



CHAPTER

14

CONDUCTORS, INSULATORS, AND SEMICONDUCTORS

The manufacture of glass, along with the forming of metals, is an art that goes back to prehistoric times. It always seems to me remarkable that our first understanding of the utility of metals in terms of atomic movements came *after* the discovery of the neutron... The years that passed before anyone tried to get a theoretical understanding of electrons in glass surprises me even more. After all, the striking thing about glass is that it is transparent, and that one does not have to use particularly pure materials to make it so. But, in terms of modern solid-state physics, what does "transparent" mean? It means that, in the energy spectrum of electrons in the material, there is a gap of forbidden energies between the occupied states (the valence band) and the empty states (the conduction band); light quanta corresponding to a visible wavelength do not have the energy needed to make electrons jump across it. This gap is quite a sophisticated concept, entirely dependent on quantum mechanics...

Nevill F. Mott

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In Chapter 10 we discussed the behavior of two atoms when they are close together in the formation of a molecule. In this chapter we shall be concerned with the behavior of a macroscopic quantity ($N_A \approx 10^{24}$) of atoms when they are *condensed* in the formation of a solid. We begin with a brief description of the possible forms that matter can take in the condensed state (see Figure 14-1). The simplest possibility is that the atoms form a regular array or crystalline structure. The atoms of a crystal form a periodic array, or lattice, that extends over distances thousands of times the size of an atom. In a crystal, the locations of all atoms are known with respect to the position of a given atom. This property is called *long-range order*. The motion of the atoms in a crystal is limited by neighboring atoms because the potential energy between a given atom and any one of its nearest neighbors is qualitatively the same as that of a simple molecule (see Figure 10-3). Each atom in a crystal is a quantum harmonic oscillator.

Another possibility is that the atoms are fixed but do not form a regular array. Such a material is called an *amorphous* solid. The motion of the atoms in an amorphous solid is limited by neighboring atoms just as in a crystal. The location of the neighboring atoms is known with respect to a given atom. This property is called *short-range order*. An amorphous solid differs from a crystal in that there is no long-range order. Glass and rubber are examples of amorphous solids.

A third possibility for condensed matter is that of a liquid. In a liquid the atoms are not held in a rigid pattern. A liquid has neither long-range nor short-range order.

We shall be concerned with crystalline solids in this chapter. Many materials fall into this category, including most metals. There are many possible geometries for the crystal structure. In a *simple cubic* lattice the Cartesian coordinates of the nuclei of the atoms are given by (n_1a, n_2a, n_3a) , where a is the distance between any atom and its nearest neighbors and n_1, n_2 , and n_3 are integers. The structure of a crystal is classified by a *unit cell*, which

specifies the geometrical arrangement of neighboring atoms. The unit cell for the simple cubic structure is one in which the nuclei of neighboring atoms occupy the corners of a cube. Another possibility is that the atoms could be at the corners and center of a cube. This crystal lattice is called *body-centered cubic* (bcc). Since the space occupied by each atom in any crystal configuration is roughly constant (10^{-29} m^3), the size of the unit cell depends on the number of atoms it contains. In a *face-centered cubic* (fcc), atoms are located at the corners and faces of a cube. Other common crystal structures are *hexagonal close packed* (hcp), and *diamond*. The unit cells for these crystal structures are shown in Figure 14-2.

The structure of a crystal may be determined by x-ray scattering. Figure 14-3 shows the crystalline structure of the elements. The richness of the field of condensed matter physics lies in the fact that many interesting properties of compounds depend on the details of the crystalline lattice. Fortunately, however, many basic properties of crystalline solids do not depend on the exact structure of the crystal. In our discussion of solids, we shall focus on the energy distribution of the outer electrons in the atoms. The understanding of the energy distribution of the electrons leads to the explanation of many basic properties of solids. The electron energy distribution is specified by two parts: (1) the density of available states and (2) the occupation probability according to the Fermi-Dirac distribution function.

14-1 ELECTRONIC ENERGY BANDS

When two identical atoms are far apart, their electron probability densities do not significantly overlap. The electronic energy levels are degenerate because the atoms are identical. When the same two atoms are close together, the probability densities overlap and one cannot say with absolute certainty which electron belongs to which atom. The energy levels are slightly shifted because the electrons now feel the electrical force from the charges (electrons and nuclei) of both atoms. Two electrons that had the same energies in two separated atoms will have slightly different energies and orbitals when the atoms are together. When a large number of atoms are brought together in a solid ($10^{29}/\text{m}^3$), the allowed energy levels form *electronic bands*. An electronic energy band is a collection of a great number of energy levels that are so close together that the energy of the allowed levels may be usefully approximated as a continuous variable. The electrons that would be in 1s energy levels if the atoms were separated make up a band of levels called the electronic 1s

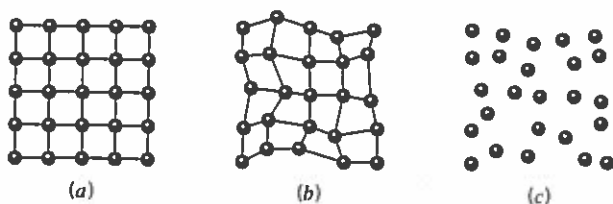


FIGURE 14-1 Condensed states of matter.
(a) Crystalline solid, (b) amorphous solid, and (c) liquid.

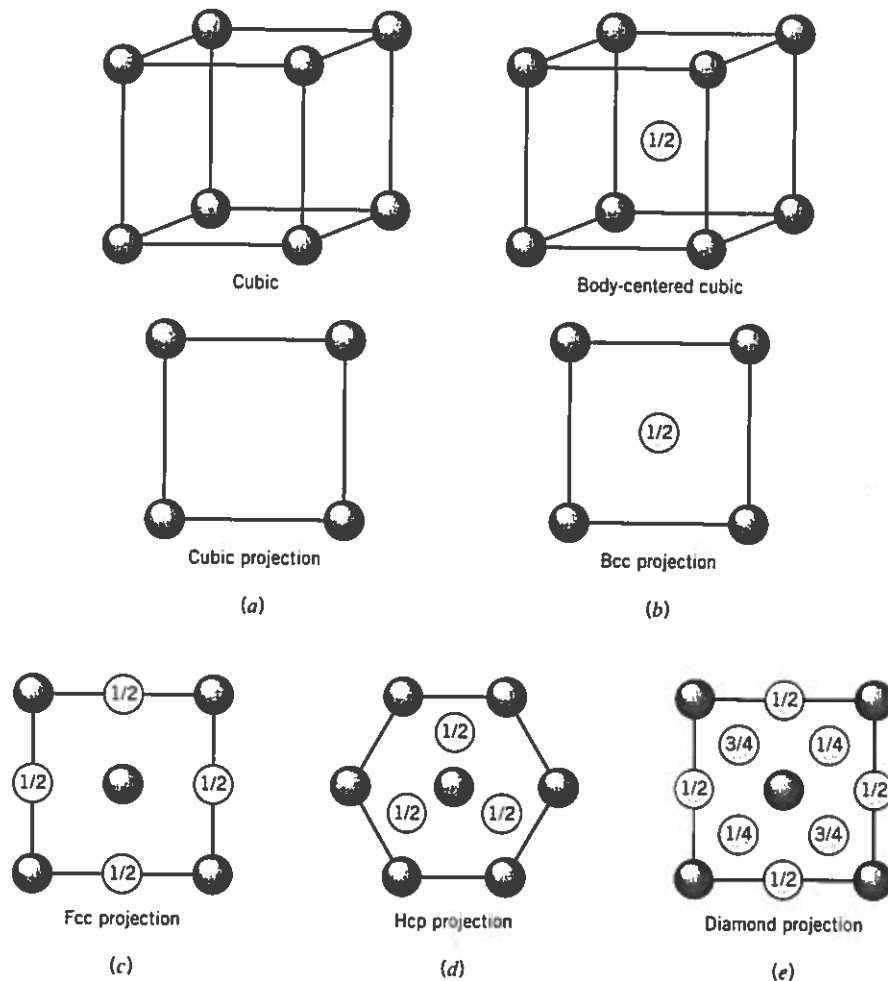


FIGURE 14-2 Crystal unit cells.

The cells are shown projected in a plane. Atoms labeled $1/4$, $1/2$, or $3/4$ are that fraction of the distance to an adjacent plane. (a) Cubic, (b) body-centered cubic, (c) face-centered cubic, (d) hexagonal close packed, and (e) diamond.

and. Similarly, other electronic bands, $2s$ and $2p$, and so on, are formed. In many cases the bands overlap.

Consider the sodium atom ($Z = 11$), which has an electron configuration of $1s^2 2s^2 2p^6 3s^1$. In a sodium crystal, the outer electron in each atom is free to move. In the neighborhood of a nucleus, the potential energy of an electron is nearly spherically symmetric, and the Schrödinger equation can be solved by separation of variables and numerical integration. The main difference between a crystal and a single atom in the solution of the Schrödinger equation is the boundary condition. In a single atom, the wave function goes to zero at infinity, whereas in a crystal the wave function is periodic. The solution is similar to ordinary s , p , d wave functions near

the nuclei and plane waves between the nuclei. The Schrödinger equation may be solved by treating the spacing between atoms in the crystal as a free parameter. The actual crystal will correspond to a specific atomic separation. The result of such a calculation for sodium is shown in Figure 14-4. The horizontal axis (x) is the distance between adjacent atoms. For an atomic separation of 1 nm, the $3s$ and $3p$ levels are clearly separated. In a sodium crystal the actual separation of the atoms (a) corresponds to $x = 0.4$ nm. For an atomic separation of 0.4 nm, the $3s$ and $3p$ levels overlap to form a continuous band. Therefore, the electrons in this band are able to gain an infinitesimally small amount of energy (for example, due to collisions or by the application of an electric field) because of

1 H hcp																	2 He hcp		
3 Li bcc	4 Be hcp													5 B rhom.	6 C diam.	7 N cub.	8 O comp.	9 F comp.	10 Ne fcc
11 Na bcc	12 Mg hcp													13 Al fcc	14 Si diam.	15 P comp.	16 S comp.	17 Cl comp.	18 Ar fcc
19 K bcc	20 Ca fcc	21 Sc hcp	22 Ti hcp	23 V bcc	24 Cr bcc	25 Mn cub.	26 Fe bcc	27 Co bcc	28 Ni bcc	29 Cu fcc	30 Zn hcp	31 Ga comp.	32 Ge diam.	33 As rhom.	34 Se hex	35 Br comp.	36 Kr fcc		
37 Rb bcc	38 Sr fcc	39 Y hcp	40 Zr hcp	41 Nb bcc	42 Mo bcc	43 Tc hcp	44 Ru hcp	45 Rh fcc	46 Pd fcc	47 Ag fcc	48 Cd hcp	49 In tet.	50 Sn diam.	51 Sb rhom.	52 Te hex	53 I comp.	54 Xe fcc		
55 Cs bcc	56 Ba bcc	71 Lu hcp	72 Hf hcp	73 Ta bcc	74 W bcc	75 Re hcp	76 Os hcp	77 Ir fcc	78 Pt fcc	79 Au fcc	80 Hg rhom.	81 Tl hcp	82 Pb fcc	83 Bi rhom.	84 Po cub.	85 At	86 Rn		
87 Fr	88 Ra	103 Lr	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une											

57 La hex.	58 Ce fcc	59 Pr hex.	60 Nd hex.	61 Pm	62 Sm comp.	63 Eu bcc	64 Gd hcp	65 Tb hcp	66 Dy hcp	67 Ho hcp	68 Er hcp	69 Tm hcp	70 Yb fcc
89 Ac fcc	90 Th fcc	91 Pa comp.	92 U comp.	93 Np comp.	94 Pu comp.	95 Am hex	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No

FIGURE 14-3 Crystalline structure of the elements.

The abbreviations are cub. = cubic, comp. = complex, hex. = hexagonal, diam. = diamond, and rhom. = rhombic. Adapted from C. Kittel, *Introduction to Solid State Physics*, Wiley (1986).

the availability of empty states. This property accounts for the electrical conductivity of metals.

The energy bands of sodium have been characterized in one dimension using the parameter x . The one-dimensional view is valid near the nucleus of a given atom because the potential is spherically symmetric. At locations corresponding to the midpoint between atoms, the potential is not spherically symmetric because the distance to the nearest atom depends on the direction that is chosen. Therefore, the details of the energy bands depend on the direction of x .

