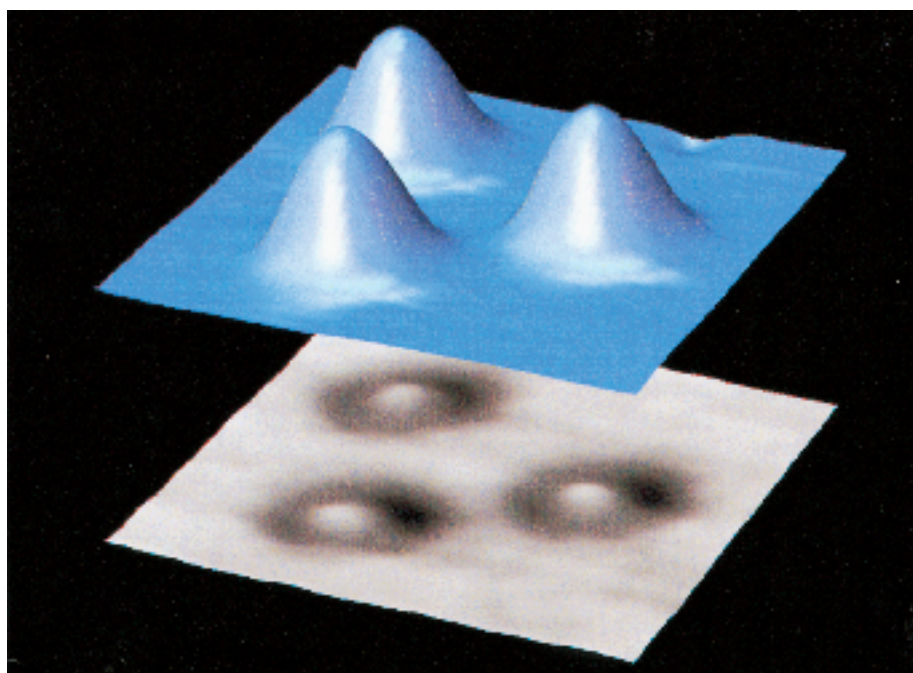**CHAPTER** **27**

The Microscopic Theory of Electrical Conduction

Simultaneously acquired topographic (top) and spectroscopic (bottom) images of three gadolinium atoms on top of a super-conducting niobium surface. In the region near the gadolinium atoms the magnetic properties of these individual atoms break up Cooper electron pairs, thereby modify-ing the superconductivity of the niobium.

In earlier chapters we used Ohm's law to find the currents in various circuits while making no attempt to relate Ohm's law to the properties of metals. Here we introduce a microscopic model of electrical conduction to relate the resistivity of a metal to the properties of electrons and the lattice ions of the metal. This model is similar to the model of a gas that we discussed in Chapter 18 to relate the pressure exerted by a gas on the walls of its container to the average energy of the gas molecules, which in turn we could relate to the absolute temperature of the gas.

The first microscopic model of electric conduction was proposed by P. Drude in 1900 and developed by Hendrik A. Lorentz about 1909. This model successfully predicts Ohm's law and relates the resistivity of conductors to the mean speed v_{av} and the mean free path λ of the free electrons within the conductor. However, when v_{av} and λ are interpreted classically, there is a disagreement between the calculated and measured values of the resistivity, and a similar disagreement between the predicted and observed temperature dependence. Thus, the classical theory fails to adequately describe the resistivity of metals. Furthermore, the classical theory says nothing about the most striking property of solids, namely that some materials are conductors, others are insulators, and still others are semiconductors, materials whose resistivity falls between that of conductors and insulators.
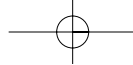
When v_{av} and λ are interpreted using quantum theory, the magnitude and temperature dependence of the resistivity are correctly predicted. In addition, quantum theory allows us to determine if a material will be a conductor, insulator, or semiconductor.

<table>
<tr><td>**27-1**</td><td># A Microscopic Picture
of Conduction</td></tr>
</table>

We consider a metal as a regular three-dimensional lattice of ions filling some volume V and containing a large number N of electrons that are free to move throughout the whole metal. Experimentally the number of free electrons in a metal is about 1 to 4 electrons per atom. In the absence of an electric field, the free electrons move about the metal randomly, much the way gas molecules move about in a container. We will often refer to these free electrons in a metal as an electron gas.

The current in a conducting wire segment is proportional to the voltage drop across the segment:

$$I = \frac{V}{R}$$

or

$$V = IR$$

The resistance R is proportional to the length L of the wire segment and inversely proportional to the cross-sectional area A:

$$R = \rho\frac{L}{A}$$

where ρ is the resistivity. According to Ohm's law, the resistance of a given wire segment is independent of the current in the segment and therefore independent of the voltage drop across the segment. For a uniform electric field E, the voltage across a segment of length L is $V = EL$. Then Ohm's law implies that the resistance, and therefore the resistivity, is independent of the applied electric field E.

Substituting $\rho L/A$ for R, and EL for V, we can write the current in terms of the electric field E and the resistivity. We have

$$I = \frac{V}{R} = \frac{EL}{\rho L/A} = \frac{1}{\rho}EA \qquad\qquad \text{27-1}$$

The current in a wire is related by Equation 26-3 to the number of electrons per unit volume $n_e = N/V$, the drift velocity v_d, the magnitude of the charge of an electron $q = e$, and the cross-sectional area A:

$$I = nqAv_d = n_e eAv_d \qquad\qquad \text{27-2}$$
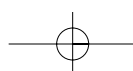
Combining Equations 27-1 and 27-2 for the current I gives

$$n_e eAv_d = \frac{1}{\rho}EA$$

or

$$\rho = \frac{E}{n_e ev_d} \qquad\qquad \text{27-3}$$

If Ohm's law holds, ρ must be independent of E, so according to Equation 27-3, the drift velocity v_d must be proportional to E.

In the presence of an electric field, a free electron experiences a force of magnitude eE. If this were the only force acting, the electron would have an acceleration eE/m_e and its velocity would steadily increase. However, Equation 27-3 implies a steady-state situation with a constant drift velocity that is proportional to the field E. In the microscopic model, it is assumed that a free electron is accelerated for a short time and then makes a collision with a lattice ion. The velocity of the electron after the collision is completely unrelated to the drift velocity. The justification for this assumption is that the drift velocity is very small compared with the random thermal velocity.

Let τ be the average time since the last collision for an electron picked at random. Since the acceleration of each electron is eE/m_e, the drift velocity of the electrons is

$$v_d = \frac{eE}{m_e}\tau \qquad\qquad 27\text{-}4$$

Using this result in Equation 27-3, we obtain

$$\rho = \frac{E}{n_e e(eE\tau/m_e)} = \frac{m_e}{n_e e^2 \tau} \qquad\qquad 27\text{-}5$$

The time τ, called the **collision time**, is also the average time between collisions.* The average distance the electron travels between collisions is $v_{av}\tau$, which is called the **mean free path** λ:

$$\lambda = v_{av}\tau \qquad\qquad 27\text{-}6$$

In terms of the mean free path and the mean speed, the resistivity is

$$\rho = \frac{m_e v_{av}}{n_e e^2 \lambda} \qquad\qquad 27\text{-}7$$

Resistivity in terms of v_{av} and λ

According to Ohm's law, the resistivity is independent of the electric field E. Since m_e, n_e, and e^2 are constants, the only quantities that could possibly depend on E are the mean speed v_{av} and the mean free path λ. Let us examine these quantities to see if they can possibly depend on the applied field E.

Classical Interpretation of λ and v_{av}

Classically, at $T = 0$ all the free electrons in a conductor should have zero kinetic energy. As the conductor is heated, the lattice ions acquire an average kinetic energy of $\frac{3}{2}kT$, which is imparted to the electron gas by the collisions between the electrons and the ions. (This is a result of the equipartition theorem studied in Chapters 18 and 19.) The electron gas would then have a Maxwell–Boltzmann distribution just like a gas of molecules. In equilibrium, the electrons would be expected to have a mean kinetic energy of $\frac{3}{2}kT$, which at ordinary temperatures ($\sim$300 K) is about 0.04 eV. At $T = 300$ K, their root mean square (rms) speed,† which is slightly greater than the mean speed, is

$$v_{av} \approx v_{rms} = \sqrt{\frac{3kT}{m_e}} = \sqrt{\frac{3(1.38 \times 10^{-23}\text{J/K})(300\text{ K})}{9.11 \times 10^{-31}\text{ kg}}}$$
$$= 1.17 \times 10^5 \text{ m/s} \qquad\qquad 27\text{-}8$$

---

* It is tempting but incorrect to think that if τ is the average time between collisions, the average time since its last collision is $\frac{1}{2}\tau$ rather than τ. If you find this confusing, you may take comfort in the fact that Drude used the incorrect result $\frac{1}{2}\tau$ in his original work.

† See Equation 18-23.
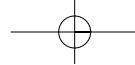
Note that this is about three billion times greater than the typical drift speed of 3.5×10^{-5} m/s calculated in Example 26-1. The very small drift velocity caused by the electric field therefore has essentially no effect on the very large mean speed of the electrons, so v_{av} in Equation 27-7 cannot depend on the electric field E.

The mean free path is related classically to the size of the lattice ions in the conductor and to the number of ions per unit volume. Consider one electron moving with speed v through a region of stationary ions, assumed to be hard spheres (Figure 27-1). The size of the electron is assumed to be negligible. The electron will collide with an ion if it comes within a distance r from the center of the ion, where r is the radius of the ion. In some time t_1, the electron moves a distance vt_1. If there is an ion whose center is in the cylindrical volume $\pi r^2 vt_1$, the electron will collide with it. The electron will then change directions and collide with another ion in time t_2 if the center of the ion is in the volume $\pi r^2 vt_2$. Thus, in the total time $t = t_1 + t_2 + \cdots$, the electron will collide with the number of ions whose centers are in the volume $\pi r^2 vt$. The number of ions in this volume is $n_{ion}\pi r^2 vt$, where n_{ion} is the number of ions per unit volume. The total path length divided by the number of collisions is the mean free path:

$$\lambda = \frac{vt}{n_{ion}\pi r^2 vt} = \frac{1}{n_{ion}\pi r^2} = \frac{1}{n_{ion}A} \qquad \text{27-9}$$

where $A = \pi r^2$ is the cross-sectional area of a lattice ion.

Neither n_{ion} nor r depends on the electric field E, so λ also does not depend on E. Thus, according to the classical interpretation of v_{av} and λ, neither depend on E, so the resistivity ρ does not depend on E, in accordance with Ohm's law. However, the classical theory gives an incorrect temperature dependence for the resistivity. Since λ depends only on the number density of lattice ions and their radius, the only quantity in Equation 27-7 that depends on temperature in the classical theory is v_{av}, which is proportional to $\sqrt{T}$. But experimentally, ρ varies linearly with temperature. Furthermore, when ρ is calculated at $T = 300$ K using the Maxwell–Boltzmann distribution for v_{av} and Equation 27-9 for λ, the numerical result is about six times greater than the measured value.

