the same displacement, i.e., no change in shape occurs in the simple case of an electric field only.

With reference to Eq. (7.56), the suitability of the relaxation-time approximation to this case can be tested by seeing whether $\phi(\mathbf{k}')/\phi(\mathbf{k})$ is independent of the type of the perturbation. From Eq. (7.66),

$$\frac{\phi(\mathbf{k}')}{\phi(\mathbf{k})} = \frac{\tau(\mathbf{k}') e\mathscr{E}_x v_x(\mathbf{k}')}{\tau(\mathbf{k}) e\mathscr{E}_x v_x(\mathbf{k})} = \frac{\tau(\mathbf{k}') v_x(\mathbf{k}')}{\tau(\mathbf{k}) v_x(\mathbf{k})} \tag{7.70}$$

We conclude that scattering processes for an electric field only can be described by a relaxation time provided that the scattering processes are elastic.

THERMAL GRADIENT ONLY

For a thermal gradient only, $\mathbf{B} = 0$ and $\mathscr{E} = 0$. From Eq. (7.65),

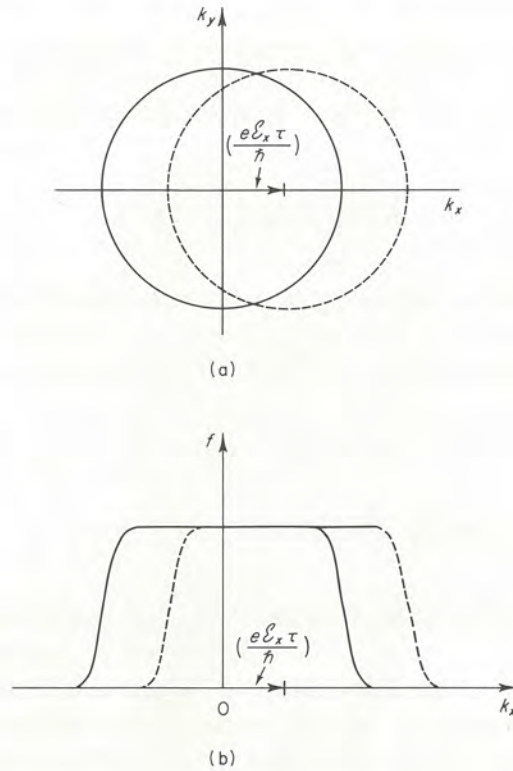$$\phi = \tau [-(E - E_F) \nabla \ln T] \cdot \mathbf{v} \tag{7.71}$$

(a)

(b)

Fig. 7.3 (a) Displacement of the Fermi sphere in **k** space as the result of the application of an electric field only, in the x direction. (b) Displacement of the distribution function as the result of the application of an electric field only, in the x direction.

For a thermal gradient in the x direction,

$$f' = -\phi \frac{\partial f_0}{\partial E} = \tau(E - E_F) \frac{1}{T} \frac{\partial T}{\partial x} \frac{1}{\hbar} \frac{\partial f_0}{\partial E} \frac{\partial E}{\partial k_x} \qquad (7.72)$$

Consider the simple case of spherical equal-energy surfaces such that

$$(E - E_F) = \frac{\hbar^2 k_0}{m^*} (k - k_0) \qquad (7.73)$$

which follows from $E_F = \hbar^2 k_0^2 / 2m^*$, $|E - E_F| \ll E_F$, and $E = E_F \pm (k - k_0)(\partial E_F / \partial k)$. Then the expression for f' in Eq. (7.72) becomes

$$f' = \frac{\tau \hbar k_0}{m^* T} (k - k_0) \frac{\partial T}{\partial x} \frac{\partial f_0}{\partial k_x} \qquad (7.74)$$

The total distribution function is expressible as

$$f(k_x, k_y, k_z) = f\left[k_x + \frac{\tau \hbar k_0}{m^* T} (k - k_0) \frac{\partial T}{\partial x}, k_y, k_z \right] \qquad (7.75)$$

This is a more complicated variation from the equilibrium distribution than found for the case of an electric field only. Displacements of the Fermi surface and of the distribution function are shown in Fig. 7.4. For the case of a thermal gradient, the displacement depends on the energy of the surface being considered with respect to the Fermi energy E_F. For $E = E_F$,
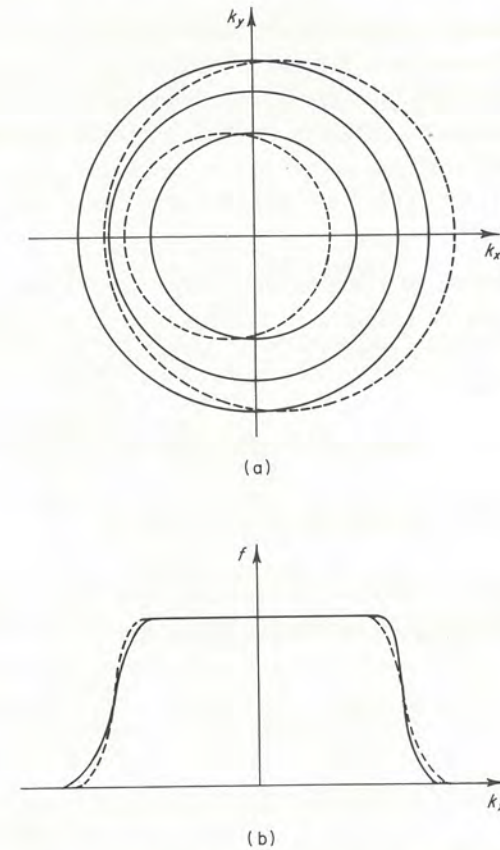

(a)

(b)

Fig. 7.4 (a) Displacement of the Fermi sphere in **k** space as the result of the application of a thermal gradient only, in the x direction. The magnitude and direction of the displacement depends on the energy of the surface with respect to the Fermi energy. (b) Displacement of the distribution function as the result of the application of a thermal gradient only, in the x direction.

there is no shift, while shifts in opposite directions are found for $E > E_F$ and $E < E_F$. Comparison of Figs. 7.3 and 7.4 show how strongly the departure from equilibrium can depend on the nature of the specific perturbation causing this departure.

Again with Eq. (7.56) in mind, we can check the suitability of a relaxation-time approximation to the case of a thermal gradient only.

$$\frac{\phi(\mathbf{k}')}{\phi(\mathbf{k})} = \frac{\tau(\mathbf{k}')[E(\mathbf{k}') - E_F] \, \nabla \ln T \cdot \mathbf{v}(\mathbf{k}')}{\tau(\mathbf{k})[E(\mathbf{k}) - E_F] \, \nabla \ln T \cdot \mathbf{v}(\mathbf{k})} = \frac{\tau(\mathbf{k}') \, v_x(\mathbf{k}')[E(\mathbf{k}') - E_F]}{\tau(\mathbf{k}) \, v_x(\mathbf{k})[E(\mathbf{k}) - E_F]} \tag{7.76}$$

This ratio is indeed independent of the thermal gradient. Comparison of Eq. (7.76) for the case of a thermal gradient only with Eq. (7.70) for the case of an electric field only shows that the *same* relaxation time can be used for both processes, however, only in the case of elastic scattering, i.e., only if $E(\mathbf{k}') = E(\mathbf{k})$.