We now examine the consequences of a partially filled energy band in sodium by considering the propagation of an electron plane wave in a given direction, i_x . Taking the nucleus of an arbitrary atom to be the origin, we choose the direction i_x to be in the direction of one of the closest neighbors, as indicated in Figure 14-5a. Since the crystal structure of sodium is bcc, this direction corresponds to propagation along the diagonal of the unit cell (see Figure 14-2). Figure 14-5b shows the electron energy versus its

wave number (k). In this plot we define a negative wave number to be propagation in the $-i_x$ direction. The energy at $k = 0$ corresponds to the minimum energy of an electron in the 3s band (see Figure 14-4). From this plot we see that the increase in energy with increasing k corresponds very nearly to a free electron, which is characterized by

$$E_k = \frac{p^2}{2m} = \frac{(\hbar k)^2}{2m}. \quad (14.1)$$

This is especially true of electrons that reside near the bottom of the 3s band.

We also notice that there is a discontinuity in the allowed energy at certain values of the wave number. The energy gap occurs when an integer (n) number of electron half-wavelengths is equal to the spacing between atoms:

$$n \frac{\lambda}{2} = a. \quad (14.2)$$

In terms of the electron wave number k , this corresponds to

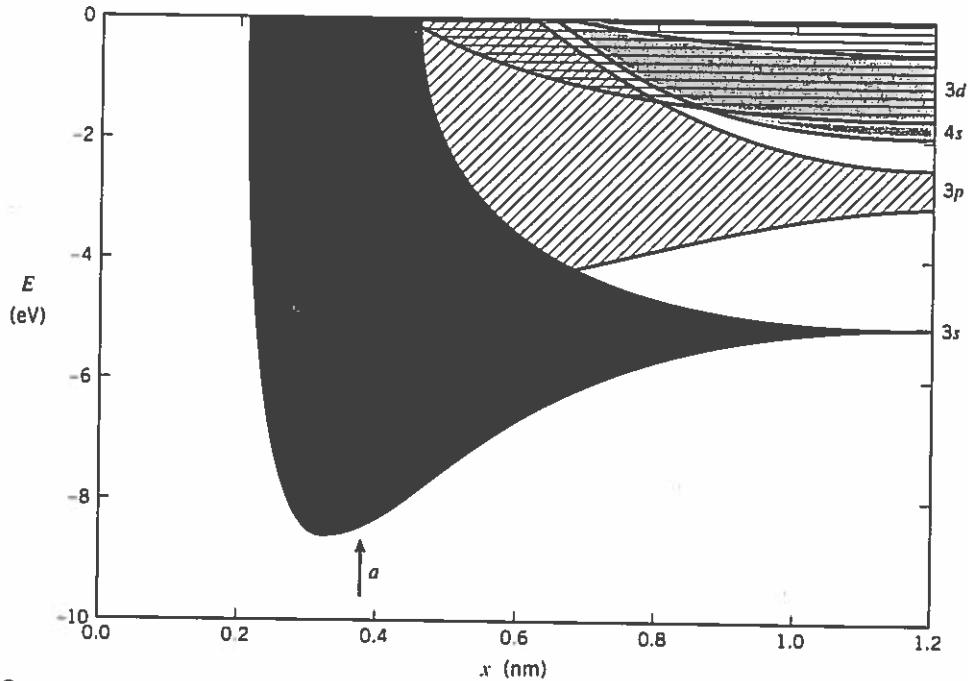


FIGURE 14-4 Outer energy bands in sodium.

The Schrödinger equation is solved for a sodium crystal treating the distance between atoms as a variable (x). At large distances the energy levels are separated, but at small distances they overlap. This explains the conductivity of metals. After J. C. Slater, "Electronic Energy Bands in Metals," *Phys. Rev.* **45**, 794 (1934).

$$k = \pm \frac{2\pi}{\lambda} = \pm \frac{n\pi}{a}. \quad (14.3)$$

This is precisely the Bragg condition for electron scattering first observed by Davison and Germer. Electrons that are incident on the crystal at a certain angle are totally reflected if they have an energy corresponding to the location of the band gap. These electrons cannot exist in the crystal because there are no states! The location of the energy gaps in k space separate the crystal into regions called *Brillouin zones*. The *first* Brillouin zone is bounded by

$$-\frac{\pi}{a} < k < \frac{\pi}{a}, \quad (14.4)$$

the *second* Brillouin zone is bounded by

$$\frac{2\pi}{a} < k < -\frac{\pi}{a} \quad \text{or} \quad \frac{\pi}{a} < k < \frac{2\pi}{a}, \quad (14.5)$$

and so on.

For energetic electrons corresponding to wave numbers in the second zone (see Figure 14-5b), the increase in energy with increasing k is smaller than that of a free

particle. Electrons in this zone may still be described as free particles provided we assign them an effective mass (m^*) that is larger than the electron mass. A particle treated in this fashion is referred to as a quasiparticle. (In some crystals m^* may be smaller than the electron mass.)

EXAMPLE 14-1

Use Figure 14-6b to make an estimate of the effective mass of an electron in zone 2.

SOLUTION:

For a free particle the energy difference (ΔE) between $k = 0$ and $k = 2\pi/a$ is

$$\Delta E \approx 14 \text{ eV} \approx \frac{(\hbar \Delta k)^2}{2m},$$

where $\Delta k = 2\pi/a$. For an electron in the crystal, the actual difference is about 6 eV. Therefore, the effective mass of the electron is given by

$$6 \text{ eV} \approx \frac{(\hbar \Delta k)^2}{2m^*}.$$

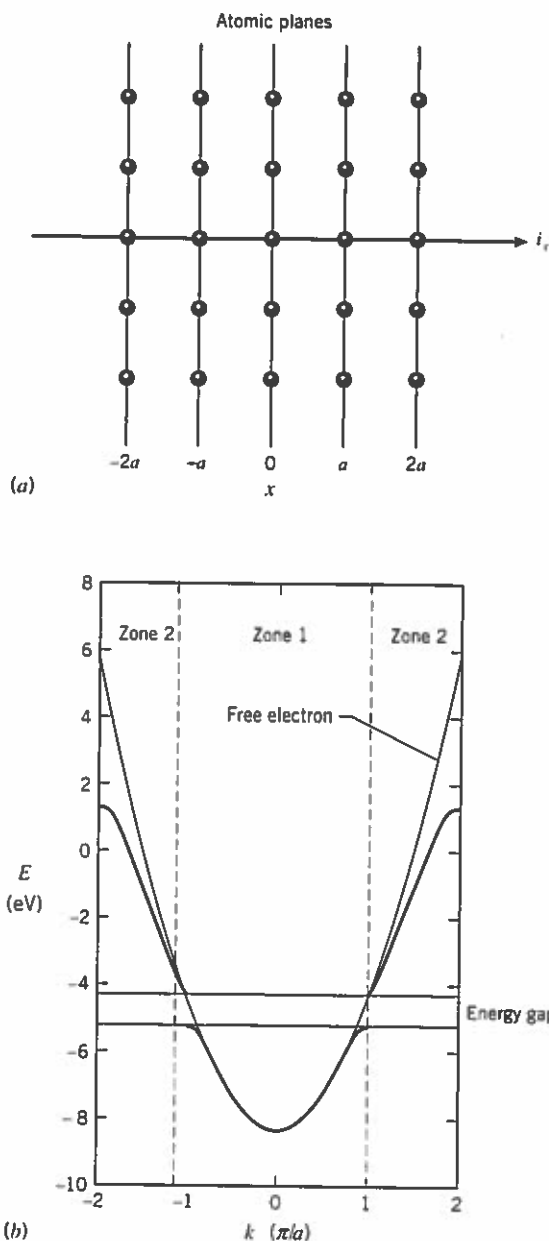


FIGURE 14-5 Electron plane waves propagating in a sodium crystal.

(a) The direction of propagation is chosen to be in the direction from one atom to its nearest neighbor, which is separated by a distance $x = a$. (b) Electron energy versus wave number k . The parabola corresponds to a free electron. After J. C. Slater, "Electronic Energy Bands in Metals," *Phys. Rev.* 45, 794 (1934).

or

$$m^* \approx \left(\frac{14 \text{ eV}}{6 \text{ eV}} \right) m \approx \left(\frac{7}{3} \right) (0.5 \text{ MeV}) = 1.2 \text{ MeV}. \blacksquare$$

All metals have a similar electronic band structure. The outer electronic energy bands of copper ($Z = 29$), which has an electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$, are shown in Figure 14-6. In copper the atomic separation is about 0.27 nanometer. At this separation distance, the $3d$, $4s$, and $4p$ bands overlap to form a single electronic band.

The properties of a solid depend on the details of its electronic band structure. There are three main classes of band structure in solids: (1) the outer band is partially filled, (2) the outer band is completely filled and there is a large energy gap between it and the next band, which is empty, and (3) the outer band is completely filled and there is a small energy gap between it and the next band. The generic band structure of solids is illustrated in Figure 14-7. The case of a partially filled outer band corresponds to a metal. The outer band is called the *conduction band*. The electrons that occupy states in the outer band are called conduction electrons. The electrons are free to move in the partially filled conduction band because there are empty energy levels with infinitesimally higher energy.

In an *insulator* the outermost band that contains electrons is completely full and is separated from the next available empty band by several electronvolts. The electrons cannot move without acquiring enough energy to cross the gap. In an *intrinsic semiconductor* the outer band is also completely full but is separated from the next band by a relatively small energy, roughly 1 electronvolt.

In a metal, the outer electrons occupy a partially filled outer band and are free to move within the metal. In an insulator, the outer electrons completely fill the outer band and the next available band is separated by an energy gap.

EXAMPLE 14-2

Estimate the probability that an energetic electron in an insulator at room temperature is in the conduction band. Take the band gap to be 4 eV.

SOLUTION:

The occupation probability (P) for an electron to be in the next highest band is given by the Fermi-Dirac factor

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

where ΔE is the energy difference between the top of the filled band and the Fermi energy. Since the Fermi energy is in the middle of the energy gap (E_g), we have

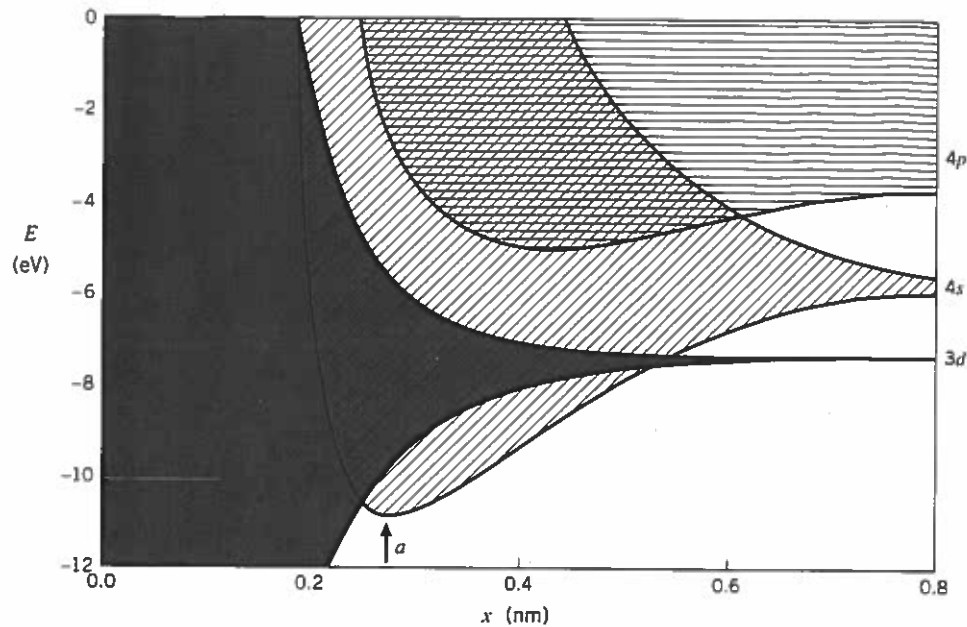


FIGURE 14-6 Energy bands of the outer electrons in copper. After H. M. Kutter, "Energy Bands in Copper," *Phys. Rev.* 48, 664 (1935).

$$\Delta E = \frac{E_g}{2} \approx 2 \text{ eV}.$$

at room temperature,

$$kT \approx \frac{1}{40} \text{ eV},$$

and

$$P = e^{-\Delta E/kT} \approx e^{-80} \approx 10^{-35}.$$

4-2 FERMI ENERGY

Electrons are fermions and obey the Pauli exclusion principle: No two electrons can be found in the same state. The maximum occupation probability for any given state is 1. The Fermi-Dirac distribution function specifies the probability that a given state with energy E is occupied:

$$f_{FD} = \frac{1}{e^{(E-E_F)/kT} + 1}, \quad (14.6)$$

where E_F is the Fermi energy of the metal. At $T = 0 \text{ K}$, the factor $e^{(E-E_F)/kT}$ is either zero if $E < E_F$ or infinite if $E > E_F$. Thus, at $T = 0 \text{ K}$, $f_{FD} = 1$ if $E < E_F$, $f_{FD} = 1/2$ if $E = E_F$, and $f_{FD} = 0$ if $E > E_F$. The physical interpretation of the Fermi

energy at $T = 0 \text{ K}$ is the energy boundary between filled states and empty states. All states with an energy greater than E_F are empty, and all states with an energy less than E_F are filled.