The classical theory of conduction fails because electrons are not classical particles. The wave nature of the electrons must be considered. Because of the wave properties of electrons and the exclusion principle (to be discussed below), the energy distribution of the free electrons in a metal is not even approximately given by the Maxwell–Boltzmann distribution. Furthermore, the collision of an electron with a lattice ion is not similar to the collision of a baseball with a tree. Instead, it involves the scattering of electron waves by the lattice. To understand the quantum theory of conduction, we need a qualitative understanding of the energy distribution of free electrons in a metal. This will also help us understand the origin of contact potentials between two dissimilar metals in contact, and the contribution of free electrons to the heat capacity of metals.
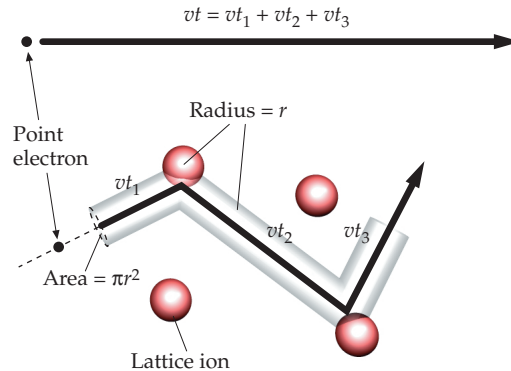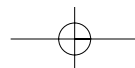

Figure 27-1 Model of an electron moving through the lattice ions of a conductor. The electron, which is considered to be a point, collides with an ion if it comes within a distance r of the center of the ion, where r is the radius of the ion. If the electron speed is v, it collides in time t with all the ions whose centers are in the volume $\pi r^2 vt$.

27-2   The Fermi Electron Gas

We have used the term *electron gas* to describe the free electrons in a metal. Whereas the molecules in an ordinary gas such as air obey the classical Maxwell–Boltzmann energy distribution, the free electrons in a metal do not. Instead they obey a quantum energy distribution called the Fermi–Dirac dis-

tribution. Because the behavior of this electron gas is so different from a gas of molecules, the electron gas is often called a **Fermi electron gas**. The main features of a Fermi electron gas can be understood by considering an electron in a metal to be a particle in a box, a problem whose one-dimensional version we studied extensively in Chapter 17. We discuss the main features of a Fermi electron gas semiquantitatively in this section and leave the details of the Fermi–Dirac distribution to Section 27-6.

Energy Quantization in a Box

In Chapter 17 we found that the wavelength associated with an electron of momentum p is given by the de Broglie relation:

$$\lambda = \frac{h}{p} \tag{27-10}$$

where h is Planck's constant. When a particle is confined to a finite region of space such as a box, only certain wavelengths λ_n given by standing-wave conditions are allowed. For a one-dimensional box of length L, the standing-wave condition is

$$n\frac{\lambda_n}{2} = L \tag{27-11}$$

This results in the quantization of energy:

$$E_n = \frac{p_n^2}{2m} = \frac{(h/\lambda_n)^2}{2m} = \frac{h^2}{2m}\frac{1}{\lambda_n^2} = \frac{h^2}{2m}\frac{1}{(2L/n)^2}$$

or

$$E_n = n^2\frac{h^2}{8mL^2} \tag{27-12}$$

The wave function for the nth state is given by

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L} \tag{27-13}$$

The quantum number n characterizes the wave function for a particular state and the energy of that state. In three-dimensional problems, three quantum numbers arise, one associated with each dimension.

The Pauli Exclusion Principle

The distribution of electrons among the possible energy states is dominated by the exclusion principle, which was first enunciated by Wolfgang Pauli in 1925 to explain the electronic structure of atoms:

> No two electrons in an atom can be in the same quantum state; that is, they cannot have the same set of values for their quantum numbers.

Pauli exclusion principle

The exclusion principles applies to all "spin one-half" particles, which include electrons, protons, and neutrons.* These particles have a *spin* quantum number m_s which has two possible values, $+\frac{1}{2}$ and $-\frac{1}{2}$. The quantum state of

---

* Intrinsic spin is discussed briefly in Chapter 10, Section 5.

optional

a particle is characterized by the spin quantum number m_s, plus the quantum numbers associated with the spatial part of the wave function. Because the spin quantum numbers have just two possible values, the exclusion principle can be stated in terms of the spatial states:

> There can be at most two electrons with the same set of values for their *spatial* quantum numbers.

Exclusion principle in terms of spatial states

When there are more than two electrons in a system such as an atom or metal, only two can be in the lowest energy state. The third and fourth must go into the second-lowest state, and so on.

Particles that obey the exclusion principle are called **fermions**. Other particles such as α particles, deuterons, photons, and mesons do not obey the exclusion principle. These particles are called **bosons** and have either zero intrinsic spin, or integral spin quantum numbers.

Example 27-1

Compare the total energy of the ground state of 5 identical bosons of mass m in a one-dimensional box with that of 5 identical fermions of mass m in the same box.

Picture the Problem The ground state is the lowest possible energy state. The energy levels in a one-dimensional box are given by $E_n = n^2 E_1$, where $E_1 = (h^2/8mL^2)$. The lowest energy for 5 bosons occurs when all the bosons are in the state $n = 1$ as shown in Figure 27-2a. For fermions, the lowest state occurs with two in state $n = 1$, two in $n = 2$, and one in $n = 3$ as shown in Figure 27-2b.
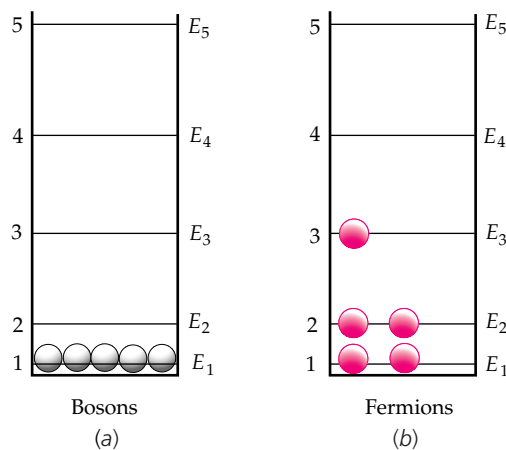

Figure 27-2

1. The energy of 5 bosons in the state $n = 1$ is:

$$E = 5E_1$$

2. The energy of two fermions in the state $n = 1$, two in state $n = 2$, and one in state $n = 3$ is:

$$E = 2E_1 + 2E_2 + 1E_3 = 2E_1 + 2(2)^2 E_1 + 1(3)^2 E_1$$
$$= 2E_1 + 8E_1 + 9E_1 = 19E_1$$

Remark We see that the exclusion principle has a large effect on the energy of a multiple-particle system.

The Fermi Energy

When there are many electrons in a box, at $T = 0$ the electrons will occupy the lowest energy states consistent with the exclusion principle. If we have N electrons, we can put two electrons in the lowest energy level, two in the next lowest, and so on. The N electrons thus fill up the lowest $N/2$ energy levels

(Figure 27-3). The energy of the last filled (or half-filled) level at $T = 0$ is called the **Fermi energy** E_F. If the electrons moved in a one-dimensional box, the Fermi energy would be given by Equation 27-12 with $n = N/2$:

$$E_F = \left(\frac{N}{2}\right)^2 \frac{h^2}{8m_e L^2} = \frac{h^2}{32m_e}\left(\frac{N}{L}\right)^2$$

27-14

Fermi energy at T = 0 in one dimension

In a one-dimensional box, the Fermi energy depends on the number of free electrons per unit length of the box.

> **Exercise** Suppose there is an ion, and therefore a free electron, every 0.1 nm in a one-dimensional box. Calculate the Fermi energy. (*Hint:* Write Equation 27-14 as
>
> $$E_F = \frac{(hc)^2}{32m_e c^2}\left(\frac{N}{L}\right)^2 = \frac{(1240 \text{ eV·nm})^2}{32(0.511 \text{ MeV})}\left(\frac{N}{L}\right)^2$$

(*Answer* $E_F = 9.4$ eV)

In our model of conduction, the free electrons move in a *three-dimensional* box of volume V. The derivation of the Fermi energy in three dimensions is somewhat difficult, so we will just give the result. In three dimensions, the Fermi energy at $T = 0$ is given by

$$E_F = \frac{h^2}{8m_e}\left(\frac{3N}{\pi V}\right)^{2/3}$$

27-15*a*

Fermi energy at T = 0 in three dimensions

The Fermi energy depends on the number of electrons per unit volume (the number density) N/V. Substituting numerical values for the constants gives

$$E_F = (0.365 \text{ eV·nm}^2)\left(\frac{N}{V}\right)^{2/3}$$

27-15*b*

Fermi energy at T = 0 in three dimensions

Table 27-1 lists the free-electron number densities and Fermi energies at $T = 0$ for several metals.
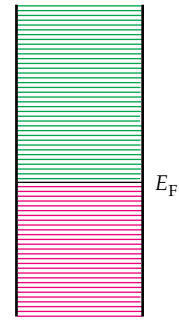

Figure 27-3 At $T = 0$ the electrons fill up the allowed energy states to the Fermi energy E_F. The levels are so closely spaced they can be assumed to be continuous.

Table 27-1

Free-Electron Number Densities and Fermi Energies at $T = 0$ for Selected Elements

	Element	N/V, Electrons/cm^3	E_F, eV
Al	Aluminum	18.1×10^{22}	11.7
Ag	Silver	5.86×10^{22}	5.50
Au	Gold	5.90×10^{22}	5.53
Cu	Copper	8.47×10^{22}	7.04
Fe	Iron	17.0×10^{22}	11.2
K	Potassium	1.4×10^{22}	2.11
Li	Lithium	4.70×10^{22}	4.75
Mg	Magnesium	8.60×10^{22}	7.11
Mn	Manganese	16.5×10^{22}	11.0
Na	Sodium	2.65×10^{22}	3.24
Sn	Tin	14.8×10^{22}	10.2
Zn	Zinc	13.2×10^{22}	9.46

optional

Example **27-2**

The number density for electrons in copper was calculated in Example 26-1 and found to be $8.47 \times 10^{22}/\text{cm}^3$. Calculate the Fermi energy at $T = 0$ for copper.

1. The Fermi energy is given by Equation 27-15:

$$E_F = (0.365 \text{ eV} \cdot \text{nm}^2) \left(\frac{N}{V}\right)^{2/3}$$

2. Substitute the given number density for copper:

$$E_F = (0.365 \text{ eV} \cdot \text{nm}^2)(84.7/\text{nm}^3)^{2/3}$$

$$= 7.04 \text{ eV}$$

Remark Note that the Fermi energy is much greater than kT at ordinary temperatures. For example, at $T = 300$ K, kT is only about 0.026 eV.