GENERAL SOLUTION

A general solution of the Boltzmann equation in the relaxation-time approximation can be obtained in fairly simple form if spherical equal-energy surfaces are assumed, i.e., $E = \hbar^2 k^2 / 2m^*$, and $\mathbf{v} = \hbar \mathbf{k}/m^*$. Then Eq. (7.65) becomes

$$\phi = \tau[e\mathscr{E} - (E - E_F)\nabla \ln T] \cdot \frac{\hbar \mathbf{k}}{m^*} + \frac{e\tau}{c\hbar^2}\mathbf{B} \cdot \left[\frac{\hbar^2 \mathbf{k}}{m^*} \times \nabla_\mathbf{k}\phi \right] \tag{7.77}$$

The solution of this equation can be expressed as

$$\phi = \mathbf{k} \cdot \boldsymbol{\theta}(E, \mathscr{E}, \mathbf{B}, \nabla T) \tag{7.78}$$

where $\boldsymbol{\theta}$ is not a function of $\mathbf{k}$. The equation for $\boldsymbol{\theta}$ is

$$\boldsymbol{\theta} = \tau \frac{\hbar}{m^*} \left[e\mathscr{E} - (E - E_F)\nabla \ln T \right] - \frac{e\tau}{cm^*}\left[\mathbf{B} \times \boldsymbol{\theta} \right] \tag{7.79}$$

which has the solution

$$\boldsymbol{\theta} = \frac{\frac{\hbar\tau}{m^*} \left[\left[e\mathscr{E} - (E - E_F)\nabla \ln T \right] - \frac{e\tau}{m^*c}\mathbf{B} \times \left[e\mathscr{E} - (E - E_F)\nabla \ln T \right] \right.}{1 + \left(\frac{e\tau B}{m^*c} \right)^2} $$
$$\frac{\left. + \left(\frac{e\tau}{m^*c} \right)^2 \mathbf{B}\{\mathbf{B} \cdot \left[e\mathscr{E} - (E - E_F)\nabla \ln T \right] \} \right]}{1 + \left(\frac{e\tau B}{m^*c} \right)^2} \tag{7.80}$$

We consider this equation in more detail in Chapter 10 in connection with galvanomagnetic effects. We note here only the simplification that results if $\mathbf{B}$ is in the same direction as $\mathscr{E}$ and ∇T. Multiplication of Eq. (7.80) by $\mathbf{k}$ in this case (the second term in the numerator is zero) shows that ϕ reduces to the same form as that obtained from Eq. (7.65) with $\mathbf{B} = 0$. It is possible to conclude directly without further calculation, therefore, that *longitudinal* galvanomagnetic and thermomagnetic effects are not observed in the case of spherical equal-energy surfaces and sufficiently small $\mathbf{B}$ that the relaxation-time approximation holds.

7.6   Electrical Conductivity in the Relaxation-Time Approximation

For the case of electrical conductivity we are concerned with the effect of applying an electric field only; and hence the distribution function is given by Eq. (7.67). This relationship written explicitly for electrons with charge of $-e$ and for an electric field in the x direction is

$$f = f_0 + \tau e \mathscr{E}_x v_x \frac{\partial f_0}{\partial E} \tag{7.81}$$

The electric current density (current per unit area) j_x is given by the product of the electron charge and electron velocity, summed over all the electrons contributing,

$$j_x = -e \int f(\mathbf{k}') \, N(\mathbf{k}') \, v_x \, d\mathbf{k}'$$
$$= -\frac{e}{4\pi^3} \int f(\mathbf{k}') \, v_x \, d\mathbf{k}' \tag{7.82}$$

since $(1/4\pi^3)$ is the density per unit volume of allowed values of $\mathbf{k}'$, including a factor of 2 for electron spin. The integration of Eq. (7.82) is to be taken over all partially filled bands. Inserting f from Eq. (7.81) gives

$$j_x = -\frac{e^2\mathscr{E}_x}{4\pi^3} \int \tau v_x^2 \frac{\partial f_0}{\partial E} \, d\mathbf{k}' \tag{7.83}$$

since the integration over the equilibrium distribution f_0 is zero. Sometimes j_x is written simply as

$$j_x = e^2\mathscr{E}_x K_1 \tag{7.84}$$

in terms of the transport integral K_n, defined by

$$K_n \equiv -\frac{1}{4\pi^3} \int \tau v_x^2 E^{n-1} \frac{\partial f_0}{\partial E} \, d\mathbf{k}' \tag{7.85}$$

In most cases of electrical conductivity, only one partially occupied band is involved. In such a case, if the lower edge of the band is at $E = 0$ and the upper edge of the band is at $E = E_m$, the band contains n electrons per unit volume, given by

$$n = \frac{1}{4\pi^3} \int_0^{E_m} f_0 \, d\mathbf{k}' \qquad (7.86)$$

In terms of n, Eq. (7.83) can be rewritten as

$$j_x = -e^2 \mathscr{E}_x n \frac{\int_0^{E_m} \tau v_x^2 (\partial f_0 / \partial E) \, d\mathbf{k}'}{\int_0^{E_m} f_0 \, d\mathbf{k}'} \qquad (7.87)$$

This expression may be rewritten using $(\partial f_0 / \partial E) = -f_0(1 - f_0)/kT$:

$$j_x = \frac{e^2 \mathscr{E}_x n}{kT} \frac{\int_0^{E_m} \tau v_x^2 f_0 (1 - f_0) \, d\mathbf{k}'}{\int_0^{E_m} f_0 \, d\mathbf{k}'} \qquad (7.88)$$

Further simplification is possible if the equal-energy surfaces involved may be assumed to be spherical, so that

$$E = \frac{m^* |\mathbf{v}|^2}{2} = \frac{\hbar^2 |\mathbf{k}'|^2}{2m^*}$$

$$d\mathbf{k}' \propto k'^2 \, dk' \propto E^{1/2} \, dE$$

$$v_x^2 \approx \frac{|\mathbf{v}|^2}{3} = \frac{2E}{3m^*}$$

The final result for the current density for spherical equal-energy surfaces is

$$j_x = \frac{2e^2 \mathscr{E}_x n}{3m^* kT} \frac{\int_0^{E_m} \tau(E) E^{3/2} f_0 (1 - f_0) \, dE}{\int_0^{E_m} E^{1/2} f_0 \, dE}$$

$$= \frac{e^2 \mathscr{E}_x n}{m^*} \frac{\int_0^{E_m} \tau(E) E^{3/2} f_0 (1 - f_0) \, dE}{\int_0^{E_m} E^{3/2} f_0 (1 - f_0) \, dE} \qquad (7.89)$$

since

$$\int_0^{E_m} E^{3/2} f_0 (1 - f_0) \, dE = -kT \int_0^{E_m} E^{3/2} \frac{\partial f_0}{\partial E} \, dE = \frac{3kT}{2} \int_0^{E_m} E^{1/2} f_0 \, dE$$