The energy levels of electrons in a metal may be viewed in the context of a finite square-well, as shown in Figure 14-8. The electron energy levels are quantized and only one electron occupies each state, but the levels are very close together so that kinetic energy is treated as a continuous variable. The density of the levels is proportional to the square root of the kinetic energy, as in the case of an ideal gas. The levels are filled to the Fermi energy and empty above the Fermi energy. The work function of the metal (ϕ) is the difference between the height of the potential well (V_0) and the Fermi energy (E_F).

We now derive an expression for the Fermi energy of electrons in a metal. The Fermi energy depends on the number of conduction electrons per volume in the metal. Larger electron densities correspond to larger Fermi energies. In Chapter 12, we calculated the density of states (12.51) for electrons in a metal to be

$$\rho(E) = \frac{8\sqrt{2}\pi m^{3/2}}{h^3} \sqrt{E}, \quad (14.7)$$

where m and E are the electron mass and energy. The number of conduction electrons per volume per unit en-

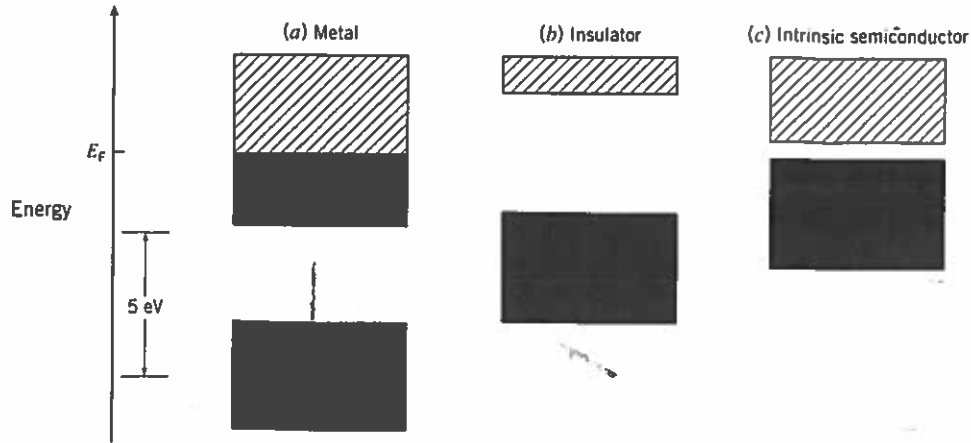


FIGURE 14-7 The generic band structure of solids.

(a) In a metal, the outer band is partially filled. (b) In an insulator, the outer band is completely full and is separated from the next band by several electronvolts. (c) In an intrinsic semiconductor, the outer band is completely full but is separated from the next band by a relatively small energy. The boundary between filled states and empty states is the Fermi energy (E_F).

ergy (dn/dE) is equal to the density of states times the Fermi-Dirac distribution function:

$$\frac{dn}{dE} = \rho(E) f_{FD} = \frac{8\sqrt{2}\pi m^{3/2}}{h^3} \sqrt{E} \frac{1}{e^{(E-E_F)/kT} + 1}. \quad (14.8)$$

An expression for the number of conduction electrons per volume in the metal is obtained by integrating dn/dE :

$$n = \int_0^\infty dE \rho(E) f_{FD} = \frac{8\sqrt{2}\pi m^{3/2}}{h^3} \int_0^\infty dE \sqrt{E} \frac{1}{e^{(E-E_F)/kT} + 1}. \quad (14.9)$$

At $T = 0$ K we may easily do the integration,

$$n = \frac{8\sqrt{2}\pi m^{3/2}}{h^3} \int_0^{E_F} dE \sqrt{E} = \frac{8\sqrt{2}\pi m^{3/2}}{h^3} \left(\frac{2}{3} E_F^{3/2} \right). \quad (14.10)$$

Solving for the Fermi energy, we have

$$E_F = \left(\frac{h^2 c^2}{8 m c^2} \right) \left(\frac{3}{\pi} \right)^{2/3} n^{2/3}. \quad (14.11)$$

The Fermi energy depends on the density of conduction electrons to the two-thirds power.

For atoms with one conduction electron and a diameter of 0.3 nm, the density of conduction electrons is

$$n \approx \left(\frac{1}{0.3 \text{ nm}} \right)^3, \quad (14.12)$$

and the Fermi energy (14.11) is

$$E_F \approx \left(\frac{3}{\pi} \right)^{2/3} \frac{(1240 \text{ eV} \cdot \text{nm})^2}{(0.3 \text{ nm})^2 (8) (5.11 \times 10^5 \text{ eV})} \approx 4 \text{ eV}. \quad (14.13)$$

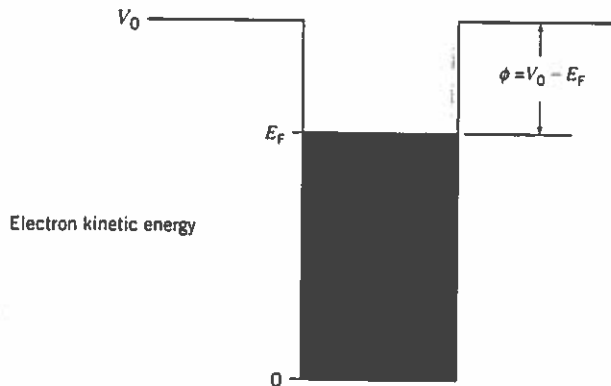


FIGURE 14-8 Electrons in a finite square-well.

The levels are filled up to the Fermi energy and empty above the Fermi energy. The work function of the metal (ϕ) is the difference between the height of the potential well (V_0) and the Fermi energy (E_F). For copper, $V_0 \approx 11$ eV, $E_F \approx 7$ eV, and $\phi = 4$ eV.

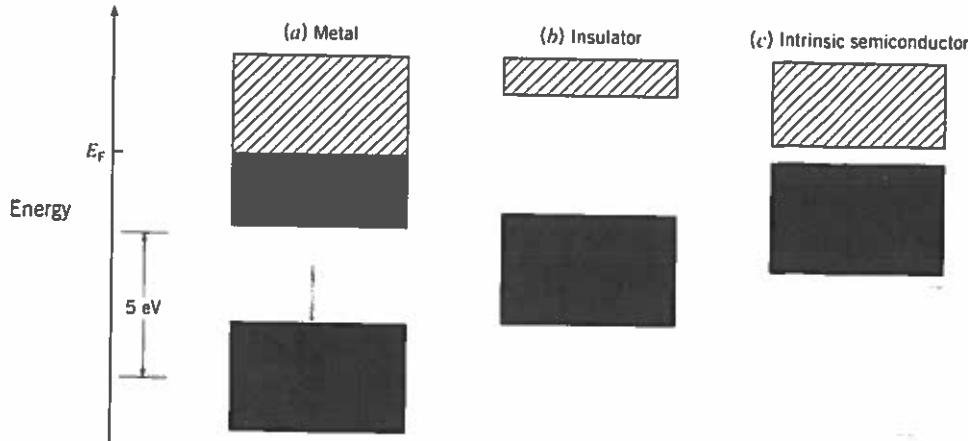


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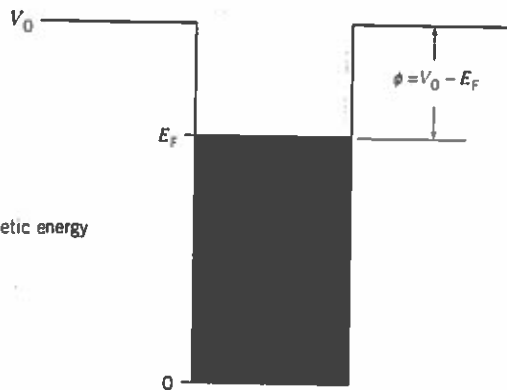


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This is a typical value for the Fermi energy of a metal.

We have calculated the Fermi energy (14.11) at $T = 0$. At temperatures above zero kelvin but well below E_F/k , only those electrons that have energies near the Fermi energy may be thermally excited to higher energy levels because all states with lower energies are completely filled. Therefore, the Fermi energy does not depend on temperature, provided that $E_F \gg kT$, because the Fermi-Dirac distribution does not depend strongly on the temperature as shown in Figure 12-7 (and of course, the density of states is independent of temperature). This is the reason we have chosen to write the temperature dependence of the parameter A (12.35) as $e^{-E_F/kT}$.

EXAMPLE 14-3

The Fermi energy of potassium is determined to be 2.1 eV. The atomic mass of potassium is 39 and the density of potassium is $8.6 \times 10^2 \text{ kg/m}^3$. Calculate the number of conduction electrons per atom.

SOLUTION:

Since 0.039 kg of potassium is one mole of atoms, the number of atoms per volume (n_a) is

$$n_a = \frac{\rho N_A}{0.039 \text{ kg}} = \frac{(8.6 \times 10^2 \text{ kg/m}^3)(6.0 \times 10^{23})}{0.039 \text{ kg}} \\ \approx 1.3 \times 10^{28} \text{ m}^{-3}.$$

The number of conduction electrons per volume is

$$n = \frac{8\pi}{3h^3 c^3} (2E_F mc^2)^{3/2} \\ = \frac{8\pi [(2)(2.1 \text{ eV})(0.51 \times 10^6 \text{ eV})]^{3/2}}{(3)(1240 \text{ eV} \cdot \text{nm})^3} \\ \approx 1.4 \times 10^{28} \text{ m}^{-3}.$$

The number of conduction electrons per atom is

$$\frac{N}{\text{atom}} = \frac{n}{n_a} \approx \frac{1.4 \times 10^{28} \text{ m}^{-3}}{1.3 \times 10^{28} \text{ m}^{-3}} \approx 1.$$

The electron configuration of potassium ($Z = 19$) is $1s^2 2s^2 2p^6 3s^2 3p^4 4s$. The conduction electron is the 4s electron. ■

EXAMPLE 14-4

Estimate the Fermi energy of copper, which has a density $8.9 \times 10^3 \text{ kg/m}^3$.

SOLUTION:

Since copper has a single 4s electron (see Figure 9-7), there is one conduction electron per atom. The atomic mass of copper is $A = 63.5$. The density of conduction electrons is

$$n = \frac{N_A \rho}{A(10^{-3} \text{ kg})} = \frac{(6.02 \times 10^{23})(9 \times 10^3 \text{ kg/m}^3)}{(63.5)(10^{-3} \text{ kg})} \\ = 8.5 \times 10^{28} \text{ m}^{-3}.$$

The Fermi energy (14.11) is

$$E_F = \left(\frac{h^2 c^2}{8mc^2} \right) \left(\frac{3}{\pi} \right)^{2/3} n^{2/3} \\ = \frac{(1240 \text{ eV} \cdot \text{nm})^2}{(8)(5.11 \times 10^5 \text{ eV})} \left(\frac{3}{\pi} \right)^{2/3} (8.5 \times 10^{28} \text{ m}^{-3})^{2/3} \\ \approx 7.0 \text{ eV}. \quad \blacksquare$$

EXAMPLE 14-5

Estimate the average energy of a conduction electron in copper at low temperatures.