Exercise Use Equation 27-15b to calculate the Fermi energy at $T = 0$ for gold, which has a number density of 5.90×10^{22}. (*Answer* 5.53 eV)

The average energy of a free electron can be calculated from the complete energy distribution of the electrons, which is discussed in Section 27-6. At $T = 0$, the average energy turns out to be

$$E_{av} = \tfrac{3}{5}E_F \qquad\qquad \text{27-16}$$

Average energy of electrons in a Fermi gas at T = 0

For copper, E_{av} is about 4 eV. This average energy is huge compared with typical thermal energies of about $kT \approx 0.026$ eV at a normal temperature of $T = 300$ K. This result is very different from the classical, Maxwell–Boltzmann distribution result that at $T = 0$, $E = 0$, and that at some temperature T, E is of the order of kT.

The Fermi Factor at *T* = 0

The probability of an energy state being occupied is called the **Fermi factor**, $f(E)$. At $T = 0$ all the states below E_F are filled, whereas all those above this energy are empty, as shown in Figure 27-4. Thus, at $T = 0$ the Fermi factor is simply

$$f(E) = 1, \qquad E < E_F$$
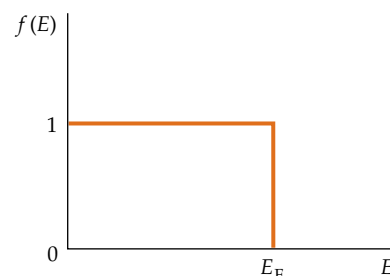$$f(E) = 0, \qquad E > E_F \qquad\qquad \text{27-17}$$

Figure 27-4 Fermi factor versus energy at $T = 0$.

The Fermi Factor for *T* > 0

At temperatures greater than $T = 0$, some electrons will occupy higher energy states because of thermal energy gained during collisions with the lattice. However, an electron cannot move to a higher or lower state unless it is unoccupied. Since the kinetic energy of the lattice ions is of the order of kT, electrons cannot gain much more energy than kT in collisions with the lattice ions. Therefore, only those electrons with energies within about kT of the Fermi energy can gain energy as the temperature is increased. At 300 K, kT is only 0.026 eV, so the exclusion principle prevents all but a very few electrons near the top of the energy distribution from gaining energy through random

collisions with the lattice ions. Figure 27-5 shows the Fermi factor for some temperature T. Since for $T > 0$ there is no distinct energy that separates filled from unfilled levels, the definition of the Fermi energy must be slightly modified. At temperature T, the Fermi energy is defined to be that energy for which the probability of being occupied is $\frac{1}{2}$. For all but extremely high temperatures, the difference between the Fermi energy at temperature T and that at $T = 0$ is very small.

The **Fermi temperature** T_F is defined by

$$kT_F = E_F \qquad \text{27-18}$$

For temperatures much lower than the Fermi temperature, the average energy of the lattice ions will be much less than the Fermi energy, and the electron energy distribution will not differ greatly from that at $T = 0$.
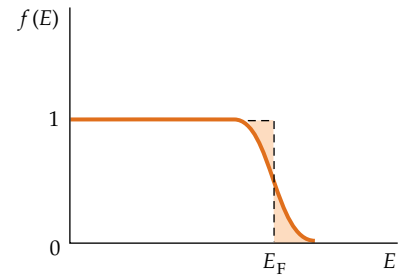

Figure 27-5 The Fermi factor for some temperature T. Some electrons with energies near the Fermi energy are excited, as indicated by the shaded regions. The Fermi energy is that value of E for which $f(E) = \frac{1}{2}$.

Example 27-3

Find the Fermi temperature for copper.

Use $E_F = 7.04$ eV and $k = 8.62 \times 10^{-5}$ eV/K in Equation 27-18:

$$T_F = \frac{E_F}{k} = \frac{7.04 \text{ eV}}{8.62 \times 10^{-5} \text{ eV/K}} = 81{,}700 \text{ K}$$

Remark We can see from this example that the Fermi temperature of copper is much greater than any temperature T for which copper remains a solid.

Because an electric field in a conductor accelerates all of the conduction electrons together, the exclusion principle does not prevent the free electrons in filled states from participating in conduction. Figure 27-6 shows the Fermi factor in one dimension versus *velocity* for an ordinary temperature. The factor is approximately 1 for speeds v_x in the range $-u_F < v_x < u_F$, where the Fermi speed u_F is related to the Fermi energy by $E_F = \frac{1}{2}mu_F^2$. Then

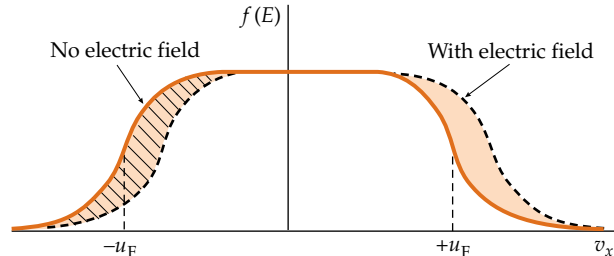$$u_F = \sqrt{\frac{2E_F}{m_e}} \qquad \text{27-19}$$

Figure 27-6 Fermi factor versus velocity in one dimension with no electric field (solid) and with an electric field in the $+x$ direction (dashed). The difference is greatly exaggerated.


Example 27-4

Calculate the Fermi speed for copper.

Use Equation 27-19 with $E_F = 7.04$ eV:

$$u_F = \sqrt{\frac{2(7.04 \text{ eV})}{9.11 \times 10^{-31} \text{ kg}}\left(\frac{1.6 \times 10^{-19} \text{ J}}{1 \text{ eV}}\right)} = 1.57 \times 10^6 \text{ m/s}$$

The dashed curve in Figure 27-6 shows the Fermi factor after the electric field has been acting for some time t. Although all of the electrons have been shifted to higher velocities, the net effect is equivalent to shifting only the electrons near the Fermi energy.

optional
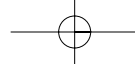
Contact Potential

When two different metals are placed in contact, a potential difference $V_{contact}$ called the **contact potential** develops between them. The contact potential depends on the work functions of the two metals, ϕ_1 and ϕ_2 (we encountered work functions when the photoelectric effect was introduced in Chapter 17), and the Fermi energies of the two metals. When the metals are in contact, the total energy of the system is lowered if electrons near the boundary move from the metal with the higher Fermi energy into the metal with the lower Fermi energy until the Fermi energies of the two metals are the same, as shown in Figure 27-7. When equilibrium is established, the metal with the lower initial Fermi energy is negatively charged and the other is positively charged, so that between them there is a potential difference $V_{contact}$ given by

$$V_{contact} = \frac{\phi_1 - \phi_2}{e} \qquad\qquad 27\text{-}20$$

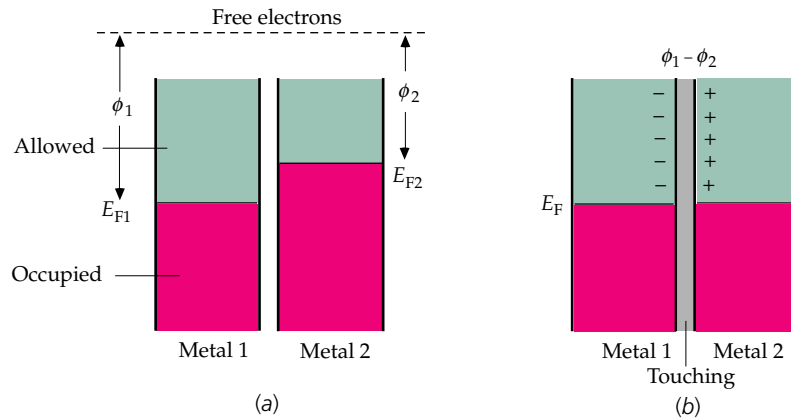Table 27-2 lists the work functions for several metals.

Figure 27-7 (a) Energy levels for two different metals with different Fermi energies and work functions. (b) When the metals are in contact, electrons flow from the metal that initially has the higher Fermi energy to the metal that initially has the lower Fermi energy until the Fermi energies are equal.

Table 27-2

Work Functions for Some Metals

	Metal	ϕ, eV
Ag	Silver	4.7
Au	Gold	4.8
Ca	Calcium	3.2
Cu	Copper	4.1
K	Potassium	2.1
Mn	Manganese	3.8
Na	Sodium	2.3
Ni	Nickel	5.2

Example 27-5

The threshold wavelength for the photoelectric effect is 271 nm for tungsten and 262 nm for silver. What is the contact potential developed when silver and tungsten are placed in contact?

Picture the Problem The contact potential is proportional to the difference in the work functions for the two metals. The work function ϕ can be found from the given threshold wavelengths using $\phi = hc/\lambda_t$ (Equation 17-4).

1. The contact potential is given by Equation 27-20:

$$V_{contact} = \frac{\phi_1 - \phi_2}{e}$$

2. The work function is related to the threshold wavelength:

$$\phi = \frac{hc}{\lambda_t}$$

3. Substitute $\lambda_t = 271$ nm for tungsten:

$$\phi_W = \frac{hc}{\lambda_t} = \frac{1240 \text{ eV·nm}}{271 \text{ nm}} = 4.58 \text{ eV}$$

4. Substitute $\lambda_t = 262$ nm for silver:

$$\phi_{Ag} = \frac{1240 \text{ eV·nm}}{262 \text{ nm}} = 4.73 \text{ eV}$$

5. The contact potential is thus:

$$V_{contact} = \frac{\phi_{Ag} - \phi_W}{e} = 4.73 \text{ V} - 4.58 \text{ V}$$

$$= 0.15 \text{ V}$$
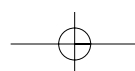
Heat Capacity Due to Electrons in a Metal

The quantum-mechanical modification of the electron distribution in metals allows us to understand why the contribution of the electron gas to the heat capacity of a metal is much less that of the ions. According to the classical equipartition theorem, the energy of the lattice ions in n moles of a solid is $3nRT$, and thus the molar heat capacity is $C' = 3R$, where R is the universal gas constant (see Section 19-7). In a metal there is a free electron gas containing a number of electrons approximately equal to the number of lattice ions. If these electrons obey the classical equipartition theorem, they should have an energy of $\frac{3}{2}nRT$ and contribute an additional $\frac{3}{2}R$ to the molar heat capacity. But measured heat capacities of metals are just slightly greater than those of insulators. We can understand this because at some temperature T, only those electrons with energies near the Fermi energy can be excited by random collisions with the lattice ions. The number of these electrons is of the order of $(kT/E_F)N$, where N is the total number of electrons. The energy of these electrons is increased from that at $T = 0$ by an amount that is of the order of kT. So the total increase in thermal energy is of the order of $(kT/E_F)N \times kT$. We can thus express the energy of N electrons at temperature T as

$$E = NE_{av}(0) + \alpha N \frac{kT}{E_F} kT \qquad\qquad 27\text{-}21$$

where α is some constant that we expect to be of the order of 1 if our reasoning is correct. The calculation of α is quite difficult. The result is $\alpha = \pi^2/4$. Using this result and writing E_F in terms of the Fermi temperature, $E_F = kT_F$, we obtain the following for the contribution of the electron gas to the heat capacity at constant volume:

$$C_v = \frac{dU}{dT} = 2\alpha Nk \frac{kT}{E_F} = \frac{\pi^2}{2} nR \frac{T}{T_F}$$

where we have written Nk in terms of the gas constant R ($Nk = nR$). The molar heat capacity at constant volume is then

$$C'_v = \frac{\pi^2}{2} R \frac{T}{T_F} \qquad\qquad 27\text{-}22$$

We can see that because of the large value of T_F, the contribution of the electron gas is a small fraction of R at ordinary temperatures. Because $T_F = 81{,}700$ K for copper, the molar heat capacity of the electron gas at $T = 300$ K is

$$C'_v = \frac{\pi^2}{2} \left(\frac{300 \text{ K}}{81{,}700} \right) R \approx 0.02R$$

which is in good agreement with experiment.