A relatively simple physical interpretation of Eq. (7.89) can be made. It can be rewritten as

$$j_x = \frac{e^2 \mathscr{E}_x n}{m^*} \langle \tau(E) \rangle \qquad (7.90)$$

where the average value of the relaxation time $\langle \tau(E) \rangle$ is defined by the expression of Eq. (7.89). Physically the relaxation time is defined as the mean free time of the carrier between scattering events. Thus if an electron makes a scattering collision at $t = 0$ in the presence of an electric field $\mathscr{E}_x$ and loses all previous velocity in the direction of $\mathscr{E}_x$ (this velocity is called the *drift velocity* v_x and is expressible as $v_x = -\mu \mathscr{E}_x$, where μ is the electron *mobility*), its velocity at some later time t is

$$v_x = -\frac{e\mathscr{E}_x t}{m_e^*} \qquad (7.91)$$

where m_e^* is the effective mass of the electron in the crystal. The average value of the velocity over time is

$$\bar{v}_x = -\frac{e\mathscr{E}_x}{m_e^*} \tau_e \qquad (7.92)$$

where τ_e is the relaxation time for the electron. In view of the definition of mobility,

$$\mu_e = \frac{e}{m_e^*} \tau_e \qquad (7.93)$$

The current density is given by

$$j_x = -ne\bar{v}_x = \frac{e^2 \mathscr{E}_x n}{m_e^*} \tau_e \qquad (7.94)$$

which is identical to Eq. (7.90). In any real crystal we must consider also the average of the relaxation time τ_e over the distribution of electron energies. When this average is taken into account, τ_e in Eq. (7.94) is replaced by $\langle \tau(E) \rangle$, according to the procedure set forth in Eq. (7.89).

7.7 Electrical Conductivity in Semiconductors and Metals

Many different kinds of scattering processes are possible in semiconductors and metals, some of which allow a description in terms of a relaxation-time approximation and some of which do not. In this section we consider only two of the most generally encountered mechanisms: (1) scattering by acoustic phonons, and (2) scattering by charged imperfections. Other types of scattering are discussed in Chapter 8. The nature of these two scattering processes is such that a relaxation-time approximation in semiconductors is appropriate for both processes over the entire temperature

range of interest. In metals, however, scattering by acoustic phonons becomes inelastic at low temperatures and cannot be adequately described by the relaxation-time approximation.

SEMICONDUCTORS

In semiconductors the carriers contributing to electrical conductivity have **k** values near $\mathbf{k}_{ext}$ for the conduction or valence band extrema. Initial and final states have **k** values not greatly different for scattering by acoustic phonons, and it is found in general that scattering by acoustic phonons in nondegenerate semiconductors (i.e., with Fermi level in the forbidden gap between valence and conduction bands) is elastic. Scattering by charged imperfections involves no change in carrier energy, and hence is always elastic. Thus, for the two scattering processes under consideration here, the relaxation-time approximation is appropriate for semiconductors.

For a nondegenerate semiconductor, $f_0(1 - f_0) \approx f_0$, and Eq. (7.89) simplifies to

$$j_x = \frac{e^2 \mathscr{E}_x n}{m^*} \frac{\int_0^{E_m} \tau(E)\, E^{3/2} f_0\, dE}{\int_0^{E_m} E^{3/2} f_0\, dE} \tag{7.95}$$

If $\tau(E)$ can be expressed in the form of a simple power, e.g., $\tau(E) = AE^{-s}$, where A is not a function of E, an expression for $<\tau(E)>$ can be calculated as a function of s. For the nondegenerate semiconductor, the Fermi function f_0 reduces to the Boltzmann distribution, and the integrals of Eq. (7.95) can be evaluated directly to give

$$\langle \tau(E) \rangle = \frac{A}{(kT)^s} \frac{\Gamma(\tfrac{5}{2} - s)}{\Gamma(\tfrac{5}{2})} \tag{7.96}$$

As we show in Chapter 8, $s = \tfrac{1}{2}$ for acoustic phonon scattering, and $s = -\tfrac{3}{2}$ for charged imperfection scattering. When the relaxation time $\tau(E)$ is written in the form $\tau(E) = AE^{-s}$, it follows that

$$\langle \tau(E) \rangle_{\text{ac.ph.}} = \frac{4A}{3(\pi kT)^{1/2}} \tag{7.97}$$

$$\langle \tau(E) \rangle_{\text{ch.imp.}} = \frac{8A'(kT)^{3/2}}{\pi^{1/2}} \tag{7.98}$$

An alternative way of some physical interest to look at the calculation of $\langle \tau(E) \rangle$ for a nondegenerate semiconductor can be obtained by returning to Eq. (7.88) rewritten as

$$j_x = \frac{e^2 \mathscr{E}_x n}{3kT} \langle \tau v^2 \rangle \tag{7.99}$$

Now we may associate $m^* \langle v^2 \rangle / 2 = 3kT/2$, where $\langle v^2 \rangle$ is the root-mean-square velocity of a Maxwellian distribution, and we conclude that

$$\langle \tau \rangle = \frac{\langle \tau v^2 \rangle}{\langle v^2 \rangle} \tag{7.100}$$

The average relaxation time $\langle \tau \rangle$ is a weighted average of the relaxation times over the particles of the distribution, each particle being given a weight v^2, proportional to the energy E.

If more than one type of scattering process is contributing appreciably to the actual mobility of a charge carrier, we may expect as a first approximation that the rates of scattering add linearly, i.e., that the relaxation times or mobilities add reciprocally

$$\left(\frac{1}{\mu} \right)_{\text{total}} \approx \left(\frac{1}{\mu} \right)_{\text{ac.ph.}} + \left(\frac{1}{\mu} \right)_{\text{ch.imp.}} \tag{7.101}$$

This type of linear combination is not strictly correct, because of the different energy dependence of the relaxation time for the two processes. A more exact calculation taking proper averages results in the type of correction shown in Fig. 7.5. At the point of the largest correction, which is when 40% of the resistance is due to charged imperfection scattering and 60% due to acoustic phonon scattering, the total mobility calculated according to Eq. (7.101) is about 30% too large.