SOLUTION:

The average energy is

$$\langle E \rangle = \frac{\int_0^\infty dE E \rho(E) f_{FD}}{\int_0^\infty dE \rho(E) f_{FD}}.$$

At low temperatures the Fermi-Dirac distribution function is unity for

$$E < E_F,$$

and zero for

$$E > E_F.$$

The average conduction electron energy is

$$\langle E \rangle = \frac{\int_0^{E_F} dE E \rho(E)}{\int_0^{E_F} dE \rho(E)}.$$

Since the density of states is proportional to $E^{1/2}$, we have

$$\langle E \rangle = \frac{\int_0^{E_F} dE E^{3/2}}{\int_0^{E_F} dE \sqrt{E}} = \frac{\frac{2}{5} E_F^{5/2}}{\frac{2}{3} E_F^{3/2}} = \frac{3}{5} E_F.$$

The Fermi energy for copper was calculated in the previous example. The average energy is 3/5 of the Fermi energy:

$$\langle E \rangle \approx \left(\frac{3}{5} \right) (7.0 \text{ eV}) \approx 4 \text{ eV}. \quad \blacksquare$$

14-3 HEAT CAPACITY

The Law of Dulong and Petit

The heat capacity is defined to be the amount of energy needed to raise the temperature of a specified amount of material (usually taken to be 1 mole) by 1 K. The heat capacity is usually expressed with either the volume (C_V) or the pressure (C_P) held constant. The heat capacity at constant volume is

$$C_V = \left(\frac{\partial E_{\text{tot}}}{\partial T} \right)_V, \quad (14.14)$$

where E_{tot} is the total energy of the atoms. When energy is added to a solid, it takes the form of atomic vibrations. In the nineteenth century, motivated by the observation that the heat capacities of many solids at room temperature were identical, Dulong and Petit used the equipartition theorem (2.73) to calculate the energy associated with each atom. For six degrees of freedom corresponding to vibration and translation in three dimensions, atomic oscillators in a solid should have an average energy of $3kT$ per atom. This gives a heat capacity that is independent of temperature:

$$\begin{aligned} C_V &= \frac{\partial E_{\text{tot}}}{\partial T} = \frac{\partial}{\partial T} (3kTN_A/\text{mole}) \\ &= 3kN_A/\text{mole} \approx 25 \text{ J/K} \cdot \text{mole}. \end{aligned} \quad (14.15)$$

For many solids at room temperature, the law of Dulong and Petit (14.15) gives the observed value of the heat capacity. When the technology became available to measure heat capacities of solids at low temperatures, an interesting puzzle was discovered. For insulators, the heat capacity is observed to vary as T^3 at low temperatures ($T \ll 300 \text{ K}$). Figure 14-9a shows the heat capacity

of pure silicon plotted as a function of T^3 . Pure silicon is an insulator at sufficiently low temperatures because it has a band gap of 1.1 eV (see Figure 14-7). All insulators have a similar variation of the heat capacity with temperature except that the coefficient of the T^3 term varies from material to material.

The law of Dulong and Petit ignores the contribution of electrons to the heat capacity. If each atom in a metal had

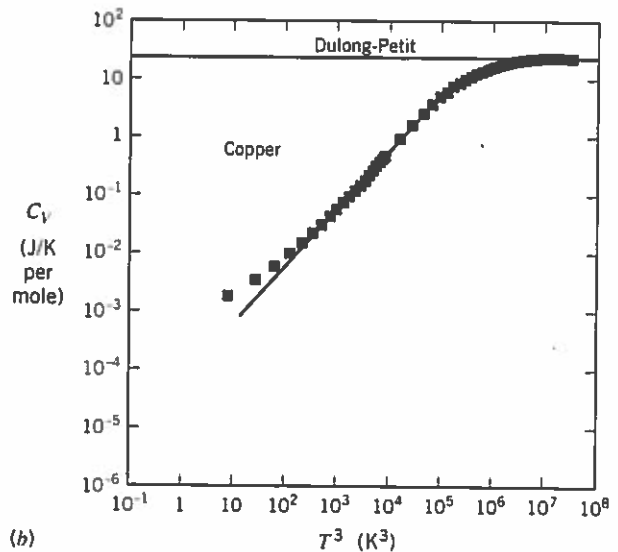
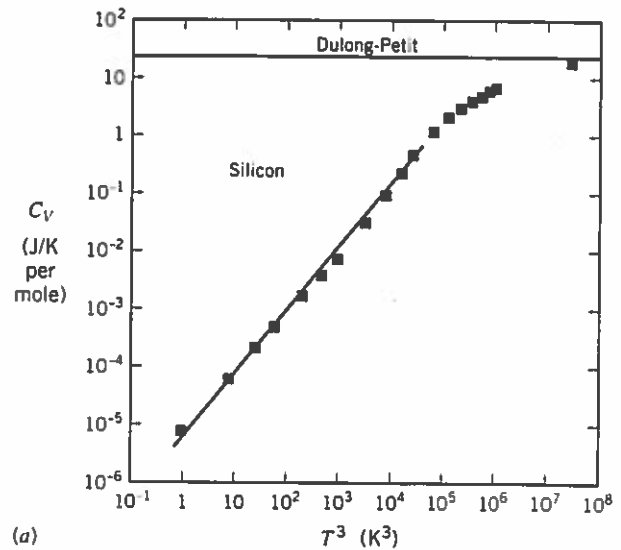


FIGURE 14-9 Temperature dependence of heat capacity.

The sloped solid line indicates a T^3 behavior. (a) Pure silicon, an insulator, and (b) copper, a metal.

ne free electron, then the motion of these electrons would contribute $3N_A k/2$ per mole to the heat capacity. Free electrons should increase the heat capacity of a metal by 0% in this simple analysis! The lack of understanding of heat capacities was *the* central problem in physics at the turn of the century. *How can free electrons account for the electrical conductivity of metals without contributing significantly to the heat capacity?*

The measured heat capacity of copper as a function of temperature is shown in Figure 14-9b. The temperature dependence of the heat capacity of a metal is qualitatively the same as for an insulator, except that there is a deviation from the T^3 dependence at the very lowest temperatures ($T < 10$ K). This deviation is caused by the electrons. The temperature dependence of the heat capacity of insulators and metals is explained in the following sections.

The Result of Einstein

In 1907, Einstein was qualitatively able to explain the temperature variation in the heat capacity of solids by applying the Planck distribution to the energies of the atomic oscillators. The average energy of a one-dimensional atomic oscillator with a vibrational frequency f is

$$\langle E \rangle = \frac{hf}{e^{hf/kT} - 1}. \quad (14.16)$$

The total energy for a collection of oscillators vibrating in three dimensions is

$$E_{\text{tot}} = \langle E \rangle \left(\frac{N_A}{\text{mole}} \right) = \frac{3hfN_A}{e^{hf/kT} - 1} \text{ mole}^{-1}. \quad (14.17)$$

This gives a heat capacity of

$$C_V = \frac{\partial E_{\text{tot}}}{\partial T} = \frac{3N_A k \left(\frac{hf}{kT} \right)^2 e^{hf/kT}}{(e^{hf/kT} - 1)^2} \text{ mole}^{-1}. \quad (14.18)$$

EXAMPLE 14-6

Show that the heat capacity (C_V) in the Einstein model (14.18) agrees with the law of Dulong and Petit (14.15) at high temperatures.

SOLUTION:

For large temperatures ($kT \gg hf$) we have

$$e^{hf/kT} \approx 1 + \frac{hf}{kT}.$$

The heat capacity (14.31) becomes

$$\begin{aligned} C_V &\approx \frac{3N_A k \left(\frac{hf}{kT} \right)^2 \left(1 + \frac{hf}{kT} \right)}{\left(\frac{hf}{kT} \right)^2} \text{ mole}^{-1} \\ &= 3N_A k \left(1 + \frac{hf}{kT} \right) \approx 3N_A k \text{ mole}^{-1}. \quad \blacksquare \end{aligned}$$

At large temperatures, the Einstein heat capacity (14.18) approaches the result of Dulong and Petit ($3kN_A/\text{mole}$). The appropriate frequency (f) for each element was determined empirically. The quantity hf/k is called the *Einstein temperature* (T_E). The Einstein result for the temperature dependence gives reasonable but *not exact* agreement with experiments.

The Debye Model

In 1912, Peter Debye developed a model for solids in which the crystal vibrates as a whole. Debye considered the vibrations in the solid to be stationary sound waves analogous to electromagnetic standing waves in a cavity. The vibrational energy of the crystal is quantized in units of hf and one quantum is called a *phonon*. For phonons in a crystal, the calculation of the total energy is similar to that for electromagnetic waves in a cavity. The principle difference is that the number of modes is not infinite at small frequencies, as it is for electromagnetic waves, but is limited by the total number of degrees of freedom of all the atoms in the crystal.

We first calculate the density of states, the number of photon states per volume per unit energy. The density of states is proportional to the phonon energy squared, the same as for a photon (i.e., the energy of a phonon is proportional to its momentum). We write this as

$$\rho(E) = AE^2, \quad (14.19)$$

where A is a constant. To account for the finite number of modes, Debye imposed a cutoff in the density of states corresponding to the maximum number of degrees of freedom of the atoms in the crystal. The maximum allowed phonon frequency is called the *Debye frequency* (f_D). The total number of degrees of freedom for a single atom is 3, corresponding to vibration in the x , y , and z directions. The total number of degrees of freedom for 1

mole ($3N_A$) is equal to the total number of states:

$$\begin{aligned} 3N_A &= V \int_0^{hf_D} dE \rho(E) = VA \int_0^{hf_D} dE E^2 \\ &= VA \frac{(hf_D)^3}{3}, \end{aligned} \quad (14.20)$$

where V is the volume. Solving for the constant A , we have

$$A = \frac{9N_A}{V(hf_D)^3}, \quad (14.21)$$

and the density of states is

$$\rho(E) = AE^2 = \frac{9N_A E^2}{V(hf_D)^3}. \quad (14.22)$$

The total energy per volume of 1 mole of atoms in the crystal is

$$\begin{aligned} \frac{E_m}{V} &= \int_0^{hf_D} dE \frac{\rho(E) E}{e^{E/kT} - 1} \\ &= \frac{9N_A}{V(hf_D)^3} \int_0^{hf_D} dE \frac{E^3}{e^{E/kT} - 1}. \end{aligned} \quad (14.23)$$

With the change of variables,

$$x \equiv \frac{E}{kT}, \quad (14.24)$$

the total energy for 1 mole becomes

$$E_m = \frac{9N_A (kT)^4}{(hf_D)^3} \int_0^{hf_D/kT} dx \frac{x^3}{e^x - 1}. \quad (14.25)$$

The integral may not be evaluated in closed form. At small temperatures, the total energy in phonons is proportional to the fourth power of the temperature. The same is true for the total energy of photons in a cavity; indeed, the two calculations are nearly identical.

The molar heat capacity (C_V) is obtained by differentiating E_m (14.25) with respect to T . At small temperatures, the integral is equal to $\pi^4/15$ and the molar heat capacity is

$$\begin{aligned} C_V &= \frac{\partial E_m}{\partial T} \approx \frac{\partial}{\partial T} \left(\frac{9\pi^4 N_A (kT)^4}{15(hf_D)^3} \right) \\ &= \frac{12\pi^4 N_A k (kT)^3}{5(hf_D)^3}. \end{aligned} \quad (14.26)$$

With the definition of *Debye temperature* (T_D),

$$T_D \equiv \frac{hf_D}{k}, \quad (14.27)$$

the molar heat capacity becomes

$$C_V = \frac{12\pi^4}{5} N_A k \left(\frac{T}{T_D} \right)^3. \quad (14.28)$$

The Debye model gives a quantitative account of the temperature dependence of the heat capacity of an insulator (see Figure 14-9a). The slope of C_V versus T^3 for small T in an insulator is proportional to T_D^{-3} . Measurement of the temperature dependence of the heat capacity gives a Debye temperature of 645 K for silicon and 2230 K for diamond.

The physical meaning of the Debye temperature is that kT_D is the maximum energy of a vibrational mode (phonon). There is a relationship between the temperature at which a solid melts (T_m) and the Debye temperature. The total energy that a solid can absorb at the melting point is proportional to kT_m . The potential energy of a single atom oscillating with frequency (ω) is

$$V = \frac{1}{2} M \omega^2 x^2, \quad (14.29)$$

where M is the mass of the atom and x is its displacement. The total energy of all the atoms is proportional to $\omega^2 = (kT_D/\hbar)^2$. With the assumption that the crystal melts when the amplitude of the oscillations reaches a certain fraction of the spacing between atoms (d_{atom}), we have

$$kT_m \propto M (kT_D)^2 d_{\text{atom}}^2, \quad (14.30)$$

or

$$T_D \propto \frac{1}{d_{\text{atom}}} \sqrt{\frac{T_m}{M}}. \quad (14.31)$$

The relationship between Debye temperature and melting temperature of solids is illustrated in Figure 14-10 for two different crystal types, diamond and fcc.

The vibrational energy in a solid is quantized; the quanta are called phonons. The quantization leads to a total vibrational energy which is proportional to T^4 and a heat capacity which is proportional to T^3 at low temperatures. The maximum phonon energy is a characteristic of the solid and is written as kT_D , where T_D is called the Debye temperature.

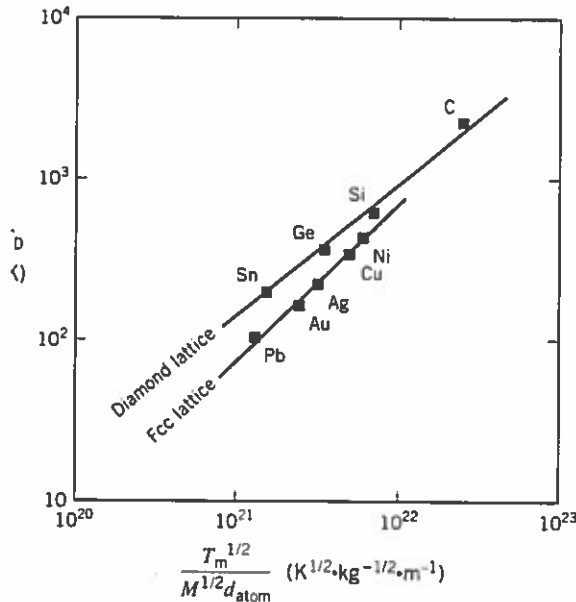


FIGURE 14-10 Relationship between the Debye temperature and the melting point of solids.