27-3   Quantum Theory of Electrical Conduction

We can use Equation 27-7 for the resistivity if we use the Fermi speed u_F in place of v_{av}:

$$\rho = \frac{m_e u_F}{ne^2 \lambda} \qquad\qquad 27\text{-}23$$

We now have two problems. First, since the Fermi speed u_F is approximately independent of temperature, the resistivity given by Equation 27-23 is inde-

pendent of temperature unless the mean free path depends on it. The second problem concerns magnitudes. As mentioned earlier, the classical expression for resistivity using v_{av} calculated from the Maxwell–Boltzmann distribution gives values that are about 6 times too large at $T = 300$ K. Since the Fermi speed u_F is about 16 times the Maxwell–Boltzmann value of v_{av}, the magnitude of ρ predicted by Equation 27-23 will be about 100 times greater than the experimentally determined value. The resolution of both of these problems lies in the calculation of the mean free path λ.

The Scattering of Electron Waves

In Equation 27-9 for the classical mean free path ($\lambda = 1/n_{ion}A$), the quantity $A = \pi r^2$ is the area of the lattice ion as seen by an electron. In the quantum calculation, the mean free path is related to the scattering of electron waves by the crystal lattice. Detailed calculations show that, for a *perfectly* ordered crystal, $\lambda = \infty$, that is, there is no scattering of the electron waves. The scattering of electron waves arises because of *imperfections* in the crystal lattice, which have nothing to do with the actual area of the lattice ions. According to the quantum theory of electron scattering, A depends merely on *deviations* of the lattice ions from a perfectly ordered array and not on the size of the ions. The most common causes of such deviations are thermal vibrations of the lattice ions or impurities.

We can use $\lambda = 1/n_{ion}A$ for the mean free path if we reinterpret the area A. Figure 27-8 compares the classical and quantum pictures of this area. In the quantum picture, the lattice ions are points that have no size but present an area $A = \pi r_0^2$, where r_0 is the amplitude of thermal vibrations. In Chapter 14 we saw that the energy of vibration in simple harmonic motion is proportional to the square of the amplitude, which is r_0^2. Thus, the effective area A is proportional to the energy of vibration of the lattice ions. From the equipartition theorem, we know that the average energy of vibration is proportional to kT.* Thus, A is proportional to T, and λ is proportional to $1/T$. Then the resistivity given by Equation 27-7 is proportional to T, in agreement with experiment.

The effective area A due to thermal vibrations can be calculated, and the results give values for the resistivity that are in agreement with experiment. At $T = 300$ K, for example, the effective area turns out to be about 100 times smaller than the actual area of a lattice ion. We see, therefore, that the free-electron model of metals gives a good account of electrical conduction if the classical mean speed v_{av} is replaced by the Fermi speed u_F and if the collisions between electrons and the lattice ions are interpreted in terms of the scattering of electron waves, for which only deviations from a perfectly ordered lattice are important.

The presence of impurities in a metal also causes deviations from perfect regularity in the crystal lattice. The effects of impurities on resistivity are approximately independent of temperature. The resistivity of a metal containing impurities can be written $\rho = \rho_t + \rho_i$, where ρ_t is the resistivity due to the thermal motion of the lattice ions and ρ_i is the resistivity due to impurities. Figure 27-9 shows typical resistance-versus-temperature curves for metals with impurities. As the temperature approaches zero, ρ_t approaches zero and the resistivity approaches the constant ρ_i due to impurities.
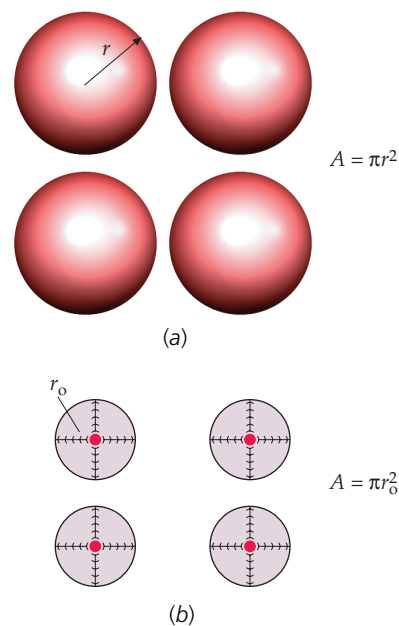

Figure 27-8 (*a*) Classical picture of the lattice ions as spherical balls of radius r that present an area πr^2 to the electrons. (*b*) Quantum-mechanical picture of the lattice ions as points that are vibrating in three dimensions. The area presented to the electrons is πr_0^2, where r_0 is the amplitude of oscillation of the ions.
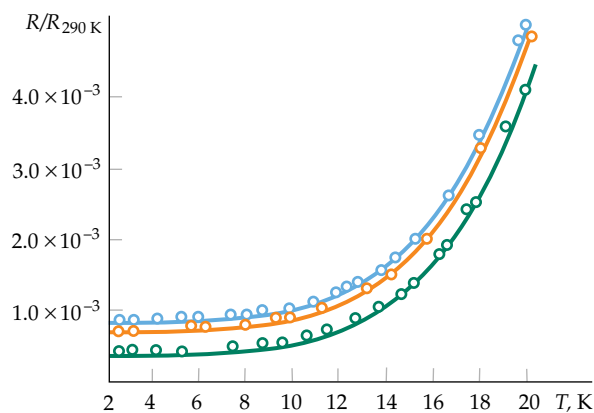

Figure 27-9 Relative resistance versus temperature for three samples of sodium. The three curves have the same temperature dependence but different magnitudes because of differing amounts of impurities in the samples.

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* The equipartition theorem *does* hold for the lattice ions, which obey the Maxwell–Boltzmann energy distribution.

27-4   Band Theory of Solids

Resistivities vary enormously between insulators and conductors. For a typical insulator, such as quartz, $\rho \sim 10^{16}$ $\Omega \cdot$m, whereas for a typical conductor, $\rho \sim 10^{-8}$ $\Omega \cdot$m. The reason for this enormous variation is the variation in the number density of free electrons n_e. To understand this variation, we consider the effect of the lattice on the electron energy levels.

We begin by considering the energy levels of the individual atoms as they are brought together. The allowed energy levels in an isolated atom are often far apart. For example, in hydrogen, the lowest allowed energy ($E_1 = -13.6$ eV) is 10.2 eV below the next lowest ($E_2 = -13.6$ eV)$/4 = -3.4$ eV).* Let us consider two identical atoms and focus our attention on one particular energy level. When the atoms are far apart, the energy of a particular level is the same for each atom. As the atoms are brought closer together, the energy level for each atom changes because of the influence of the other atom. As a result, the level splits into two levels of slightly different energies for the two-atom system. If we bring three atoms close together, a particular energy level splits into three separate levels of slightly different energies. Figure 27-10 shows the energy splitting of two energy levels for six atoms as a function of the separation of the atoms.
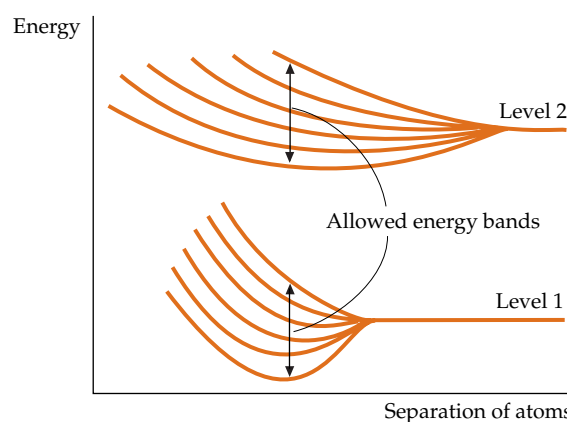
If we have N identical atoms, a particular energy level in the isolated atom splits into N different, closely spaced energy levels when the atoms are close together. In a macroscopic solid, N is very large—of the order of 10^{23}—so each energy level splits into a very large number of levels called a **band**. The levels are spaced almost continuously within the band. There is a separate band of levels for each particular energy level of the isolated atom. The bands may be widely separated in energy, they may be close together, or they may even overlap, depending on the kind of atom and the type of bonding in the solid.

The lowest-energy bands, corresponding to the lowest energy levels of the atom in the lattice, are filled with electrons that are bound to the atom. The electrons that can take part in conduction occupy the higher energy bands. The highest energy band that contains electrons is called the **valence band**. The valence band may be completely filled with electrons or only partially filled, depending on the kind of atom and type of bonding in the solid.

We can now understand why some solids are conductors and others are insulators. If the valence band is only partially full, there are many available empty energy states in the band, and the electrons in the band can easily be raised to a higher energy state by an electric field. Accordingly, this material is a good conductor. If the valence band is full and there is a large energy gap between it and the next available band, a typical applied electric field will be too weak to excite an electron from the upper energy levels of the filled band across the large gap into the energy levels of the empty band, so the material is an insulator. The lowest band in which there are unoccupied states is called the **conduction band**. In a conductor, the valence band is only partially filled, so the valence band is also the conduction band. An energy gap between allowed bands is called a **forbidden energy band**.

The band structure for a conductor such as copper is shown in Figure

Figure 27-10 Energy splitting of two energy levels for six atoms as a function of the separation of the atoms. When there are many atoms, each level splits into a near-continuum of levels called a band.
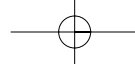
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* The energy levels in hydrogen are discussed in Chapter 37.

27-11*a*. The lower bands (not shown) are filled with the inner electrons of the atoms. The valence band is only about half full. When an electric field is established in the conductor, the electrons in the conduction band are accelerated, which means that their energy is increased. This is consistent with the Pauli exclusion principle because there are many empty energy states just above those occupied by electrons in this band. These electrons are thus the conduction electrons.