Whether or not the electrical conductivity is a simple scalar or a more complex tensor quantity depends on the nature of the energy bands of the
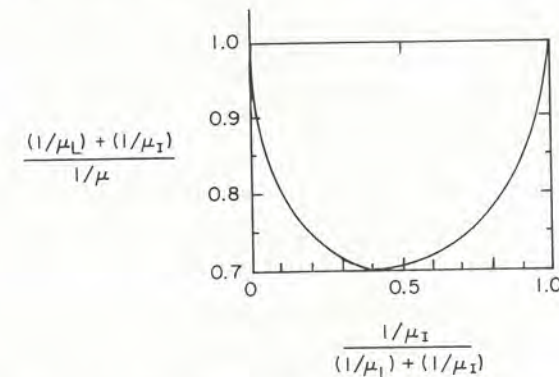

Fig. 7.5 Correction to be applied to the total mobility, as calculated by the simple sum of Eq. (7.101), in the presence of both acoustic lattice scattering (L) and charged-impurity scattering (I), when a proper average over energy is used. [After V. A. Johnson and K. Lark-Horovitz, *Phys. Rev.* **82**, 977 (1951).]

crystal. In the calculations following Eq. (7.88) we have been assuming spherical equal-energy surfaces with a scalar effective mass, $E(\mathbf{k}) = \hbar^2 k^2/2m^*$. As an example of a more complicated situation, consider an n-type semiconductor with a single conduction band minimum at $\mathbf{k} = 0$ with non-spherical equal-energy surfaces:

$$E(\mathbf{k}) = \frac{\hbar^2}{2} \left(\frac{k_1^2}{m_1^*} + \frac{k_2^2}{m_2^*} + \frac{k_3^2}{m_3^*} \right)$$

Electrical conductivity is conveniently described if the axes of the equal-energy surfaces are chosen as the coordinate axes for the description of the components of the electric field. An electric field applied in the $+x$ direction produces a current flow in the x direction,

$$j_x = -en\bar{v}_{xe} = en\frac{e}{m_1^*}\langle \tau_e \rangle \mathscr{E}_x = en\mu_{e1}\mathscr{E}_x \qquad (7.102)$$

A similar result is obtained for electric fields applied in the y or z directions. Under these conditions, therefore, the conductivity takes the form of a diagonalized tensor,

$$\sigma = \begin{pmatrix} ne\mu_{e1} & 0 & 0 \\ 0 & ne\mu_{e2} & 0 \\ 0 & 0 & ne\mu_{e3} \end{pmatrix} \qquad (7.103)$$

with

$$j_i = \sum_j \sigma_{ij}\mathscr{E}_j \qquad (7.104)$$

Such a crystal exhibits anisotropic conductivity, and except for electric fields in the direction of the equal-energy surface axes, the current flow is not in the same direction as the applied electric field.

Another example is a semiconductor with several equivalent minima in the conduction band, like that found for Ge or Si. Equal-energy surfaces for a band structure like that of Si are represented by the ellipsoids of Fig. 7.6. In this case the sum of the electrons in all the minima must be made. If, for example, the applied electric field is in the x direction,

$$j_x = \tfrac{1}{6}(2ne\mu_{e1} + 2ne\mu_{e2} + 2ne\mu_{e3})\mathscr{E}_x$$
$$= \tfrac{1}{3}ne(\mu_{e1} + \mu_{e2} + \mu_{e3})\mathscr{E}_x \qquad (7.105)$$

Each ellipsoid corresponds to one sixth of the total number of electrons, and there are two ellipsoids of each type to be included in the sum. For an electric field in the x direction, $j_y = j_z = 0$. For a general orientation
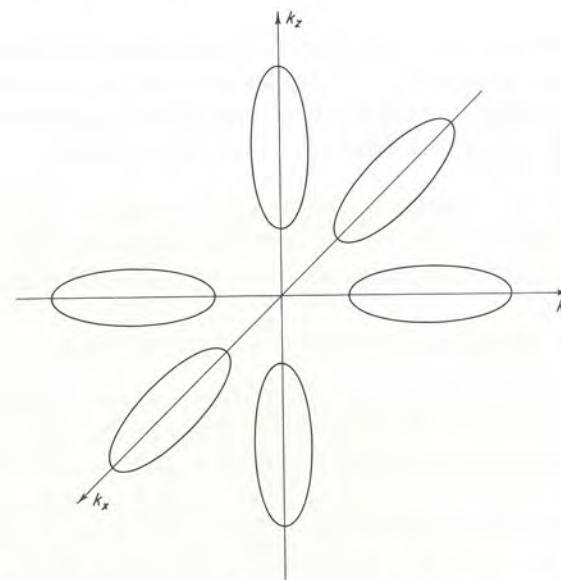
Fig. 7.6 Ellipsoidal equal-energy surfaces found for electrons in silicon.

of $\mathscr{E}$, the conductivity for this case remains a scalar, and it is common practice to define a *conductivity mobility*,

$$\mu_{e,con} \equiv \tfrac{1}{3}(\mu_{e1} + \mu_{e2} + \mu_{e3}) \qquad (7.106)$$

so that it is possible to write

$$\sigma_e = ne\mu_{e,con} \qquad (7.107)$$

It is also common to define a *conductivity effective mass*,

$$\frac{1}{m_{e,con}^*} \equiv \frac{1}{3}\left(\frac{1}{m_{e1}^*} + \frac{1}{m_{e2}^*} + \frac{1}{m_{e3}^*} \right) \qquad (7.108)$$

so that it is also possible to write

$$\mu_{e,con} = \frac{e}{m_{e,con}^*}\langle \tau_e \rangle \qquad (7.109)$$

In general, of course, the conductivity effective mass is not the same as the effective mass that enters the density of states, this latter *density-of-states effective mass* being given by

$$m^* = (m_1^* m_2^* m_3^*)^{1/3} \qquad (7.110)$$

as derived in Problem 6.11b.

In a crystal with cubic symmetry, the equal-energy surfaces shown in Fig. 7.6 are spheroids, so that the two transverse effective masses are equal and may be set equal to a transverse mass m_t^*, the longitudinal mass being represented by m_ℓ^*, as discussed previously in Eq. (6.40).

Example 7.1   If a maximum uncertainty in energy of the order of kT is to be allowed in order for the suitability of the band picture to be justified, what is the minimum mobility that is consistent with a band interpretation?

From the Heisenberg indeterminacy principle, we have

$$\Delta E \cdot \Delta t \geq \frac{\hbar}{2}$$

or

$$\Delta t \geq \frac{\hbar}{2kT}$$

Now we may take

$$\Delta t \approx \langle \tau \rangle$$

so that the smallest value of mobility that would be consistent is

$$\mu = \frac{e\hbar}{2m_e^* kT}$$

in view of Eq. (7.93). If we take $m_e^* = m$, this minimum value of mobility estimated in this way is about 20 cm²/V-sec at room temperature.

Example 7.2   In a cubic semiconductor crystal with spheroidal equal-energy surfaces, a mobility of 1000 cm²/V-sec is measured for electrons, for which the average scattering relaxation time is 10^{-13} sec. If the transverse effective mass is $0.5m$, what is the longitudinal effective mass?