Electronic Heat Capacity

The heat capacity of a metal deviates from the Debye model (14.28) at extremely small temperatures e.g., $T < 1$ K for copper as shown in Figure 14-9b. The Debye model works well for a metal except at the lowest temperatures. Evidently, the contribution of electrons to the heat capacity of a metal plays no role unless T is very small. We now examine this property in more detail.

The central problem is to understand how a conduction electron behaves as a free particle and does not contribute a relatively large amount to the heat capacity. A metal contains a large number of free electrons, one or more per atom. When thermal energy is supplied to the metal, the classical theory predicts that the free conduction electrons increase their kinetic energy in proportion to the temperature increase of the metal. Thus, the electronic heat capacity is predicted to be large, that is, a large amount of energy would make a small increase in temperature because there are so many free electrons that can gain kinetic energy. Since the average kinetic energy of a free electron is $3kT/2$, we expect that the contribution to the electronic heat capacity (C_{el}) from conduction electrons to be

$$C_{el} = \frac{3kN_A}{2} \text{ mole}^{-1}. \quad (14.32)$$

The observed electronic heat capacities of metals are smaller than this by more than an order of magnitude.

Furthermore, the electronic heat capacity is not the same for all metals and is temperature dependent.

The solution of the electronic heat capacity problem comes from the kinetic energy distribution of the conduction electrons in the metal. These conduction electrons do not obey Maxwell-Boltzmann statistics. It is the Maxwell-Boltzmann distribution that leads to an average particle kinetic energy of $3kT/2$ and therefore an electronic heat capacity of $3k/2$ per particle.

The electrons in the metal obey Fermi-Dirac statistics. When energy is supplied to the metal, the average conduction electron cannot be promoted to higher energy because the neighboring energy levels are all occupied. The Pauli exclusion principle prevents most of the electrons from gaining kinetic energy. Only those electrons that have energies near the Fermi energy can be excited to higher energy levels. The fraction of conduction electrons that can be excited is just the fraction that have an energy within a few times kT of the Fermi energy. We may write this fraction as

$$f_{el} \approx \frac{kT}{E_F}. \quad (14.33)$$

The increase in kinetic energy for each conduction electron that is excited is approximately kT . Therefore, the electronic heat capacity of free electrons is roughly

$$\begin{aligned} C_{el} &\approx N_A \frac{d}{dT} \left[(kT) \left(\frac{kT}{E_F} \right) \right] \text{ mole}^{-1} \\ &= \frac{2N_A k^2 T}{E_F} \text{ mole}^{-1}. \end{aligned} \quad (14.34)$$

This approximation of the electronic heat capacity gives the correct order of magnitude and the correct temperature dependence.

The conduction electrons do not contribute significantly to the heat capacity of a metal at room temperature because only a small fraction of the electrons, those near the Fermi energy, may gain energy when the temperature is increased.

We now make a more accurate determination of C_{el} . Consider a metal at a temperature T_1 . The average energy per conduction electron is

$$\langle E_k(T_1) \rangle = \frac{1}{n} \int_0^\infty dE E \rho(E) f_{FD}(E, T_1), \quad (14.35)$$

where n is the density of electrons, $\rho(E)$ is the density of states, and f_{FD} is the probability that a given state is occupied. Recall that the density of states is proportional to $E^{1/2}$. At a slightly higher temperature, $T_2 = T_1 + \Delta T$, the average kinetic energy per conduction electron is

$$\langle E_k(T_2) \rangle = \frac{1}{n} \int_0^\infty dE E \rho(E) f_{FD}(E, T_2). \quad (14.36)$$

The electronic heat capacity is

$$C_{el} = \frac{N_A}{n} \frac{\langle E_k(T_2) \rangle - \langle E_k(T_1) \rangle}{T_2 - T_1} \text{mole}^{-1}. \quad (14.37)$$

The temperature dependence is due to the Fermi-Dirac distribution function. The change in electron energies occurs only near the Fermi energy. Thus, we may write the electronic heat capacity as

$$C_{el} = \frac{N_A}{n} \text{mole}^{-1} \int_0^\infty dE (E - E_F) \rho(E) \frac{df_{FD}}{dT}. \quad (14.38)$$

We now reduce this integral for the heat capacity to a simpler form. With the change of variables

$$x \equiv \frac{E - E_F}{kT}, \quad (14.39)$$

the Fermi-Dirac distribution function is

$$f_{FD} = \frac{1}{e^x + 1}. \quad (14.40)$$

The derivative is

$$\frac{df_{FD}}{dx} = -\frac{e^x}{(e^x + 1)^2}, \quad (14.41)$$

or

$$\begin{aligned} \frac{df_{FD}}{dT} &= \frac{df_{FD}}{dx} \frac{dx}{dT} \\ &= \frac{e^x}{(e^x + 1)^2} \frac{(E_F - E)}{kT^2} \\ &= \frac{1}{T} \frac{xe^x}{(e^x + 1)^2}. \end{aligned} \quad (14.42)$$

The electronic heat capacity is

$$\begin{aligned} C_{el} &= \frac{N_A}{n} \text{mole}^{-1} \int_0^\infty dE (E - E_F) \rho(E) \frac{df_{FD}}{dT} \\ &= \frac{N_A k^2 T}{n} \text{mole}^{-1} \int_{-E_F/kT}^\infty dx \rho(x) \frac{x^2 e^x}{(e^x + 1)^2}. \end{aligned} \quad (14.43)$$

The integrand is almost zero except when x is near zero, which corresponds to E near E_F . This allows us to remove the density of states factor from the integrand and evaluate it at the Fermi energy. We can also change the limits of integration from minus infinity to infinity without significantly changing the result. Therefore,

$$C_{el} = \frac{N_A k^2 T}{n} \text{mole}^{-1} \rho(E_F) \int_{-\infty}^{\infty} dx \frac{x^2 e^x}{(e^x + 1)^2}. \quad (14.44)$$

The integral is equal to $\pi^2/3$. The electronic heat capacity is

$$C_{el} = \frac{\pi^2 N_A k^2 T \rho(E_F)}{3n} \text{mole}^{-1}. \quad (14.45)$$

We now need to evaluate the density of states at the Fermi energy divided by the electron density. The number of states per volume (12.50) is

$$n_s = \frac{N}{V} = \frac{8\sqrt{2}\pi m^{3/2}}{h^3} \left(\frac{2}{3} E_F^{3/2} \right). \quad (14.46)$$

Taking the logarithm, we have

$$\ln(n_s) = \frac{3}{2} \ln E_F + B, \quad (14.47)$$

where B is a constant. Taking the derivative, we find

$$\frac{dn_s}{n} = \frac{3}{2} \frac{dE_F}{E_F}, \quad (14.48)$$

$$\rho(E) = \frac{dn_s}{dE} = \frac{3n_s}{2E_F}, \quad (14.49)$$

and

$$\frac{\rho(E_F)}{n} = \frac{3}{2E_F}. \quad (14.50)$$

Finally, we arrive at the result for the electronic heat capacity:

$$C_{el} = \frac{\pi^2 N_A k^2 T}{2 E_F} \text{ mole}^{-1}. \quad (14.51)$$

The typical value of the Fermi energy is 4 eV. The contribution to the heat capacity per electron calculated using Fermi-Dirac statistics is smaller than the classical value $(3kN_A/2)$ by a factor of

$$\begin{aligned} \frac{\left(\frac{\pi^2 N_A k^2 T}{2 E_F} \right)}{\left(\frac{3 N_A k}{2} \right)} &= \frac{\pi^2}{3} \frac{kT}{E_F} \\ &\approx 3 \frac{\left(\frac{1}{40} \text{ eV} \right)}{4 \text{ eV}} \approx 0.02. \end{aligned} \quad (14.52)$$

Thus, the prediction of the electronic heat capacity at room temperature using quantum statistics is lower than the classical prediction by about a factor of 50.

Electronic heat capacities of metals at room temperature are shown in Figure 14-11. Our simple application of

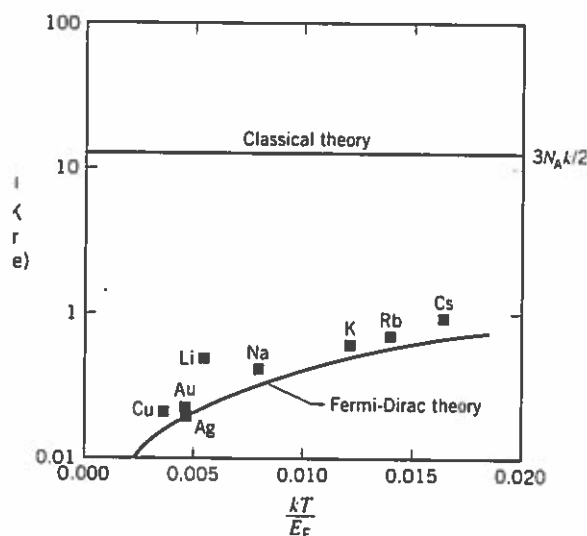


FIGURE 14-11 Electronic heat capacities of metals at room temperature.

The units are eV/K per conduction electron. The classical prediction is $(3/2)k$, independent of temperature. The prediction using Fermi-Dirac statistics is $(\pi^2/2)(T/T_F)k$. The measured electronic heat capacities are shown as solid squares. The Fermi-Dirac theory gives the correct order of magnitude for the electronic heat capacity, whereas the classical prediction is too high by factors of 10 to 50.

Fermi-Dirac statistics gives the correct order of magnitude for the electronic heat capacity, while the classical prediction is too high by factors of 10 to 50. Our application of the Fermi-Dirac theory does not predict the electronic heat capacities exactly because we have ignored interactions of the electrons with the metallic lattice and with other electrons.

The total heat capacity of a metal is obtained by adding the electronic contribution (14.51) to the phonon contribution (14.28),

$$\begin{aligned} C_{tot} &= C_{el} + C_V \\ &= \left(\frac{\pi^2 k^2 N_A}{2 E_F} \text{ mole}^{-1} \right) T \\ &\quad + \left(\frac{12 \pi^4 N_A k}{5 T_D^3} \text{ mole}^{-1} \right) T^3. \end{aligned} \quad (14.53)$$

Note that we have assumed that there is one conduction electron per atom. The electronic heat capacity is the dominant contribution to the total heat capacity of a metal at low temperatures because it varies with temperature as T , while the phonon contribution varies as T^3 . If we plot C_{tot}/T versus T^2 , we expect a linear relationship. This is shown for copper in Figure 14-12.

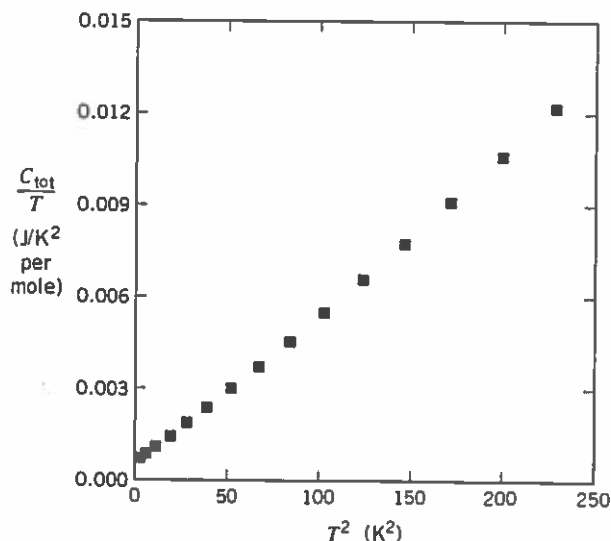


FIGURE 14-12 Heat capacity of copper at low temperature.

14-4 OHM'S LAW

We now discuss the electrical properties of metals and insulators. We shall concentrate on metals first. There is a remarkably simple relationship between the voltage and current in a conductor. Ohm's law states that the potential difference (V) along the length of an electrical conductor is directly proportional to the current (I) in the conductor. The constant of proportionality is called the resistance (R) of the conductor. The familiar form of Ohm's law is

$$V = IR. \quad (14.54)$$

Ohm's law is due to the properties of electrons in materials and hence does not have universal application. For example, Ohm's law does not hold for electrons in a vacuum! (Recall the example of the vacuum tubes discussed in Chapter 2.)