Figure 27-11 Four possible band structures for a solid. (*a*) A typical conductor. The valence band is only partially full, so electrons can be easily excited to nearby energy states. (*b*) A conductor in which the allowed energy bands overlap. (*c*) A typical insulator. There is a forbidden band with a large energy gap between the filled valence band and the conduction band. (*d*) A semiconductor. The energy gap between the filled valence band and the conduction band is very small, so some electrons are excited to the conduction band at normal temperatures, leaving holes in the valence band.

Figure 27-11*b* shows the band structure for magnesium, which is also a conductor. In this case, the highest occupied band is full, but there is an empty band above it that overlaps it. The two bands thus form a combined valence–conduction band that is only partially filled.

Figure 27-11*c* shows the band structure for a typical insulator. At $T = 0$ K, the valence band is completely full. The next energy band containing empty energy states, the conduction band, is separated from the valence band by a large energy gap. At $T = 0$, the conduction band is empty. At ordinary temperatures, a few electrons can be excited to states in this band, but most cannot be because the energy gap is large compared with the energy an electron might obtain by thermal excitation. Very few electrons can be thermally excited to the nearly empty conduction band, even at fairly high temperatures. When an electric field of ordinary magnitude is established in the solid, electrons cannot be accelerated because there are no empty energy states at nearby energies. We describe this by saying that there are no free electrons. The small conductivity that is observed is due to the very few electrons that are thermally excited into the nearly empty conduction band. When an electric field applied to an insulator is sufficiently strong to cause an electron to be excited across the energy gap to the empty band, dielectric breakdown occurs.

In some materials, the energy gap between the filled valence band and the empty conduction band is very small, as shown in Figure 27-11*d*. At $T = 0$, there are no electrons in the conduction band and the material is an insulator. However, at ordinary temperatures, there are an appreciable number of electrons in the conduction band due to thermal excitation. Such a material is called an **intrinsic semiconductor**. For typical semiconductors such as silicon and germanium, the energy gap is only about 1 eV. In the presence of an electric field, the electrons in the conduction band can be accelerated because there are empty states nearby. Also, for each electron in the conduction band there is a vacancy, or hole, in the nearly filled valence band. In the presence of an electric field, electrons in this band can also be excited to a vacant energy level. This contributes to the electric current and is most easily described as the motion of a hole in the direction of the field and opposite to the motion of the electrons. The hole thus acts like a positive charge. To visualize the conduction of holes, think of a two-lane, one-way road with one lane full of parked cars and the other empty. If a car moves out of the filled lane into the empty lane, it can move ahead freely. As the other cars move up to occupy the space left, the empty space propagates backward in the direction opposite the motion of the cars. Both the forward motion of the car in the nearly empty lane and the backward propagation of the empty space contribute to a net forward propagation of the cars.

An interesting characteristic of semiconductors is that the resistivity of the material decreases as the temperature increases, which is contrary to the case for normal conductors. The reason is that as the temperature increases, the number of free electrons increases because there are more electrons in the
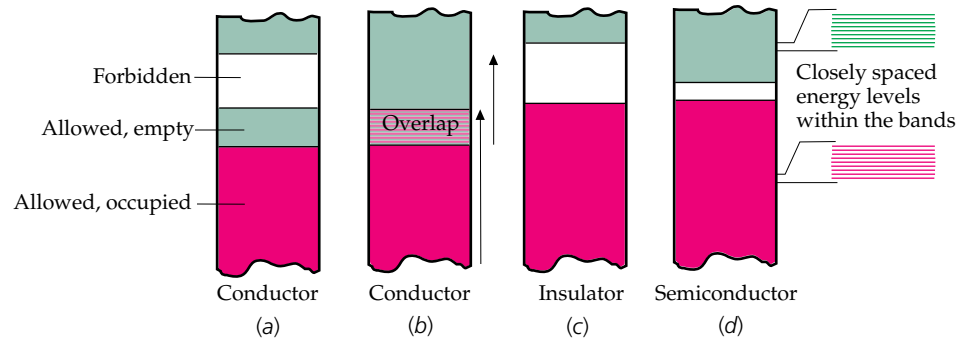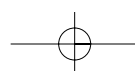
conduction band. The number of holes in the valence band also increases, of course. In semiconductors, the effect of the increase in the number of charge carriers, both electrons and holes, exceeds the effect of the increase in resistivity due to the increased scattering of the electrons by the lattice ions due to thermal vibrations. Semiconductors therefore have a negative temperature coefficient of resistivity.

27-5   Superconductivity

There are some materials for which the resistivity suddenly drops to zero below a certain temperature T_c, called the **critical temperature**. This amazing phenomenon, called **superconductivity**, was discovered in 1911 by the Dutch physicist H. Kamerlingh Onnes, who had developed a technique for liquefying helium (boiling point 4.2 K) and was putting his technique to work exploring the properties of materials at extremely low temperatures. Figure 27-12 shows his plot of the resistance of mercury versus temperature. The critical temperature for mercury is the same as the boiling point of helium, 4.2 K. Critical temperatures for other superconducting elements range from less than 0.1 K for hafnium and iridium to 9.2 K for niobium. The temperature range for superconductors goes much higher for a number of metallic compounds. For example, the superconducting alloy Nb_3Ge, discovered in 1973, has a critical temperature of 23.2 K, which was the highest known until 1986, when the discoveries of Bednorz and Müller launched the era of high-temperature superconductors, now defined as materials that exhibit superconductivity at temperatures above 77 K. To date (mid 1998), the highest temperature at which superconductivity has been demonstrated, using compounds containing mercury, is 125 K at atmospheric pressure and 164 K at high pressure.

The resistivity of a superconductor is zero. There can be a current in a superconductor even when the electric field in the superconductor is zero. Indeed, in superconducting rings in which there was no electric field, steady currents have been observed to persist for years without apparent loss. Despite the cost and inconvenience of refrigeration with expensive liquid helium, many superconducting magnets have been built using superconducting materials, because such magnets require no power expenditure to maintain the large current needed to produce a large magnetic field.

The discovery of high-temperature superconductors has revolutionized the study of superconductivity because relatively inexpensive liquid nitrogen, which boils at 77 K, can be used for a coolant. However, many problems, such as brittleness and the toxicity of the materials, make these new superconductors difficult to use. The search continues for new materials that will superconduct at even higher temperatures.

Figure 27-12 Plot by Kamerlingh Onnes of the resistance of mercury versus temperature, showing the sudden decrease at the critical temperature of $T = 4.2$ K.

The BCS Theory

It had been recognized for some time that superconductivity is due to a collective action of the conducting electrons. In 1957, John Bardeen, Leon Cooper, and Robert Schrieffer published a successful theory of superconductivity now known by the initials of the inventors as the **BCS theory**. According to this theory, the electrons in a superconductor are coupled in pairs at low temperatures. The coupling comes about because of the interaction between electrons and the crystal lattice. One electron interacts with the lattice and perturbs it. The perturbed lattice interacts with another electron in such a way that there is an attraction between the two electrons that at low tem-
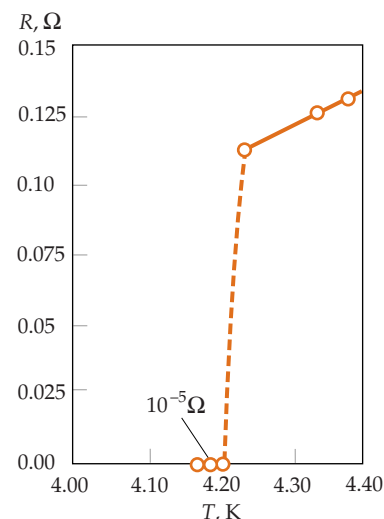
peratures can exceed the Coulomb repulsion between them. The electrons form a bound state called a **Cooper pair**. The electrons in a Cooper pair have equal and opposite spins, so they form a system with zero spin. Each Cooper pair acts as a *single particle* with zero spin—in other words, as a boson. Bosons do not obey the exclusion principle. Any number of Cooper pairs may be in the same quantum state with the same energy. In the ground state of a superconductor (at $T = 0$), all the electrons are in Cooper pairs and all the Cooper pairs are in the same energy state. In the superconducting state, the Cooper pairs are correlated so that they all act together. An electric current can be produced in a superconductor because all of the electrons in this collective state move together. But energy cannot be dissipated by individual collisions of electron and lattice ions unless the temperature is high enough to break the binding of the Cooper pairs. The energy needed to break up a Cooper pair is similar to that needed to break up a molecule into its constituent atoms. This energy is called the **superconducting energy gap** E_g. In the BCS theory, this energy at absolute zero is related to the critical temperature by

$$E_g = 3.5kT_c \hspace{3cm} \text{27-24}$$

The energy gap can be determined by measuring the current across a junction between a normal metal and a superconductor as a function of voltage. Consider two metals separated by a layer of insulating material, such as aluminum oxide, that is only a few nanometers thick. The insulating material between the metals forms a barrier that prevents most electrons from traversing the junction. But, as mentioned in Chapter 15, waves can tunnel through a barrier if the barrier is not too thick even if the energy of the wave is less than that of the barrier (see Figures 15-21 and 15-22).

When the materials on either side of the gap are normal nonsuperconducting metals, the current resulting from the tunneling of electrons through the insulating layer obeys Ohm's law for low applied voltages (Figure 27-13a). When one of the metals is a normal metal and the other is a superconductor, there is no current (at absolute zero) unless the applied voltage V is greater than a critical voltage $V_c = E_g/2e$, where E_g is the superconductor energy gap. Figure 27-13b shows the plot of current versus voltage for this situation. The current jumps abruptly when the energy $2eV_c$ absorbed by a Cooper pair is great enough to break up the pair. (The small current visible in Figure 27-13b before the critical voltage is reached is present because at any temperature above absolute zero some of the electrons in the superconductor are thermally excited above the energy gap and are therefore not paired.) The superconducting energy gap can thus be accurately measured by measuring the critical voltage V_c.
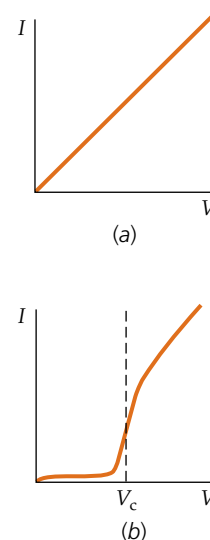

(a)

(b)

Figure 27-13 Tunneling current versus voltage for a junction of two metals separated by a thin oxide layer. (*a*) When both metals are normal metals, the current is proportional to the voltage, as predicted by Ohm's law. (*b*) When one metal is a normal metal and one is a superconductor, the current is approximately zero until the applied voltage exceeds the critical voltage $V_c = E_g/2e$.

Example **27-6**

Calculate the superconducting energy gap for mercury (T_c = 4.2 K) predicted by the BCS theory.