If the measured mobility is determined from conductivity, then $\mu_{con} = 1000$ cm²/V-sec. From Eq. (7.109)

$$m_{con}^* = \frac{e\langle \tau_e \rangle}{\mu_{con}} = \frac{4.8 \times 10^{-10} \times 10^{-13}}{3 \times 10^2 \times 10^3}$$

$$= 1.6 \times 10^{-28} \text{ g}$$

$$= 0.18m$$

Now from Eq. (7.108),

$$\frac{1}{m_{con}^*} = \frac{1}{0.18m} = \frac{1}{3}\left(\frac{1}{m_\ell^*} + \frac{2}{0.5m}\right)$$

Solution gives

$$m_\ell^* = 0.079m$$

These equal-energy surfaces are pancake shaped.

METALS

In metals there are free electrons at the Fermi surface, and scattering by acoustic phonons is not necessarily elastic. The wave vector for the most energetic phonons is of the same order of magnitude as the wave vector at the Fermi surface, but the energy of the most energetic phonons is much less than the Fermi energy. If the energy of the most energetic phonons is written as $k\Theta_D$, in terms of the Debye temperature Θ_D, then large-angle elastic scattering by acoustic phonons is expected at higher temperatures such that $kT > k\Theta_D$, and small-angle inelastic scattering by acoustic phonons is expected at lower temperatures such that $kT < k\Theta_D$. This means that the relaxation-time approximation for electrical conductivity is appropriate for metals at temperatures above Θ_D, and again at sufficiently low temperatures that charged imperfection scattering dominates over acoustic phonon scattering. But it is not appropriate over the intermediate temperature range, nor of course at very low temperatures where *superconductivity* may become a possibility.

Where the relaxation-time approximation is applicable, Eq. (7.89) can be evaluated for a metal (or degenerate semiconductor), for which the Fermi level lies in the midst of an allowed energy band. The quantity $\partial f_0/\partial E$ is appreciable only over a narrow range of energies within about kT of the Fermi level. The integrals of Eq. (7.89) can be approximated to first order by

$$\int_0^{E_m} \tau(E) E^{3/2}\left(\frac{\partial f_0}{\partial E}\right) dE \approx -\tau(E_F) E_F^{3/2} \qquad (7.111)$$

considering $(\partial f_0/\partial E)$ to be essentially a delta function at $E = E_F$, and

$$\int_0^{E_m} E^{3/2}\left(\frac{\partial f_0}{\partial E}\right) dE = -E_F^{3/2} \qquad (7.112)$$

so that

$$j_x = \frac{e^2 \mathscr{E}_x n}{m^*} \tau(E_F) \qquad (7.113)$$

Although all the electrons take part in the conductivity process, as shown by the appearance of n in the expression for the current density, the mobility with which they contribute to the conductivity is that appropriate for an electron with energy equal to the Fermi energy. If it turns out in a specific case that $\tau(E)$, $N(E)$, or $\nabla_k E(\mathbf{k})$ is a rapidly varying function of E at E_F, then the inclusion of second-order terms in the integration of Eq. (7.89) may be desirable [see Eq. (7.131)].

In the temperature range in which the relaxation-time approximation is not valid, the electrical conductivity can be calculated from a variational solution of the Boltzmann equation, as referred to earlier. Such a calculation, the details of which we will not enter into here, shows that for $T \ll \Theta_D$,

$$\sigma(T)_{lo} \propto \left(\frac{\Theta_D}{T}\right)^5 \qquad (7.114)$$

This can be compared to the high-temperature range in which the relaxation-time approximation is valid in which

$$\sigma(T)_{hi} \propto \left(\frac{\Theta_D}{T}\right) \qquad (7.115)$$

since for acoustic phonon scattering in a metal or degenerate semiconductor, the relaxation time is inversely proportional to the average lattice energy, i.e., inversely proportional to kT, as we see in more detail in Chapter 8.

The total resistivity of a metal can be expressed, following Eq. (7.101) as

$$\varrho_{total} = \varrho_{lattice} + \varrho_{impurities} \qquad (7.116)$$

This expression is sometimes known as *Matthiessen's rule*. At low temperatures, scattering by lattice acoustic phonons becomes negligible compared to scattering by charged impurities. Purity of a metal can therefore be specified by quoting the ratio of the measured resistance at room temperature to that at liquid-helium temperature,

$$p = \frac{R_{300°K}}{R_{4°K}} \qquad (7.117)$$

For 99.999% pure Cu, for example, $p = 10^3$.

Considerable interest in metals is directed toward the effects of alloying on electrical conductivity. *Linde's rule* provides an empirical guide to the effects of alloying,

$$\varrho_I = a + bZ^2 \qquad (7.118)$$

where ϱ_I is the "residual resistivity" (the resistivity due to charged imper-

fections only) per atomic percent of solute, and Z is the valence difference between solute and solvent atoms. Linde's rule is suitable only for small concentrations of solute. The effects of alloying on the electrical conductivity may be attributed to a variety of effects, including, in addition to an increase in impurity scattering directly, changes in band structure, Fermi energy, density of states, effective mass, and phonon spectrum. For concentrated alloys, the empirical *Nordheim rule* provides a reasonable description, indicating that the residual resistivity is proportional to $c(1 - c)$ for a concentration c of solute which is not $\ll 1$, provided that no phase transitions occur that would change the band structure, and provided that transition elements are not involved as solute.

Electrical resistivity of metals is also increased by plastic deformation of the metal. Small effects are caused by dislocations introduced by the plastic deformation; larger effects are caused by vacancy and interstitial atoms produced (see Chapter 9).

At very low temperatures metals may become *superconducting*. The superconducting state is a new state of matter in which the normal scattering mechanisms that contribute to electrical resistivity are made ineffective. The superconducting state is the result of a mutual attraction between pairs of electrons, coupled by a phonon-interaction process involving the local polarization of the metal (similar to that described for a polaron in Section 6.6), which becomes greater than the mutual repulsion between the pair of electrons due to their charge. When such pairs of electrons become stable (one with $+\mathbf{k}$, and the other with $-\mathbf{k}$), a *new state* of the system is produced that is separated by a small energy gap from the normal free electrons. The magnitude of this superconducting energy gap is sufficient, compared to the energy of available phonons, to prevent the normal scattering processes that result in electrical resistivity. The highest temperature at which a known metallic alloy is superconducting is about 20°K to date, and this appears to be close to an upper limit for the phonon-interaction mechanism. Efforts are being made to see if materials can be made in which an excitonic interaction between electrons might replace a phonon interaction, and thus permit superconductivity to exist at much higher temperatures.

7.8   Thermal Conductivity Due to Electrons

Thermal conductivity in solids is due both to lattice vibrations, i.e., phonons, and to electrons. In insulators and semiconductors, in which the "free" carrier density is small, thermal conductivity is usually dominated

by phonons. In metals or degenerate semiconductors, electrons can make an appreciable contribution to the thermal conductivity. In this section we calculate from the Boltzmann equation the electronic thermal conductivity.