The resistance of a wire is proportional to the length (L) and inversely proportional to the cross-sectional area (A),

$$R = \frac{\rho L}{A}, \quad (14.55)$$

where the constant of proportionality (ρ) is called the *resistivity*. The resistivity is a property of the material. Ohm's law (14.54) for the wire becomes

$$V = \frac{I\rho L}{A}. \quad (14.56)$$

The electric field inside the wire is

$$E = \frac{V}{L}. \quad (14.57)$$

We define J to be the current per cross-sectional area in the wire,

$$J = \frac{I}{A}. \quad (14.58)$$

Combining these results, we get the following expression for Ohm's law:

$$J = \frac{E}{\rho}. \quad (14.59)$$

The *conductivity* (σ) is defined to be the reciprocal of the resistivity

$$\sigma \equiv \frac{1}{\rho}, \quad (14.60)$$

and Ohm's law (14.59) may be written

$$J = \sigma E. \quad (14.61)$$

The SI unit of resistance is the ohm (Ω). One ohm is equal to one volt per ampere:

$$1\Omega = 1\text{ V/A} = 1\text{ V}\cdot\text{s/C}. \quad (14.62)$$

The units of resistivity are ohm-meters. The units of conductivity are inverse ohm-meters. Metals have a large conductivity. The best electrical conductor is silver, which has a conductivity of $6.2 \times 10^7 \Omega^{-1}\cdot\text{m}^{-1}$ at room temperature. In contrast, the electrical conductivity of diamond is about $10^{-12} \Omega^{-1}\cdot\text{m}^{-1}$.

The conduction electrons in a metal may be thought of as a gas of particles in thermal equilibrium obeying Fermi-Dirac statistics. The electrons behave as free particles (see Figure 14-5b) except they interact with the lattice. We may view this electron-lattice interaction as electron-phonon scattering. The energy scale of the conduction electrons is set by E_F and the energy scale of the phonons is set by kT_D . Since $E_F \gg kT_D$, the energy of the electrons is much larger than the energy of the phonons. Therefore, in electron-phonon collisions the direction of the electron is easily changed but its energy does not change. The electron-phonon interaction is the cause of resistance in a metal because the time between collisions limits the length of time that an electron can be accelerated between collisions before its direction of travel is randomly changed. Recall that a typical value for the Fermi energy (E_F) in a metal is about 4 eV. The speed of an electron that has a kinetic energy equal to the Fermi energy is called the *Fermi speed* (v_F). The typical Fermi speed of an electron is

$$\begin{aligned} v_F &= c \sqrt{\frac{2E_F}{mc^2}} \\ &= (3 \times 10^8 \text{ m/s}) \sqrt{\frac{(2)(4 \text{ eV})}{5.1 \times 10^5 \text{ eV}}} \\ &\approx 1.2 \times 10^6 \text{ m/s}. \end{aligned} \quad (14.63)$$

The speed of the most energetic outer electrons in a metal is the same order of magnitude as the speed of an electron in the hydrogen atom.

EXAMPLE 14-7

Calculate the Fermi speed for copper.

SOLUTION:

The Fermi energy is 7.0 eV. The Fermi speed (v_F) in units of c is

$$\frac{v_F}{c} = \sqrt{\frac{2E_F}{mc^2}} = \sqrt{\frac{(2)(7 \text{ eV})}{5.1 \times 10^5 \text{ eV}}} \approx 5.2 \times 10^{-3}.$$

The electron is nonrelativistic. The Fermi speed is

$$v_F = (5.2 \times 10^{-3})(3.0 \times 10^8 \text{ m/s}) = 1.6 \times 10^6 \text{ m/s.} \blacksquare$$

When an electric field is applied, the electrons acquire an average *drift speed* (v_d). This drift speed is related to the current per area (J) and density of conduction electrons (n) by

$$J = nev_d. \quad (14.64)$$

A large current is made up of a very large number of electrons having a small drift speed. We now make an estimate of the drift speed in a copper wire that has a cross-sectional area of 1 millimeter squared and carries a current of 1 ampere. The number of conduction electrons per volume is approximately 10^{29} m^{-3} . The drift speed may be calculated from the current density (14.64) to be

$$\begin{aligned} v_d &= \frac{J}{ne} \approx \frac{10^6 \text{ C} \cdot \text{s}^{-1} \cdot \text{m}^{-2}}{(10^{29} \text{ m}^{-3})(1.6 \times 10^{-19} \text{ C})} \\ &\approx 10^{-4} \text{ m/s.} \end{aligned} \quad (14.65)$$

The drift speed of the electrons is extremely small compared to the Fermi speed of the electrons. It is this property that explains Ohm's law.

The drift speed is equal to the acceleration times the average time between electron-phonon collisions, the *relaxation time*. The distance that the electron travels between collisions is the mean free path (d). The relaxation time (τ) depends on d and the Fermi speed. Writing the drift speed as the acceleration (force/mass) multiplied by the average time between collisions, we have

$$v_d = \frac{eE}{m} \tau = \frac{eE}{m} \frac{d}{v_F}. \quad (14.66)$$

The current per area (14.64) is

$$J = \frac{ne^2 d}{mv_F} E. \quad (14.67)$$

We see that Ohm's law (14.61) is satisfied with

$$\sigma = \frac{ne^2 d}{mv_F}. \quad (14.68)$$

There are two pieces of quantum mechanics in the description of the conductivity: (1) Fermi-Dirac statistics are needed to determine the Fermi speed (v_F), and (2) the mean free path between collisions (d) depends on the wave nature of the electron and the presence of impurities in the sample. The value of d is typically 100 times larger than the lattice spacing.

EXAMPLE 14-8

The conductivity of copper is measured to be $5.9 \times 10^7 \Omega^{-1} \cdot \text{m}^{-1}$ at room temperature. Calculate the mean free path for a conduction electron in copper.

SOLUTION:

The mean free path is

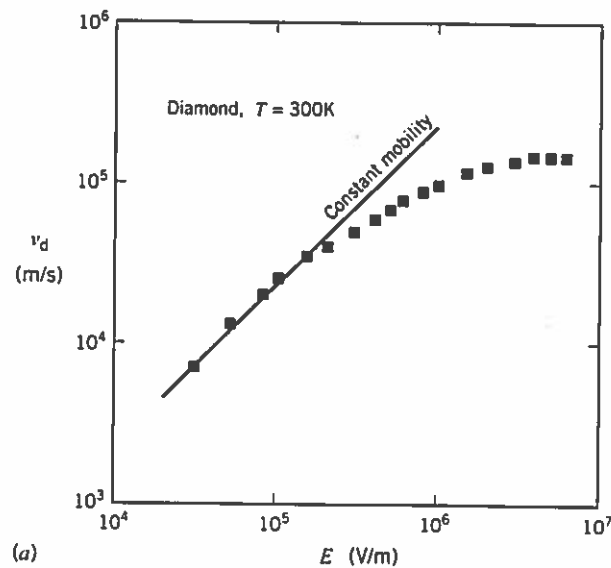
$$\begin{aligned} d &= \frac{\sigma m v_F}{ne^2} \\ &= \frac{(5.9 \times 10^7 \Omega^{-1} \cdot \text{m}^{-1})(9.1 \times 10^{-31} \text{ kg})(1.6 \times 10^6 \text{ m/s})}{(8.5 \times 10^{28} \text{ m}^{-3})(1.6 \times 10^{-19} \text{ C})^2} \\ &= 3.9 \times 10^{-8} \text{ m.} \end{aligned}$$

The mean free path is two orders of magnitude larger than the distance between two copper atoms. \blacksquare

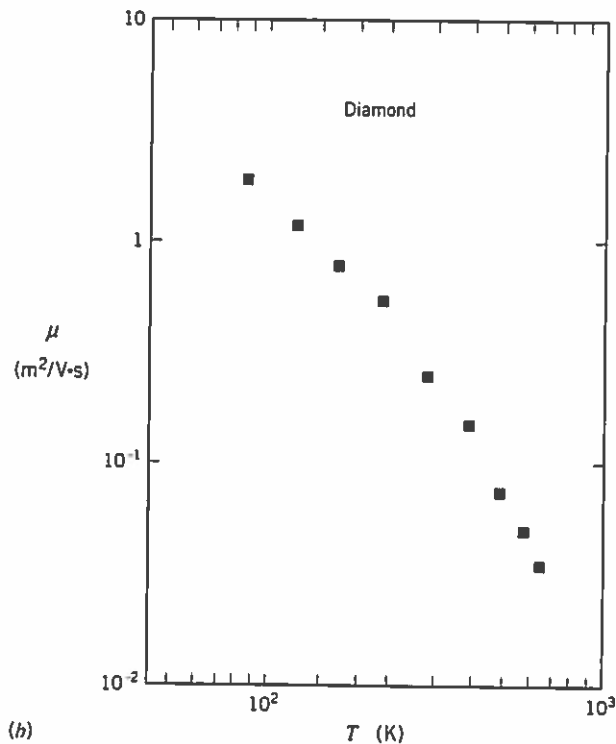
The electrical conductivity of a conductor is many orders of magnitude larger than that of an insulator. For example, at room temperature the electrical conductivity of diamond is smaller than copper by 20 orders of magnitude! It is rather remarkable then that Ohm's law is also found to hold for an insulator. To investigate this interesting property of insulators we introduce the *mobility* (μ) of an electron, defined to be the drift speed divided by the electric field. With this definition we have

$$v_d = \mu E. \quad (14.69)$$

In our derivation of Ohm's law in a metal, we have assumed that the mobility does not depend on the electric field. This is true for metals but not for insulators. The measured drift speed of electrons in diamond as a function of electric field is shown in Figure 14-13a. The slope of the curve is equal to the mobility. At small values of electric field the mobility is constant. In this region Ohm's law works. At large values of E the mobility is inversely proportional to E and Ohm's law does not hold. The mobility of electrons also depends on temperature. This is due to an interaction of the electrons with the vibrating lattice. The temperature dependence of the electron mobility in diamond is shown in Figure 14-13b.



(a)



(b)

FIGURE 14-13 Electron drift speed in the insulator diamond.

(a) Electron drift speed (v_d) measured as a function of electric field strength (E). (b) The mobility ($\mu = v_d/E$) measured as a function of temperature. The measurements were taken at small values of electric field where the mobility does not depend on E . After F. Nava et al., *Solid State Com.* 33, 475 (1980).

As a final remark we point out that in our derivation of Ohm's law we have also assumed that the number of conduction electrons remains fixed. This is true for a metal but not for an insulator at large E because additional electrons enter the conduction band. Therefore, in an insulator we may write the current density as

$$J = n(E) e v_d(E). \quad (14.70)$$

14-5 SEMICONDUCTORS

Intrinsic Semiconductors

An intrinsic semiconductor is an element in which the energy gap between the outermost filled band (called the *valence band*) and the next highest band is small compared to that of an insulator. The family of intrinsic semiconductors is made up of the first four elements in Group IV of the periodic table (see Figure 14-14). Silicon ($Z = 14$) is the most common intrinsic semiconductor. Its electron configuration is $1s^2 2s^2 2p^6 3s^2 3p^2$. In silicon, the $3s$ and $3p$ bands overlap to make a filled outer band (4 electrons per atom) with an energy gap of about 1.1 eV. The band structure of silicon is shown in Figure 14-15.

p-dopants	Intrinsic semiconductors	n-dopants
5 B $2s^2 2p^1$	6 C $2s^2 2p^2$ $E_g = 5.5 \text{ eV}$	7 N $2s^2 2p^3$
13 Al $3s^2 3p^1$	14 Si $3s^2 3p^2$ $E_g = 1.1 \text{ eV}$	15 P $3s^2 3p^3$
31 Ga $4s^2 4p^1$	32 Ge $4s^2 4p^2$ $E_g = 0.7 \text{ eV}$	33 As $4s^2 4p^3$
49 In $5s^2 5p^1$	50 Sn $5s^2 5p^2$ $E_g = 0.1 \text{ eV}$	51 Sb $5s^2 5p^3$

FIGURE 14-14 The intrinsic semiconductors diamond, silicon, germanium, and tin together with their neighboring elements in the periodic table.