1. The BCS prediction for the energy gap is: $E_g = 3.5kT_c$

2. Substitute $T_c = 4.2$ K: $E_g = 3.5kT_c$

$$= 3.5(1.38 \times 10^{-23} \text{ J/K})(4.2 \text{ K})\frac{1 \text{ eV}}{1.6 \times 10^{-19} \text{ J}}$$

$$= 1.27 \times 10^{-3} \text{ eV}$$

Note that the energy gap for a typical super-
conductor is much smaller than the energy gap
for a typical semiconductor, which is of the order
of 1 eV. As the temperature is increased from $T = 0$, some of the Cooper pairs are broken. Then there
are fewer pairs available for each pair to interact
with, and the energy gap is reduced until at $T = T_c$ the energy gap is zero (Figure 27-14).

The Josephson Effect

When two superconductors are separated by a
thin insulating barrier (for example, a layer of alu-
minum oxide a few nanometers thick), the junc-
tion is called a **Josephson junction**, based on the
prediction in 1962 by Brian Josephson that Cooper
pairs could tunnel across such a junction from one
superconductor to the other with no resistance.
The tunneling of Cooper pairs constitutes a cur-
rent, which is observed even when there is no voltage applied across the
junction. The current depends on the difference in phase of the wave func-
tions that describe the Cooper pairs. Let ϕ_1 be the phase constant for the
wave function of a Cooper pair in one superconductor. All the Cooper pairs
in a superconductor act coherently, so they all have the same phase constant.
If ϕ_2 is the phase constant for the Cooper pairs in the second superconductor,
the current across the junction is given by

$$I = I_{max} \sin (\phi_2 - \phi_1) \qquad \text{27-25}$$

where I_{max} is the maximum current, which depends on the thickness of the
barrier. This result has been observed experimentally and is known as the **dc
Josephson effect**.

Josephson also predicted that if a dc voltage V were applied across a
Josephson junction, there would be a current that alternates with frequency f
given by

$$f = \frac{2eV}{h} \qquad \text{27-26}$$

This result, known as the **ac Josephson effect**, has been observed experimen-
tally, and careful measurement of the frequency allows a precise determina-
tion of the ratio e/h. Because frequency can be measured very accurately, the
ac Josephson effect is also used to establish precise voltage standards. The in-
verse effect, in which the application of an alternating voltage across a
Josephson junction results in a dc current, has also been observed.
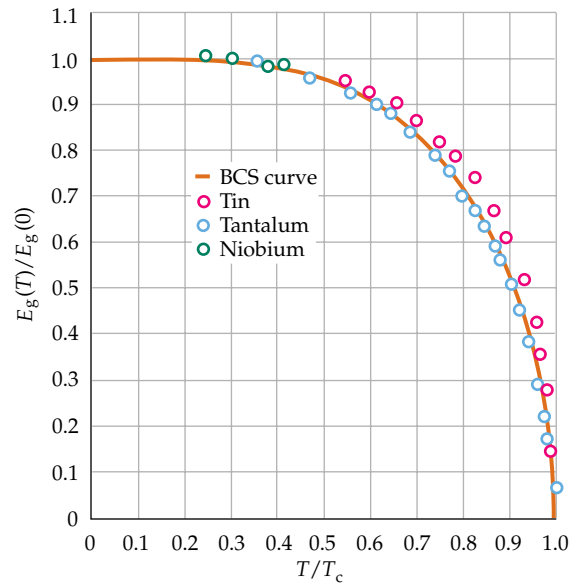
Figure 27-14 Ratio of the energy gap at
temperature T to that at $T = 0$ as a function
of the relative temperature T/T_c. The solid
curve is that predicted by the BCS theory.

Example 27-7

Using $e = 1.602 \times 10^{-19}$ C and $h = 6.626 \times 10^{-34}$ J·s, calculate the frequency of
the Josephson current if the applied voltage is 1 μV.

Substitute the given values into Equation 27-25 to
calculate f:

$$f = \frac{2eV}{h} = \frac{2(1.602 \times 10^{-19} \text{ C})(10^{-6} \text{ V})}{6.626 \times 10^{-34} \text{ J·s}}$$

$$= 4.835 \times 10^8 \text{ Hz} = 483.5 \text{ MHz}$$

optional
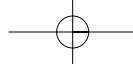
27-6   The Fermi–Dirac Distribution*

The classical Maxwell–Boltzmann distribution (Equation 18-39) gives the number of molecules with energy E in the range between E and $E + dE$. It is the product of $g(E) \, dE$ where $g(E)$ is the density of states (number of energy states in the range dE) and the Boltzmann factor $e^{-E/kT}$, which is the probability of a state being occupied. The distribution function for free electrons in a metal is called the **Fermi–Dirac distribution**. The Fermi–Dirac distribution can be written in the same form as the Maxwell–Boltzmann distribution with the density of states calculated from quantum theory and the Boltzmann factor replaced by the Fermi factor. Let $n(E) \, dE$ be the number of electrons with energies between E and $E + dE$. This number is written

$$n(E) \, dE = g(E) \, dE \, f(E) \qquad\qquad 27\text{-}27$$

Energy distribution function

where $g(E) \, dE$ is the number of states between E and $E + dE$, $g(E)$ is called the density of states, and $f(E)$ is the probability of a state being occupied, which is the Fermi factor. The density of states in three dimensions is somewhat difficult to calculate, so we just give the result. For electrons in a metal of volume V, the density of states is

$$g(E) = \frac{8\pi\sqrt{2}\,m_e^{3/2}V}{h^3} E^{1/2} \qquad\qquad 27\text{-}28$$

Density of states

As in the classical Maxwell–Boltzmann distribution, the density of states is proportional to $E^{1/2}$.

At $T = 0$, the Fermi factor is given by Equation 27-17:

$$f(E) = 1, \qquad E < E_F$$

$$f(E) = 0, \qquad E > E_F$$

The integral of $n(E) \, dE$ over all energies gives the total number of electrons N. We can derive Equation 27-15a for the Fermi energy at $T = 0$ by integrating $n(E) \, dE$ from $E = 0$ to $E = \infty$. We obtain

$$N = \int_0^\infty n(E) \, dE = \int_0^{E_F} g(E) \, dE = \frac{8\pi\sqrt{2}\,m_e^{3/2}V}{h^3} \int_0^{E_F} E^{1/2} \, dE = \frac{16\pi\sqrt{2}\,m_e^{3/2}V}{3h^3} E_F^{3/2}$$

Note that at $T = 0$, $n(E)$ is zero for $E > E_F$ so we had to integrate only from $E = 0$ to $E = E_F$. Solving for E_F gives the Fermi energy at $T = 0$:

$$E_F = \frac{h^2}{8m_e}\left(\frac{3N}{\pi V}\right)^{2/3} \qquad\qquad 27\text{-}29$$

which is Equation 27-15a. In terms of the Fermi energy, the density of states (Equation 27-28) is

$$g(E) = \frac{8\pi\sqrt{2}\,m_e^{3/2}V}{h^3} E^{1/2} = \frac{3N}{2} E_F^{-3/2} E^{1/2} \qquad\qquad 27\text{-}30$$

Density of states in terms of E_F

The average energy at $T = 0$ is calculated from

$$E_{av} = \frac{\displaystyle\int_0^{E_F} E g(E) \, dE}{\displaystyle\int_0^{E_F} g(E) \, dE} = \frac{1}{N}\int_0^{E_F} E g(E) \, dE$$

where $N = \int_0^{E_F} g(E) \, dE$ is the total number of electrons. Performing the integration, we obtain Equation 27-16

$$E_{av} = \tfrac{3}{5}E_F \qquad\qquad 27\text{-}31$$

Average energy at $T = 0$
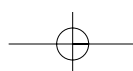
At $T > 0$, the Fermi factor is more complicated. It can be shown to be given by

$$f(E) = \frac{1}{e^{(E - E_F)/kT} + 1} \qquad \text{27-32}$$

Fermi factor

We can see from this equation that for E greater than E_F, $e^{(E - E_F)/kT}$ becomes very large as T approaches zero, so at $T = 0$, the Fermi factor is zero for $E > E_F$. On the other hand, for E less than E_F, $e^{(E - E_F)/kT}$ approaches 0 as T approaches zero, so at $T = 0$, $f(E) = 1$ for $E < E_F$. Thus the Fermi factor given by Equation 27-32 holds for all temperatures. Note also that for any nonzero value of T, $f(E) = \frac{1}{2}$ at $E = E_F$.

The complete Fermi–Dirac distribution function is thus

$$n(E)\, dE = \frac{8\pi\sqrt{2}m_e^{3/2}V}{h^3} E^{1/2} \frac{1}{e^{(E - E_F)/kT} + 1}\, dE \qquad \text{27-33}$$

Fermi–Dirac distribution

We can see that for those few electrons with energies much greater than the Fermi energy, the Fermi factor approaches $1/e^{(E - E_F)/kT} = e^{(E_F - E)/kT} = e^{E_F}e^{-E/kT}$, which is proportional to $e^{-E/kT}$. Thus, the high-energy tail of the Fermi–Dirac energy distribution decreases as $e^{-E/kT}$, just like the classical Maxwell–Boltzmann energy distribution. The reason is that in this high-energy region, there are many unoccupied energy states and few electrons, so the Pauli exclusion principle is not important, and the distribution approaches the classical distribution. This result has practical importance because it applies to the conduction electrons in semiconductors.

Example **27-8**

At what energy is the Fermi factor equal to 0.1 for copper at $T = 300$ K?

Picture the Problem We set $f(E) = 0.1$ in Equation 27-32 using $T = 300$ K and $E_F = 7.04$ eV from Table 27-1 and solve for E.

1. Solve Equation 27-32 for $e^{(E - E_F)/kT}$:

$$f(E) = \frac{1}{e^{(E - E_F)/kT} + 1} = 0.1$$

$$e^{(E - E_F)/kT} = \frac{1}{f(E)} - 1 = \frac{1}{0.1} - 1 = 9$$

2. Take the natural logarithm of both sides:

$$\frac{E - E_F}{kT} = \ln 9 = 2.20$$
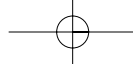
3. Solve for $E - E_F$:

$$E - E_F = 2.20 kT = 2.20(8.62 \times 10^{-5} \text{ eV/K})(300 \text{ K})$$

$$= 2.20(0.0259 \text{ eV}) = 0.0570 \text{ eV}$$

4. Solve for E using $E_F = 7.04$ eV from Table 27-1:

$$E = 7.04 \text{ eV} + 0.0570 \text{ eV} = 7.10 \text{ eV}$$

Remark The Fermi factor drops from about 1 to 0.1 at just 0.06 eV above the Fermi energy of about 7 eV.

optional

Example 27-9

Find the probability that an energy state in copper 0.1 eV above the Fermi energy is occupied at $T = 300$ K.

Picture the Problem The probability is the Fermi factor given in Equation 27-32, with $E_F = 7.04$ eV, and $E = 7.14$ eV.