For the calculation of thermal conductivity, we must begin with Eq. (7.60) for ∇f, with the term involving ∇E_F included. With this addition, a combination of Eqs. (7.66) and (7.71), allowing for the simultaneous presence of an electric field and a thermal gradient, gives

$$\phi = \left\{ \tau e \mathscr{E} - \tau \left[(E - E_F) + T \frac{\partial E_F}{\partial T} \right] \nabla \ln T \right\} \cdot \mathbf{v} \tag{7.119}$$

$$j_x = \frac{e}{4\pi^3} \left\{ \int -\tau e \mathscr{E}_x \frac{\partial f_0}{\partial E} v_x{}^2 \, d\mathbf{k}' \right.$$
$$\left. + \int \tau \left(E - E_F + T \frac{\partial E_F}{\partial T} \right) \nabla \ln T \, v_x{}^2 \frac{\partial f_0}{\partial E} \, d\mathbf{k}' \right\} \tag{7.120}$$

replacing Eq. (7.83) for this case of a temperature gradient in the x direction, an associated electric field in the x direction, and in the relaxation-time approximation. In terms of the transport integrals K_n defined in Eq. (7.85),

$$j_x = K_1 \left[e^2 \mathscr{E}_x - eT \nabla \left(\frac{E_F}{T} \right) \right] - K_2 \left(\frac{e}{T} \right) \nabla T \tag{7.121}$$

since $\nabla(E_F/T) = -(E_F/T^2)\nabla T + (1/T)\nabla E_F$.

The heat current can similarly be written as

$$Q_x = \int f(\mathbf{k}') N(\mathbf{k}') E v_x \, d\mathbf{k}'$$
$$= K_2 \left[e \mathscr{E}_x - T \nabla \left(\frac{E_F}{T} \right) \right] - K_3 \left(\frac{1}{T} \right) \nabla T \tag{7.122}$$

The measurement of Q_x usually involves the requirement that $j_x = 0$, i.e.,

$$\mathscr{E}_x = \frac{1}{e} \left[\nabla E_F + \left(\frac{K_2}{K_1 T} - \frac{E_F}{T} \right) \nabla T \right] \tag{7.123}$$

which gives, for the heat current,

$$Q_x = \frac{K_2{}^2 - K_1 K_3}{K_1 T} \nabla T \tag{7.124}$$

The thermal conductivity $\varkappa$ is defined by

$$Q_x = -K \nabla T \tag{7.125}$$

so that

$$\varkappa = \frac{K_1 K_3 - K_2{}^2}{K_1 T} \tag{7.126}$$

The transport integrals K_n for spherical equal energy surfaces become

$$K_n = -\frac{4}{3m^*} \int \tau(E) \, N(E) \, E^n \frac{\partial f_0}{\partial E} \, dE \tag{7.127}$$

Under the first-order approximation for metals used to derive Eq. (7.113), it follows therefore that the thermal conductivity $\varkappa$ given in Eq. (7.126) is identically zero. Higher-order terms in the integration must be retained, therefore, to evaluate the thermal conductivity.

Such a second-order approximation can be accomplished by considering the integral

$$\int_0^\infty f(E) \frac{d\,F(E)}{dE} \, dE \tag{7.128}$$

where $F(E)$ is a function of E such that $F(0) = 0$. The procedure is to integrate Eq. (7.128) by parts, expand $F(E)$ in a Taylor series about E_F, place this expansion in the result of the integration by parts, and obtain

$$\int_0^\infty f(E) \frac{d\,F(E)}{dE} \, dE = F(E_F) + \frac{\pi^2}{6} (kT)^2 \frac{d^2\,F(E)}{dE^2} \bigg]_{E_F} \tag{7.129}$$

If we set

$$F(E) \equiv \int_0^E N_v{}^t(E) \, dE$$

so that Eq. (7.128) is the expression for the total electron density, we can derive an expression for the temperature dependence of the Fermi energy,

$$E_F(T) = E_F(0) \left[1 - \frac{\pi^2}{12} \left(\frac{kT}{E_F(0)} \right)^2 \right] \tag{7.130}$$

If we set

$$F(E) \equiv \int_0^E E \, N_v{}^t(E) \, dE$$

we have the means of evaluating Eq. (4.88) in Section 4.6 for the electronic contribution to the heat capacity.

Applying the expansion of Eq. (7.129) to the electrical conductivity for a metal gives, in place of Eq. (7.113),

$$\sigma = \sigma(E_F) + \frac{(\pi kT)^2}{6} \frac{\partial^2 \sigma(E)}{\partial E^2} \bigg]_{E_F} \tag{7.131}$$

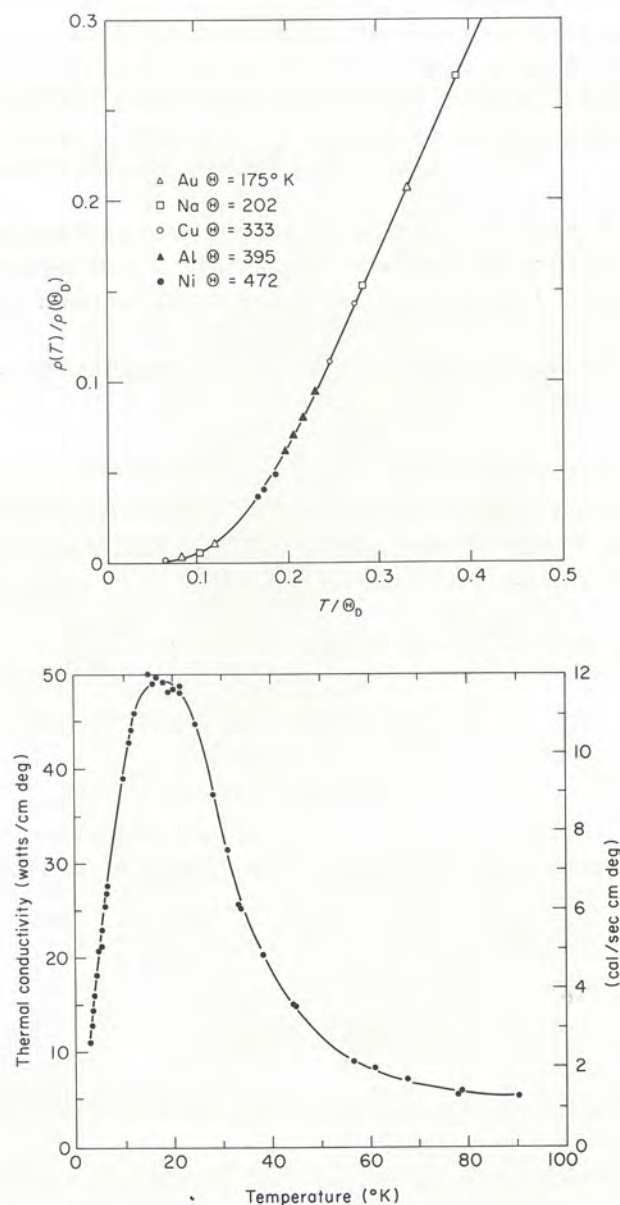Applying this expansion to the evaluation of the thermal conductivity gives

$$\varkappa = \frac{\pi^2 k^2 T}{3e^2} \sigma \tag{7.132}$$

If we write

$$\sigma = \frac{ne^2}{m^*} \tau_\sigma \tag{7.133}$$

and

$$\varkappa_e = \frac{n\pi^2 k^2 T}{3m^*} \tau_\varkappa \tag{7.134}$$

where the subscript e is added to $\varkappa$ to emphasize that only the electronic contribution is being considered, then the following correlation between electrical and thermal conductivity at high and low temperatures can be drawn.