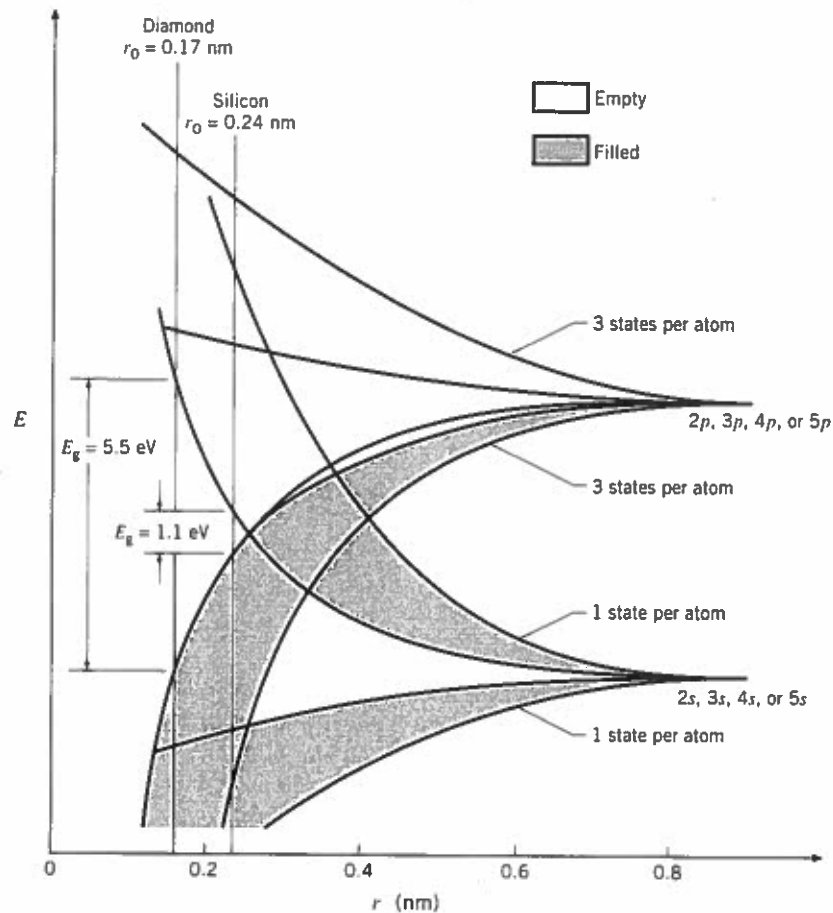


FIGURE 14-15 Band structure of the intrinsic semiconductor.

After R. L. Sproull and W. A. Phillips, *Modern Physics: The Quantum Physics of Atoms, Solids, and Molecules*, Wiley (1980).

Carbon ($Z = 6$), germanium ($Z = 32$), and tin ($Z = 50$) have the same outer electron configurations as silicon, except the outer shells correspond to $n = 2$, $n = 4$, and $n = 6$. The crystal structure of silicon is a diamond lattice (see Figures 14-2 and 14-3). The band structures of diamond, germanium, and tin are similar to that of silicon except that the spacing between atoms is smaller in diamond and larger in germanium and tin. This leads to an energy gap of 5.5 eV in diamond, 0.7 eV in germanium, and 0.1 eV in tin.

We should point out one subtle feature of the energy gap. The maximum of the valence band need not coincide with the minimum of the conduction band. This is illustrated in Figure 14-16 which shows a plot of electron energy versus wave number (see Figure 14-5). If the maximum of the valence band coincides with the minimum of the conduction band as in Figure 14-16a, an

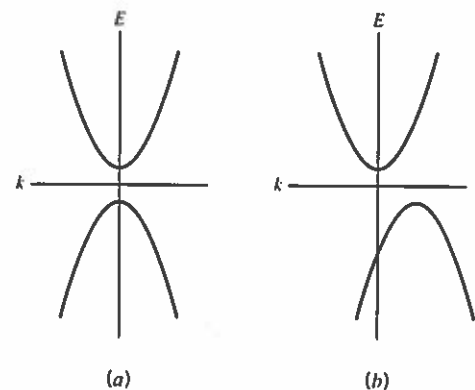


FIGURE 14-16 Semiconductor band gaps.

(a) Energy versus wave number for a semiconductor in which the minimum of the conduction band coincides with the maximum of the valence band. (b) The valence and conduction bands do not coincide.

electron can cross the gap with the absorption of a photon of energy E_g , a *direct transition*. If the valence and conduction bands do not coincide as in Figure 14-16b, an electron can still absorb a photon and cross the gap provided that the appropriate momentum is supplied by a phonon, an *indirect transition*. Since the phonon also has energy of order of magnitude kT_D , the indirect transitions are caused by photons with energies smaller than the energy gap. This effect can be especially important for those semiconductors with small band gaps.

In an intrinsic semiconductor, the band gap is small enough that some electrons are thermally excited to the conduction band, leaving unfilled states, or *holes*, in the valence band. Therefore, the conductivity of a semiconductor increases with temperature.

EXAMPLE 14-9

Make an estimate of the density of electrons in the conduction band in diamond, silicon, germanium, and tin at room temperature.

SOLUTION:

The occupation probability for an electron to be in the conduction band (see Example 14-2) is given by the Maxwell-Boltzmann factor

$$P = e^{-\Delta E / kT},$$

where

$$\frac{\Delta E}{kT} = \frac{E_g}{2kT} = \frac{20 E_g}{\text{eV}}.$$

The probability that an electron is excited to the conduction band is for diamond ($E_g = 5.5 \text{ eV}$)

$$P \approx e^{-\Delta E / kT} \approx e^{-(20)(5.5)} \approx e^{-110} \approx 10^{-48}.$$

for silicon ($\Delta E = 1.1 \text{ eV}$)

$$P \approx e^{-(20)(1.1)} \approx e^{-22} \approx 10^{-10},$$

for germanium ($\Delta E = 0.7 \text{ eV}$)

$$P \approx e^{-(20)(0.7)} \approx e^{-14} \approx 10^{-6},$$

and for tin

$$P \approx e^{-(20)(0.1)} \approx e^{-2} \approx 10^{-1}.$$

We may estimate that about one electron per atom is near the top of the outer band. The density of these electrons is

$$n \approx \frac{1}{(0.2 \text{ nm})^3} \approx 10^{29} \text{ m}^{-3}.$$

The density of conduction electrons (n_e) is for diamond

$$n_e \approx nP \approx (10^{-48})(10^{29} \text{ m}^{-3}) = 10^{-19} \text{ m}^{-3},$$

for silicon

$$n_e \approx nP \approx (10^{-10})(10^{29} \text{ m}^{-3}) = 10^{19} \text{ m}^{-3},$$

for germanium

$$n_e \approx nP \approx (10^{-6})(10^{29} \text{ m}^{-3}) = 10^{23} \text{ m}^{-3},$$

and for tin

$$n_e \approx nP \approx (10^{-1})(10^{29} \text{ m}^{-3}) = 10^{28} \text{ m}^{-3}. \quad \blacksquare$$

Doped Semiconductors

When impurity atoms are added to an intrinsic semiconductor, the resulting material is called a *doped* semiconductor. A modest doping fraction of 10^{-6} can greatly change the conduction properties of the material. There are two general classes of doped semiconductors as illustrated in Figure 14-17.

In an *n-type* (n for negative) doped semiconductor, the impurity atoms have one more outer electron than the intrinsic semiconductor. An example is germanium doped with arsenic (see Figure 14-14). The arsenic atoms occupy random positions in the crystal lattice. The energy levels of the arsenic atoms are slightly different from germanium. The outer electrons from arsenic reside in energy levels which are slightly below the conduction band. With a small amount of energy from thermal excitations, electrons can be boosted into the conduction band without leaving unfilled states (holes) in the valence band.

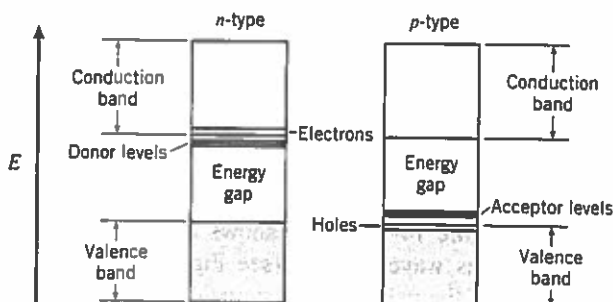


FIGURE 14-17 Energy bands in doped semiconductors.

In a *p*-type (*p* for positive) doped semiconductor, the impurity atoms have one less outer electron than the intrinsic semiconductor. An example is germanium doped with gallium (see Figure 14-14). The gallium atoms occupy random positions in the crystal lattice and leave holes in energy levels which are just above the valence band. Electrons can be thermally excited from the valence band. This creates holes in the valence band without putting electrons in the conduction band.

The *p*-*n* Junction

If we put a *p*-type and an *n*-type material in contact with each other, we create a *p*-*n* junction. An electrical device containing such a junction is called a diode. Some of the electrons near the junction boundary diffuse from the *n*-region into the *p*-region and some of the holes diffuse from a *p*-region into the *n*-region (see Figure 14-18). The movement of these mobile charges leaves behind an excess of fixed positive charge in the *n*-region near the boundary and an excess of fixed negative charge in the *p*-region near the boundary. These fixed charges create a strong electric field (10^6 – 10^8 V/m) that serves to keep the region free of mobile charge. This region is called the *depleted* region. The thickness of the depleted region is a few microns. A potential difference (V_0), called the *contact potential*, is created across the boundary.

The net current across a junction, after the initial movement that creates the contact potential, is zero. This current consists of four components, electrons and holes that can each travel in both directions. Let the current due to electrons moving from the *n*-region to the *p*-region be called I_n . The number of electrons traveling in the opposite

direction, from the *p*-region to the *n*-region, creates a current $-I_n$. Let the current due to holes moving from the *p*-region to the *n*-region be called I_p . The number of holes traveling in the opposite direction, from the *n*-region to the *p*-region, creates a current $-I_p$. Equilibrium is established and no net current is flowing across the junction:

$$I = I_n - I_n + I_p - I_p = 0. \quad (14.71)$$

Figure 14-19a shows an energy level diagram for a *p*-*n* junction. The Fermi energies for the *p*-type and the *n*-type coincide. The *p*-type region contains mobile holes at the top of the valence band that are kept from crossing into the *n*-type region by the contact potential. Similarly, the *n*-type material contains mobile electrons at the bottom of the conduction band that are kept from crossing into the *p*-type region. The contact potential and energy gap are related by $eV_0 = E_g$.

If we connect an external voltage source to the junction with the polarity selected such that an electric field is generated in the same direction as the field caused by the contact potential, this is called *reverse bias* (see Figure 14-19b). In reverse bias, the negative terminal of the voltage source is connected to the *p*-region and the positive terminal to the *n*-region. Since resistance to charge flow in the semiconductor is predominantly at the junction, the external applied voltage will appear at the junction. This destroys the equilibrium condition by making it essentially impossible for charges to cross the barrier in the direction opposing the potential, corresponding to electrons going from the *n*-region to the *p*-region or vice versa for holes. Mobile charges can still diffuse across in the other direction, creating a net current

$$I = -(I_n + I_p). \quad (14.72)$$

This current is independent of the size of the reverse bias voltage and is relatively small because there are very few mobile electrons in the *p*-region or mobile holes in the *n*-region. If the reverse-bias voltage is made large enough, electrons that are not normally mobile because they are bound in the atoms may be freed, causing an avalanche breakdown.

If we connect an external battery such that the applied electric field is opposite that due to the contact potential, this serves to help charges cross the barrier (see Figure 14-19c). This is called *forward bias*. To achieve a forward bias, the positive voltage terminal is connected to the *p*-type semiconductor and the negative to the *n*-type. The potential of the external battery will appear as a lowering

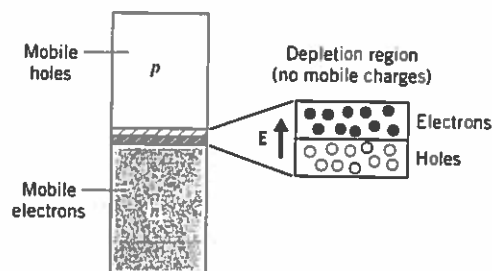


FIGURE 14-18 The *p*-*n* junction.

The depletion region is a few microns thick and contains the fixed charges left over after electrons diffuse from the *n*-region to the *p*-region and holes from the *p*-region to the *n*-region. These charges create an electric field that prevents further diffusion of charge.

In a *p-type* (*p* for positive) doped semiconductor, the impurity atoms have one less outer electron than the intrinsic semiconductor. An example is germanium doped with gallium (see Figure 14-14). The gallium atoms occupy random positions in the crystal lattice and leave holes in energy levels which are just above the valence band. Electrons can be thermally excited from the valence band. This creates holes in the valence band without putting electrons in the conduction band.