1. The probability of a state being occupied equals the Fermi factor:

$$P = f(E) = \frac{1}{e^{(E-E_F)/kT} + 1}$$

2. Calculate the dimensionless exponent in the Fermi factor:

$$\frac{E - E_F}{kT} = \frac{7.14 \text{ eV} - 7.04 \text{ eV}}{(8.62 \times 10^{-5} \text{ eV/K})(300 \text{ K})} = 3.87$$

3. Use this result to calculate the Fermi factor:

$$f = \frac{1}{e^{(E-E_F)/kT} + 1} = \frac{1}{e^{3.87} + 1}$$

$$= \frac{1}{48 + 1} = 0.0204 = 2.04\%$$

Remark The probability of an electron having an energy of 0.1 eV above the Fermi energy at 300 K is only about 2%.

Example 27-10   *try it yourself*

Find the probability that an energy state in copper 0.1 eV *below* the Fermi energy is occupied at $T = 300$ K.

Picture the Problem The probability is the Fermi factor given in Equation 27-32, with $E_F = 7.04$ eV, and $E = 6.94$ eV.
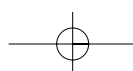
Cover the column to the right and try these on your own before looking at the answers.

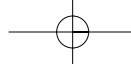| *Steps*	*Answers*
1. Write the Fermi factor.	$f(E) = \dfrac{1}{e^{(E-E_F)kT} + 1}$
2. Calculate the dimensionless exponent in the Fermi factor.	$\dfrac{E - E_F}{kT} = \dfrac{6.94 \text{ eV} - 7.04 \text{ eV}}{(8.62 \times 10^{-5} \text{ eV/K})(300 \text{ K})} = -3.87$
3. Use your result in step 2 to calculate the Fermi factor.	$f = \dfrac{1}{e^{(E-E_F)/kT} + 1} = \dfrac{1}{e^{-3.87} + 1}$ $= \dfrac{1}{0.021 + 1} = 0.979 \approx 98\%$

Remark The probability of an electron having an energy of 0.1 eV *below* the Fermi energy at 300 K is about 98%.

Exercise What is the probability of an energy state 0.1 eV below the Fermi energy being unoccupied at 300 K? (*Answer* $1 - 0.98 = 0.02$ or 2%. This is the probability of there being a hole at this energy.)

Summary

Topic	Remarks and Relevant Equations
1. Microscopic Picture of Conduction	
Resistivity	$$\rho = \frac{m_e v_{av}}{n_e e^2 \lambda} \qquad \textbf{27-7}$$ where v_{av} is the average speed of the electrons and λ is their mean free path between collisions with the lattice ions.
Mean free path	$$\lambda = \frac{1}{n_{ion}\pi r^2} = \frac{1}{n_{ion}A} \qquad \textbf{27-9}$$ where n_{ion} is the number of lattice ions per unit volume, r is their effective radius, and A is their effective cross-sectional area.
2. Classical Interpretation of v_{av} and λ	v_{av} is determined from the Maxwell–Boltzmann distribution, and r is the actual radius of a lattice ion.
3. Quantum Interpretation of v_{av} and λ	v_{av} is determined from the Fermi–Dirac distribution and is approximately constant independent of temperature. The mean free path is determined from the scattering of electron waves, which occurs only because of deviations from a perfectly ordered array. The radius r is the amplitude of vibration of the lattice ion, which is proportional to $\sqrt{T}$, so A is proportional to T.
4. Fermi Electron Gas	
Fermi energy E_F at $T = 0$	E_F is the energy of the highest filled (or half-filled) energy state.
E_F at $T > 0$	E_F is the energy at which the probability of being occupied is $\frac{1}{2}$.
Approximate magnitude of E_F	E_F is about 5 to 10 eV for most metals.
Dependence of E_F on the number density of free electrons	$$E_F = \frac{h^2}{8m_e}\left(\frac{3N}{\pi V}\right)^{2/3} = (0.365\ \text{eV·nm}^2)\left(\frac{N}{V}\right)^{2/3} \qquad \textbf{27-15}\textbf{\textit{a,b}}$$
Average energy at $T = 0$	$$E_{av} = \tfrac{3}{5}E_F \qquad \textbf{27-16}$$
Fermi factor at $T = 0$	The Fermi factor $f(E)$ is the probability of a state being occupied $$f(E) = 1, \qquad E < E_F$$ $$f(E) = 0, \qquad E > E_F \qquad \textbf{27-17}$$
Fermi temperature	$$T_F = \frac{E_F}{k} \qquad \textbf{27-18}$$
Fermi speed	$$u_F = \sqrt{\frac{2E_F}{m_e}} \qquad \textbf{27-19}$$
Contact potential	When two different metals are placed in contact, electrons flow from the metal with the higher Fermi energy to the one with the lower Fermi energy until the Fermi energies of the two metals are equal. In equilibrium, there is a potential difference be-

tween the metals that is equal to the difference in the work function of the two metals divided by the electronic charge e:

$$V_{contact} = \frac{\phi_1 - \phi_2}{e}$$ **27-20**

Heat capacity due to electrons

$$C'_v = \frac{\pi^2}{2} R \frac{T}{T_F}$$ **27-22**

5. Band Theory of Solids

When many atoms are brought together to form a solid, the individual energy levels are split into bands of allowed energies. The splitting depends on the type of bonding and the lattice separation. The highest-energy band containing electrons is called the valence band. In a conductor, the valence band is only partially full, so there are many available states for excited electrons. In an insulator, the valence band is completely full and there is a large energy gap between it and the next allowed band, the conduction band. In a semiconductor, the energy gap between the filled valence band and the empty conduction band is small; so at ordinary temperatures, an appreciable number of electrons are thermally excited into the conduction band.

6. Superconductivity

In a superconductor, the resistance drops suddenly to zero below a critical temperature T_c. Superconductors with critical temperatures as high as 125 K have been discovered.

BCS theory

Superconductivity is described by a theory of quantum mechanics called the BCS theory in which the free electrons form Cooper pairs. The energy needed to break up a Cooper pair is called the energy gap E_g. When all the electrons are paired, individual electrons cannot be scattered by a lattice ion, so the resistance is zero.

Tunneling

When a normal conductor is separated from a superconductor by a thin layer of oxide, electrons can tunnel through the energy barrier if the applied voltage across the layer is $E_g/2e$, where E_g is the energy needed to break up a Cooper pair. The energy gap E_g can be determined by a measurement of the tunneling current versus the applied voltage.

Josephson junction

A system of two superconductors separated by a thin layer of insulating material is called a Josephson junction.

dc Josephson effect

A dc current is observed to tunnel through a Josephson junction even in the absence of voltage across the junction.

ac Josephson effect

When a dc voltage V is applied across a Josephson junction, an ac current is observed with a frequency

$$f = \frac{2eV}{h}$$ **27-26**

Measurement of the frequency of this current allows a precise determination of the ratio e/h.

7. Fermi–Dirac Distribution

The number of electrons with energies between E and $E + dE$ is given by
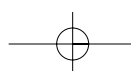
$$n(E)\, dE = g(E)\, dE\, f(E)$$ **27-27**

where $g(E)$ is the density of states and $f(E)$ is the Fermi factor.

Density of states

$$g(E) = \frac{8\pi\sqrt{2}m_e^{3/2}V}{h^3} E^{1/2}$$ **27-28**

Fermi factor at temperature T

$$f(E) = \frac{1}{e^{(E-E_F)/kT} + 1}$$ **27-32**

Problem-Solving Guide

Summary of Worked Examples

Type of Calculation	**Procedure and Relevant Examples**	
1.	**The Fermi Electron Gas**	
Calculate the Fermi energy from the number density of free electrons.	Use $E_F = (0.365 \text{ eV·nm}^2)(N/V)^{2/3}$.	**Example 27-2**
Calculate the Fermi temperature.	Use $kT_F = E_F$ and Table 27-1 for E_F.	**Example 27-3**
Calculate the Fermi speed.	Use $u_F = \sqrt{2E_F/m_e}$ and Table 27-1 for E_F.	**Example 27-4**
Calculate the contact potential developed when two metals are placed in contact.	Find the work functions from the photoelectric thresholds and use $V_{contact} = (\phi_1 - \phi_2)/e$.	**Example 27-5**
2.	**Superconductors**	
Find the superconducting gap from the critical temperature.	Use $E_g = 3.5kT_c$.	**Example 27-6**
Find the Josephson frequency for a given applied voltage.	Use $f = 2eV/h$.	**Example 27-7**
3.	**The Fermi–Dirac Distribution**	
Find the energy for a given value of $f(E)$ at a given temperature.	Use $f(E) = 1/(e^{(E - E_F)/kT} + 1)$ and solve for E.	**Example 27-8**
Find the probability that a state of a given energy will be occupied.	Calculate the Fermi factor for the given energy.	**Examples 27-9, 27-10**

Problems

> Conceptual Problems
>
> Problems from Optional and Exploring sections

In a few problems, you are given more data than you actually need; in a few other problems, you are required to supply data from your general knowledge, outside sources, or informed estimates.

- • Single-concept, single-step, relatively easy
- •• Intermediate-level, may require synthesis of concepts
- ••• Challenging, for advanced students

Use Table 27-1 for the Fermi energies and electron number densities when needed.

Microscopic Picture of Conduction

1 • In the classical model of conduction, the electron loses energy on average in a collision because it loses the drift velocity it had picked up since the last collision. Where does this energy appear?

2 • A measure of the density of the free-electron gas in a metal is the distance r_s, which is defined as the radius of the sphere whose volume equals the volume per conduction electron. (*a*) Show that $r_s = (3/4\pi n)^{1/3}$, where n is the free-electron number density. (*b*) Calculate r_s for copper in nanometers.

3 • (*a*) Given a mean free path $\lambda = 0.4$ nm and a mean speed $v_{av} = 1.17 \times 10^5$ m/s for the current flow in copper at a temperature of 300 K, calculate the classical value for the resistivity ρ of copper. (*b*) The classical model suggests that the mean free path is temperature independent and that v_{av} depends on temperature. From this model, what would ρ be at 100 K?

The Fermi Electron Gas

4 • Calculate the number density of free electrons in (*a*) Ag ($\rho = 10.5$ g/cm^3) and (*b*) Au ($\rho = 19.3$ g/cm^3), assuming one free electron per atom, and compare your results with the values listed in Table 27-1.

optional
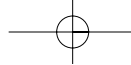
5 • The density of aluminum is 2.7 g/cm^3. How many free electrons are present per aluminum atom?

6 • The density of tin is 7.3 g/cm^3. How many free electrons are present per tin atom?

7 • Calculate the Fermi temperature for (*a*) Al, (*b*) K, and (*c*) Sn.

8 • What is the speed of a conduction electron whose energy is equal to the Fermi energy E_F for (*a*) Na, (*b*) Au, and (*c*) Sn?