At high temperatures the relaxation-time approximation holds and $\tau_\sigma = \tau_\varkappa$. The electrical conductivity σ is proportional to $1/T$ (density of scattering phonons is proportional to T) and the thermal conductivity is independent of T. The *Wiedemann–Franz ratio* is a meaningful constant quantity and is given by

$$\frac{\varkappa_e}{\sigma T} = \frac{\pi^2 k^2}{3e^2} = 0.245 \text{ erg-sec-ohm/degree}^2 \tag{7.135}$$

At low temperatures $\tau_\sigma \propto T^{-5}$ as stated in Eq. (7.114), and $\tau_\varkappa \propto T^{-3}$ (since in this range the total energy varies as T^4, the average energy per phonon $\propto T$, making the number of phonons $\propto T^3$). Thus the electrical conductivity $\propto T^{-5}$ and the thermal conductivity $\propto T^{-2}$. Over this temperature range, therefore, the Wiedemann–Franz ratio increases as T^2. Figure 7.7 shows the temperature dependence of electrical resistivity and thermal conductivity for copper.

For a semiconductor with spherical equal-energy surfaces and a relaxation time $\tau \propto E^{-s}$, the thermal conductivity can be calculated directly from

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predicts $\varrho \propto TG(\Theta_D/T)$, with

$$G(x) = x^{-4} \int_0^x \frac{y^5 \, dy}{(e^y - 1)(1 - e^{-y})}$$

which predicts $\varrho \propto T$ for $T > \Theta_D$, and $\varrho \propto T^5$ for $T < \Theta_D$. [Resistivity plot after J. Bardeen, *J. Appl. Phys.* **11**, 88 (1940); thermal conductivity after R. Berman and D. K. C. MacDonald, *Proc. Roy. Soc.* (*London*) **A209**, 368 (1951); **A211**, 122 (1952).]

Fig. 7.7 Temperature dependence of electrical resistivity and thermal conductivity for copper (Debye temperature = 333°K) and other metals with different Debye temperature. The electrical resistivity follows the semiempirical Grüneisen relation, which

Eq. (7.126). The result is

$$\varkappa_e = \frac{k^2 T}{e^2} \left(\tfrac{5}{2} - s \right) \sigma \tag{7.136}$$

The Wiedemann–Franz ratio is

$$\frac{\varkappa_e}{\sigma T} = \frac{k^2}{e^2} \left(\tfrac{5}{2} - s \right) \tag{7.137}$$

7.9   Thermoelectric Effect

If a temperature gradient is imposed on a material under conditions in which no current is drawn, a potential difference is detectable between the ends of the material. Physically the effect can be seen as the result of increased energy of electrons at the hot end of the material causing a diffusion of electrons toward the cold end; the charge imbalance caused by this diffusion sets up an electric field sufficient to make the net current flow zero. The *thermoelectric power* α_e is defined as the ratio between the electric field and the temperature gradient. From Eq. (7.123), setting $\nabla E_F = 0$ in the steady state,

$$\alpha_e = \frac{K_2 - E_F K_1}{e K_1 T} \tag{7.138}$$

For metals, the electronic thermoelectric power is given by

$$\alpha_e = \frac{\pi^2 k^2 T}{3e} \left. \frac{\partial \ln \sigma(E)}{\partial E} \right]_{E_F} \tag{7.139}$$

For an ideal metal this leads to

$$\alpha_e = \frac{\pi^2 k^2 T}{e E_F} \quad \text{for} \quad T > \Theta_D \tag{7.140}$$

and

$$\alpha_e = \frac{\pi^2 k^2 T}{3 e E_F} \quad \text{for} \quad T < \Theta_D \tag{7.141}$$

For spherical equal-energy surfaces in a semiconductor and $\tau \propto E^{-s}$, Eq. (7.138) leads directly to

$$\alpha_e = -\frac{k}{e} \left[\left(\tfrac{5}{2} - s \right) + \frac{(E_c - E_F)}{kT} \right] \tag{7.142}$$

where E_c is the energy of the bottom of the band in which the electrons are moving, and $E_c > E_F$. Comparison of Eqs. (7.142) and (7.140) shows that the thermoelectric power in a nondegenerate semiconductor is of the order of (E_F/kT) larger than that of a metal; for a metal at 300°K the thermoelectric power is of the order of $1\,\mu V/°K$, whereas for a typical semiconductor it is some 10^2–10^3 times larger.

If optical-mode scattering of carriers dominates, the relaxation-time approximation used here is no longer applicable. The thermoelectric power, however, can still be written in the form of Eq. (7.142), provided that the quantity $\left(\tfrac{5}{2} - s \right)$ is replaced by the quantity A, which is a function of temperature and is given in Fig. 7.8. The range of values for A over the normal range of temperatures does not differ widely from the value of 2 for acoustic-mode scattering.

At low temperatures another contribution to the measured thermoelectric power may arise in both metals and semiconductors in addition to that caused by the diffusion of free electrons. This additional contribution arises when the implicit assumption above, that the lattice vibrations are at equilibrium even with a temperature gradient on the material, is violated. When the interaction between phonons and electrons dominates over that between phonons and other phonons, then phonons moving in a thermal gradient tend to drag electrons along with them. This additional charge motion is called *phonon drag*, and the measured thermoelectric power is the sum of
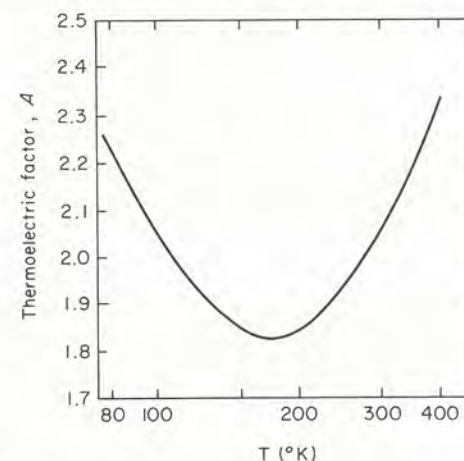