9 • Calculate the Fermi energy for (*a*) Al, (*b*) K, and (*c*) Sn using the number densities given in Table 27-1.

10 • Find the average energy of the conduction electrons at $T = 0$ in (*a*) copper and (*b*) lithium.

11 • Calculate (*a*) the Fermi temperature and (*b*) the Fermi energy at $T = 0$ for iron.

12 •• The pressure of an ideal gas is related to the average energy of the gas particles by $PV = \frac{2}{3}NE_{av}$, where N is the number of particles and E_{av} is the average energy. Use this to calculate the pressure of the Fermi electron gas in copper in newtons per square meter, and compare your result with atmospheric pressure, which is about 10^5 N/m^2. (*Note:* The units are most easily handled by using the conversion factors 1 N/m$^2 = 1$ J/m^3 and 1 eV $= 1.6 \times 10^{-19}$ J.)

13 •• The bulk modulus B of a material can be defined by

$$B = -V\frac{\partial P}{\partial V}$$

(*a*) Use the ideal-gas relation $PV = \frac{2}{3}NE_{av}$ and Equations 27-15 and 27-16 to show that

$$P = \frac{2NE_F}{5V} = CV^{-5/3}$$

where C is a constant independent of V. (*b*) Show that the bulk modulus of the Fermi electron gas is therefore

$$B = \frac{5}{3}P = \frac{2NE_F}{3V}$$

(*c*) Compute the bulk modulus in newtons per square meter for the Fermi electron gas in copper and compare your result with the measured value of 140×10^9 N/m^2.

Contact Potential

14 • Thomas refuses to believe that a potential difference can be created simply by bringing two different metals into contact with each other. John talks him into making a small wager, and is about to cash in. (*a*) Which two metals from Table 27-2 would demonstrate his point most effectively? (*b*) What is the value of that contact potential?

15 • (*a*) In Problem 14, which choices of different metals would make the least impressive demonstration? (*b*) What is the value of that contact potential?

16 • Calculate the contact potential between (*a*) Ag and Cu, (*b*) Ag and Ni, and (*c*) Ca and Cu.

Quantum Theory of Electrical Conduction

17 • When the temperature of pure copper is lowered from 300 K to 4 K, its resistivity drops by a much greater factor than that of brass when it is cooled the same way. Why?

18 • The resistivities of Na, Au, and Sn at $T = 273$ K are 4.2 $\mu\Omega\cdot$cm, 2.04 $\mu\Omega\cdot$cm, and 10.6 $\mu\Omega\cdot$cm, respectively. Use these values and the Fermi speeds calculated in Problem 8 to find the mean free paths λ for the conduction electrons in these elements.

19 •• The resistivity of pure copper is increased by about 1×10^{-8} $\Omega\cdot$m by the addition of 1% (by number of atoms) of an impurity throughout the metal. The mean free path depends on both the impurity and the oscillations of the lattice ions according to the equation

$$\frac{1}{\lambda} = \frac{1}{\lambda_t} + \frac{1}{\lambda_i}$$

(*a*) Estimate λ_i from data given in Table 27-1. (*b*) If r is the effective radius of an impurity lattice ion seen by an electron, the scattering cross section is πr^2. Estimate this area using the fact that r is related to λ_i by Equation 27-9.

Band Theory of Solids

20 • A metal is a good conductor because the valence energy band for electrons is

(*a*) completely full.
(*b*) full, but there is only a small gap to a higher empty band.
(*c*) partly full.
(*d*) empty.
(*e*) None of these is correct.

21 • Insulators are poor conductors of electricity because

(*a*) there is a small energy gap between the valence band and the next higher band where electrons can exist.
(*b*) there is a large energy gap between the full valence band and the next higher band where electrons can exist.
(*c*) the valence band has a few vacancies for electrons.
(*d*) the valence band is only partly full.
(*e*) None of these is correct.

22 • You are an electron sitting at the top of the valence band in a silicon atom, longing to jump across the 1.14-eV energy gap that separates you from the bottom of the conduction band and all of the adventures that it may contain. What you need, of course, is a photon. What is the maximum photon wavelength that will get you across the gap?

23 • Work Problem 22 for germanium, for which the energy gap is 0.74 eV.

24 • Work Problem 22 for diamond, for which the energy gap is 7.0 eV.

25 •• A photon of wavelength 3.35 μm has just enough energy to raise an electron from the valence band to the conduction band in a lead sulfide crystal. (*a*) Find the energy gap between these bands in lead sulfide. (*b*) Find the temperature T for which kT equals this energy gap.

BCS Theory of Superconductivity

26 • (*a*) Use Equation 27-24 to calculate the supercon-ducting energy gap for tin and compare your result with the measured value of 6×10^{-4} eV. (*b*) Use the measured value to calculate the wavelength of a photon having sufficient energy to break up Cooper pairs in tin at $T = 0$.

27 • Repeat Problem 26 for lead, which has a measured energy gap of 2.73×10^{-3} eV.

The Fermi–Dirac Distribution

28 •• The number of electrons in the conduction band of an insulator or intrinsic semiconductor is governed chiefly by the Fermi factor. Since the valence band in these materials is nearly filled and the conduction band is nearly empty, the Fermi energy E_F is generally midway between the top of the valence band and bottom of the conduction band, i.e., at $E_g/2$, where E_g is the band gap between the two bands and the energy is measured from the top of the valence band. (*a*) In silicon, $E_g \approx 1.0$ eV. Show that in this case the Fermi factor for electrons at the bottom of the conduction band is given by $\exp(-E_g/2kT)$ and evaluate this factor. Discuss the signifi-cance of this result if there are 10^{22} valence electrons per cu-bic centimeter and the probability of finding an electron in the conduction band is given by the Fermi factor. (*b*) Repeat the calculation in (*a*) for an insulator with a band gap of 6.0 eV.

29 •• Show that at $E = E_F$, the Fermi factor is $F = 0.5$.

30 •• What is the difference between the energies at which the Fermi factor is 0.9 and 0.1 at 300 K in (*a*) copper, (*b*) potassium, and (*c*) aluminum.

31 •• What is the probability that a conduction electron in silver will have a kinetic energy of 4.9 eV at $T = 300$ K?

32 •• Show that $g(E) = (3N/2)E_F^{-3/2} E^{1/2}$ (Equation 27-30) follows from Equation 27-28 for $g(E)$, and Equation 27-15a for E_F.

33 •• Carry out the integration $E_{av} = (1/N)\int_0^{E_F} Eg(E)\, dE$ to show that the average energy at $T = 0$ is $\frac{3}{5}E_F$.

34 •• The density of the electron states in a metal can be written $g(E) = AE^{1/2}$, where A is a constant and E is mea-sured from the bottom of the conduction band. (*a*) Show that the total number of states is $\frac{2}{3}AE_F^{3/2}$. (*b*) Approximately what fraction of the conduction electrons are within kT of the Fermi energy? (*c*) Evaluate this fraction for copper at $T = 300$ K.

35 •• What is the probability that a conduction electron in silver will have a kinetic energy of 5.49 eV at $T = 300$ K?

36 •• Use the density-of-states function, Equation 27-28, to estimate the fraction of the conduction electrons in copper that can absorb energy from collisions with the vibrating lat-tice ions at (*a*) 77 K and (*b*) 300 K.

37 •• In an intrinsic semiconductor, the Fermi energy is about midway between the top of the valence band and the bottom of the conduction band. In germanium, the forbidden energy band has a width of 0.7 eV. Show that at room temper-ature the distribution function of electrons in the conduction band is given by the Maxwell–Boltzmann distribution func-tion.

38 ••• (*a*) Show that for $E \geq 0$, the Fermi factor may be written as

$$f(E) = \frac{1}{Ce^{E/kT} + 1}$$

(*b*) Show that if $C \gg e^{-E/kT}$, $f(E) = Ae^{-E/kT} \ll 1$; in other words, show that the Fermi factor is a constant times the clas-sical Boltzmann factor if $A \ll 1$. (*c*) Use $\int n(E)\, dE = N$ and Equation 27-28 to determine the constant A. (*d*) Using the re-sult obtained in part (*c*), show that the classical approxima-tion is applicable when the electron concentration is very small and/or the temperature is very high. (*e*) Most semicon-ductors have impurities added in a process called doping, which increases the free electron concentration so that it is about $10^{17}/\text{cm}^3$ at room temperature. Show that for these systems, the classical distribution function is applicable.

39 ••• Show that the condition for the applicability of the classical distribution function for an electron gas ($A \ll 1$ in Problem 38) is equivalent to the requirement that the average separation between electrons is much greater than their de Broglie wavelength.

40 ••• The root-mean-square (rms) value of a variable is obtained by calculating the average value of the square of that variable and then taking the square root of the result. Use this procedure to determine the rms energy of a Fermi distribution. Express your result in terms of E_F and compare it to the average energy. Why do E_{av} and E_{rms} differ?

41 ••• When a star with a mass of about twice that of the sun exhausts its nuclear fuel, it collapses to a neutron star, a dense sphere of neutrons of about 10 km diameter. Neutrons are spin-$\frac{1}{2}$ particles and, like electrons, are subject to the ex-clusion principle. (*a*) Determine the neutron density of such a neutron star. (*b*) Find the Fermi energy of the neutron distri-bution.

General Problems

42 • True or false:
(*a*) Solids that are good electrical conductors are usually good heat conductors.
(*b*) The classical free-electron theory adequately explains the heat capacity of metals.
(*c*) At $T = 0$, the Fermi factor is either 1 or 0.
(*d*) The Fermi energy is the average energy of an electron in a solid.
(*e*) The contact potential between two metals is proportional to the difference in the work functions of the two metals.
(*f*) At $T = 0$, an intrinsic semiconductor is an insulator.
(*g*) Semiconductors conduct current in one direction only.

43 • How does the change in the resistivity of copper compare with that of silicon when the temperature increases?

44 • The density of potassium is 0.851 g/cm^3. How many free electrons are there per potassium atom?

optional

45   • Calculate the number density of free electrons for
(*a*) Mg ($\rho = 1.74$ g/cm^3) and (*b*) Zn ($\rho = 7.1$ g/cm^3), assuming
two free electrons per atom, and compare your results with
the values listed in Table 27-1.

46   •• Estimate the fraction of free electrons in copper
that are in excited states above the Fermi energy at (*a*) room
temperature of 300 K and (*b*) 1000 K.

47 ••• A 2-cm^2 wafer of pure silicon is irradiated with
light having a wavelength of 775 nm. The intensity of
the light beam is 4.0 W/m^2 and every photon that strikes
the sample is absorbed and creates an electron–hole pair.
(*a*) How many electron–hole pairs are produced in one sec-
ond? (*b*) If the number of electron–hole pairs in the sample
is 6.25×10^{11} in the steady state, at what rate do the elec-
tron–hole pairs recombine? (*c*) If every recombination event
results in the radiation of one photon, at what rate is energy
radiated by the sample?