Fig. 7.8   The thermoelectric factor A in the expression $\alpha = \pm (k/e)[A + (E_c - E_F)/kT]$ for optical-mode scattering in a nondegenerate semiconductor. [After S. S. Devlin, *in* "Physics and Chemistry of II–VI Compounds," (M. Aven and J. Prener, eds.), Wiley, New York, 1967, p. 561.]
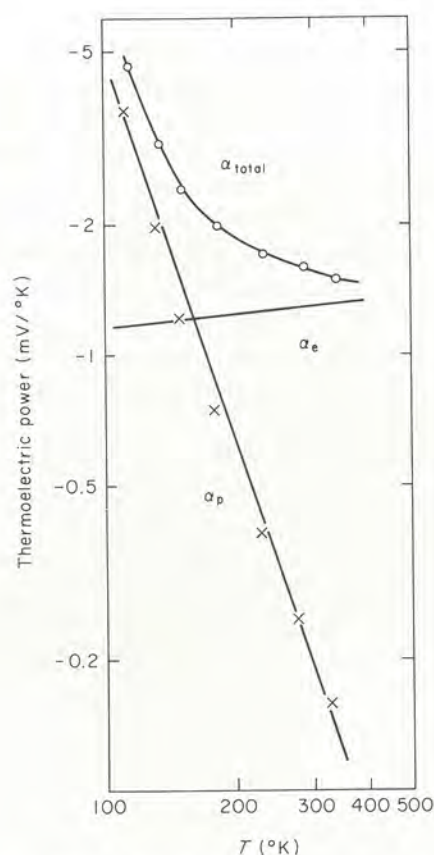
Fig. 7.9 Temperature dependence of the total measured thermoelectric power, the calculated electronic contribution to the thermoelectric power, and the phonon-drag contribution obtained by subtraction, for 10^2 Ω-cm n-type silicon. [After J. G. Harper, H. E. Matthews and R. H. Bube, *J. Appl. Phys.* **41**, 765 (1970).]

the diffusion contribution and the phonon-drag contribution. Figure 7.9 shows the temperature dependence of electron-diffusion and phonon-drag contributions to the total measured thermoelectric power for n-type silicon.

7.10 Summary

The utility of wave packets to describe the transport of particles in a wave mechanical framework rests on the fact that classical laws of motion can be applied to the wave packet as a pseudoparticle with a position given

by the expectation value of x for the packet and acted on by a force given by the expectation value of the external force. A wave packet constructed of Bloch waves corresponding to wave vectors k' in the vicinity of k has a velocity given by the group velocity $v = \hbar^{-1} \nabla_k E(k)$.

Steady-state transport properties of metals and semiconductors, such as electrical and thermal conductivity, are derived in terms of a departure from and a return to the equilibrium distribution of state occupancy. The Boltzmann equation is the key to this analysis, and the form of the relaxation of the perturbation from equilibrium back to the equilibrium state through a scattering process determines the type of solution. In those cases where scattering involves a change in energy of the carrier much less than its thermal energy, the relaxation can be described in terms of a simple relaxation-time approximation. In those cases where larger changes in energy are involved in scattering, a more general solution of the Boltzmann equation via a variational approach is required.

In this chapter we have been concerned only with scattering by acoustic-mode lattice vibrations or by charged impurities. In the following chapter we consider the actual calculation of the scattering probability for these two processes, as well as for others. Here we have seen that in semi-conductors, both of these processes may be adequately represented by the relaxation-time approximation. In metals, on the other hand, acoustic-mode scattering becomes inelastic at low temperatures and can no longer be adequately described in the relaxation-time approximation. This means that in metals the properties of electrical and thermal conductivity can be described in terms of a single relaxation time that is proportional to T^{-1} at high temperatures, but that at low temperatures rather more complicated behavior is encountered in which the electrical conductivity varies as T^{-5} while thermal conductivity varies as T^{-2}. The constancy of the Wiedemann–Franz ratio (the ratio of thermal conductivity due to electrons to the product of electrical conductivity and temperature) holds only in the higher temperature range.

If a temperature gradient is imposed on a material, an electric field results. The ratio between the electric field and the thermal gradient is called the thermoelectric power. Contributions to the thermoelectric power arise both from the diffusion of electrons in the temperature gradient and, at low temperatures, from the interaction between phonons moving in the temperature gradient and free electrons. In general the thermoelectric power is several orders of magnitude larger in semiconductors than in metals. This results from the fact that only a small fraction (about kT/E_F) of the free electrons in a metal are affected by the presence of a thermal gradient,

a condition that is also shown by the effective relaxation time for a metal being to first order just the relaxation time corresponding to electrons at the Fermi energy.

Problems

7.1 If the maximum value of a Gaussian wave packet is 10^2 times the width of the packet at $t = 0$, how far will the wave packet travel before the maximum value is equal to the width for a free electron?

7.2 The mobilities and effective masses of carriers in GaAs at room temperature are typically as follows:

	Mobility, cm²/V-sec	Effective-mass ratio
Electrons	7000	0.07
Holes	300	0.5

Calculate (a) the relaxation time for electrons and for holes, (b) the mean free path for electrons and holes, (c) the drift path length in an electric field of 100 V/cm in one relaxation time, (d) the electrical conductivity for a sample with 10^{14} cm^{-3} free electrons and 2.3×10^{15} cm^{-3} free holes.

7.3 If scattering relaxation times for electrons and holes in a semiconductor were about equal, would you in general expect electrons or holes to have the higher mobility? Why? (How do the widths of conduction and valence bands usually compare?)

7.4 In a crystal with scalar effective mass of $0.2m$ for electrons, the mobility is measured at 30°K, where it is dominated by impurity scattering, to be 20 cm²/V-sec, and at 600°K, where it is dominated by lattice scattering, to be 70 cm²/V-sec. What is the relaxation time for scattering at 200°K?

7.5 In a crystal in which scattering by both lattice vibrations and by charged imperfections is present, the following measurements were made of mobility versus T:

Mobility, cm²/V-sec	T, °K
500	100
125	400

What is the measured mobility expected for 50°K?

7.6 Suppose that the relaxation time for a particular scattering process is directly proportional to the electron velocity. Calculate the temperature dependence of the mobility for a nondegenerate semiconductor.

7.7 The measured thermal conductivity of germanium at 300°K is 0.63 W/°K, in a range where acoustic phonon scattering dominates.
(a) What fraction of this thermal conductivity is caused by free electrons if the free-electron density is 10^{17} cm^{-3} and the electron mobility is 4×10^3 cm²/V-sec?
(b) What must the concentration of free electrons in germanium at 300°K be in order for the electronic contribution to the thermal conductivity to be equal to the lattice contribution?
(c) The thermoelectric power corresponding to (a) is measured to be 0.46 mV/°K. How far below the conduction-band edge does the Fermi level lie?