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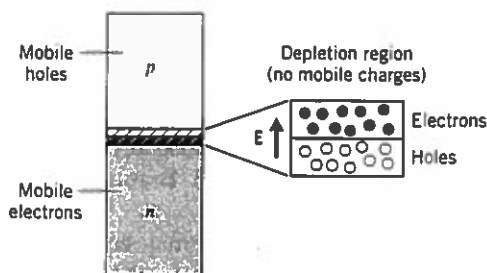


FIGURE 14-18 The *p-n* junction.

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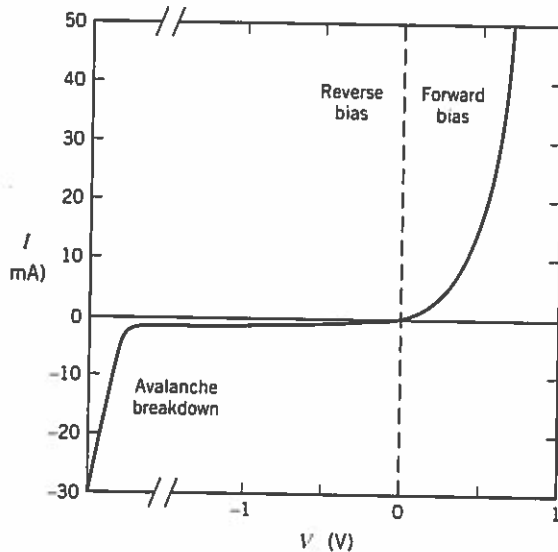


FIGURE 14-20 Current versus voltage in a p - n junction.

This barrier prevents the flow of electrons between the two regions. In order to function as an amplifier, the transistor must be biased with external power supplies. These power supplies will provide the energy source for the power amplification. Figure 14-22b shows an energy band diagram for an n - p - n transistor that is connected to external voltage sources. The base-emitter junction is forward biased so that this energy barrier is reduced. The base-collector junction is reverse biased so that this energy barrier is raised. Electrons are ready to travel from the emitter to the collector, but they are hindered from doing so because of the potential barrier in the base. This barrier

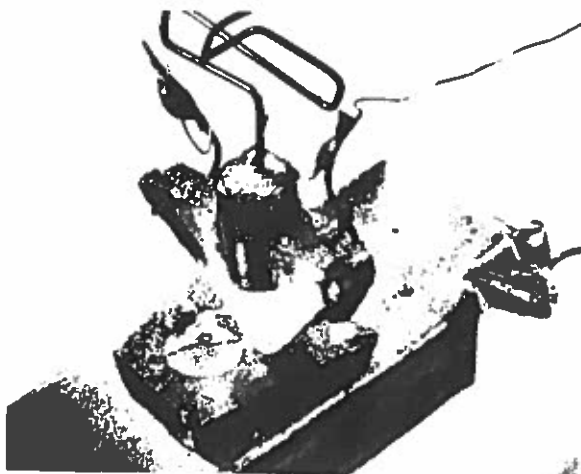


FIGURE 14-21 The first transistor.
Courtesy A. T. & T. Bell Laboratories, reprinted by permission.

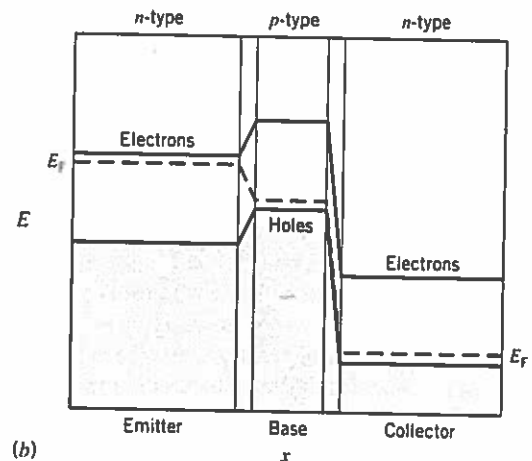
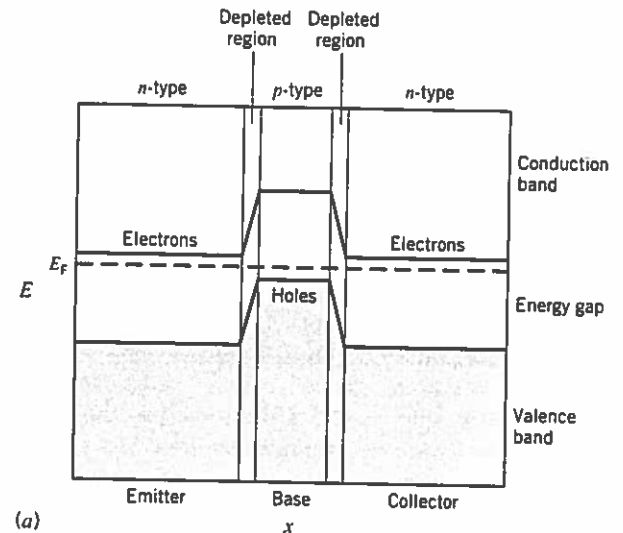


FIGURE 14-22 The n - p - n junction.

(a) No external voltage and (b) emitter-base forward biased and base-collector reverse biased.

is made up of negative charge that has accumulated in the base. If electrons are allowed a path to escape from the base, then the emitter-base barrier is lowered and a small change in height of the barrier allows a large amount of charge to flow across it. A small base-emitter current causes a large emitter-collector current (see Figure 14-23). The n - p - n transistor is designed such that essentially all of the electrons from the emitter that enter the base pass through it into the collector. This is accomplished by making the base very thin and lightly p -doped while the emitter is heavily n -doped. The collector is usually lightly n -doped. The ratio (α) of collector (I_c) to emitter currents (I_e) is of order unity,

$$\alpha = \frac{I_c}{I_e} \approx 1. \quad (14.76)$$

The ratio of collector to base (I_b) currents is called the *gain* (β) of the transistor,

$$\beta = \frac{I_c}{I_b}. \quad (14.77)$$

The numerical value of β is in the range 10–1000 with 100 being a typical value. The gains of transistors, even of the same model number, can easily vary by factors of 2 from component to component. Therefore, circuit design must not depend on the exact value of the transistor gain. In addition, every transistor has current and voltage limits beyond which it will “burn out.”

A p - n - p transistor consists of a heavily p -doped emitter and a lightly p -doped collector separated by a lightly n -doped base. The operation of a p - n - p transistor is similar to that of an n - p - n transistor except that the bias voltages are reversed and the current is dominated by the motion of holes.

The normal operation of the transistor may be summarized by noting that a small current in the base controls a large current through the collector. The base-emitter junction is forward-biased while the base-collector junction is reverse biased. Therefore, there is a small resistance between emitter and base and a large resistance between collector and base. Since almost every charge that enters the base from the emitter continues into the collector, the current across each junction is the same. Since the collector junction has higher resistance, it has a higher power ($P = I^2R$), and the transistor serves as a power amplifier. The current-voltage characteristics of a common transistor are shown in Figure 14-23*b*. To operate the transistor as an amplifier, a voltage of about 0.5 V is maintained between the collector and emitter (V_{ce}). The collector current (I_c) is then about 100 times the base current (I_b).

Field-Effect Transistors

The collector current in a bipolar transistor is controlled by the base current. In another type of transistor, the *field-effect transistor* (FET), current is controlled by an electric field. There are two main categories of FETs, the junction field-effect transistor (JFET) and the metal-oxide-semiconductor field-effect transistor (MOSFET). Both the JFET and the MOSFET come in two varieties, p -channel

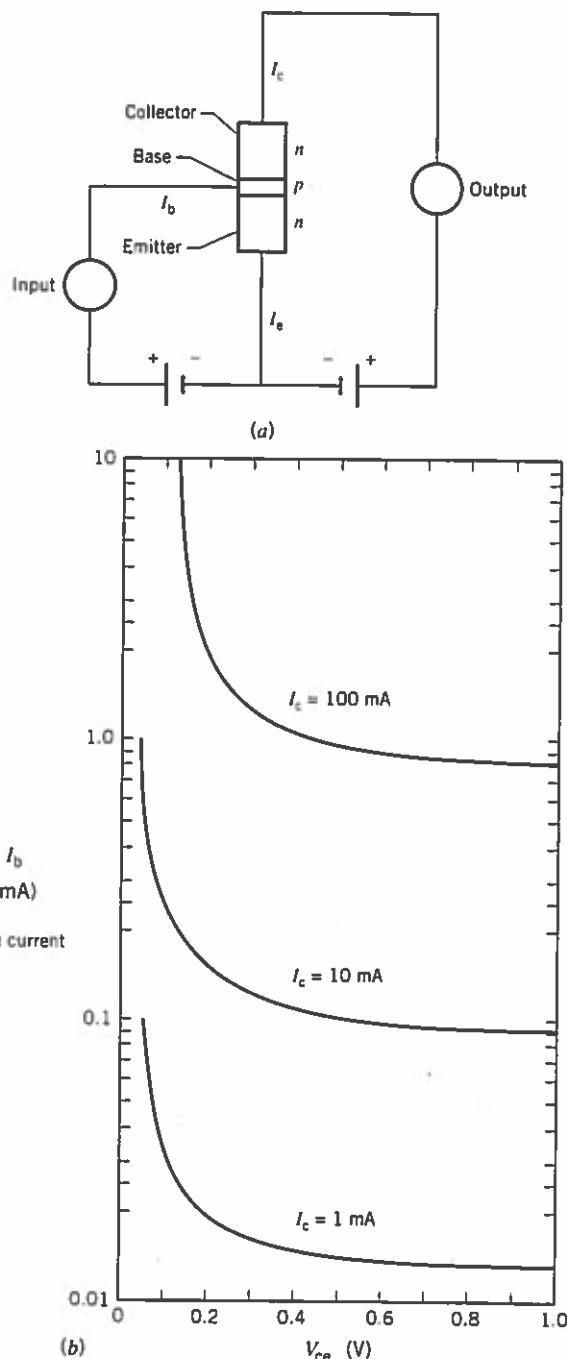


FIGURE 14-23 The transistor as an amplifier. (a) Circuit diagram for an n - p - n transistor in which the base-emitter junction is forward biased and the base-collector junction is reverse biased. (b) Current-voltage characteristics of a typical transistor amplifier. For a given collector-emitter voltage (e.g., $V_{ce} = 0.5$ V), the collector current is approximately 100 times the base current.

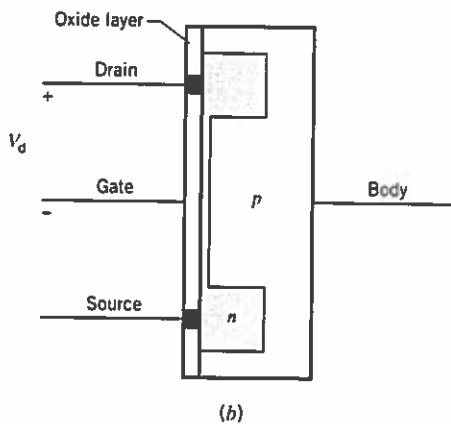
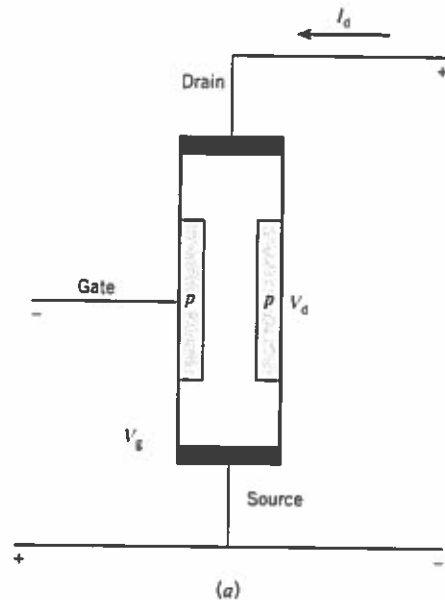


FIGURE 14-24 The field-effect transistor. (a) JFET, and (b) MOSFET.

n-channel, analogous to *p*-*n*-*p* and *n*-*p*-*n* bipolar transistors. The *n*-channel JFET is shown in Figure 14-24a. The JFET consists of a semiconductor bar, most commonly silicon, with electrical contacts, called the source and the drain, on each end. The middle of the bar contains a second semiconductor with the opposite dopant—called the gate. The gate is designed to draw essentially no current. The gate-source is reverse biased, creating an electric field in the semiconductor bar. The gate voltage arises because the amount of voltage bias determines the size of the energy gap that the mobile charges pass through. The three terminals gate, source,

and drain are analogous to the base, emitter, and collector of the bipolar transistor.

The MOSFET differs from the JFET in that the gate consists of a metal electrode that is insulated from the semiconductor by a layer of glass (SiO_2). These devices are sometimes referred to as insulated-gate FETs (IGFETs). The *n*-channel MOSFET is shown in Figure 14-24b.

14-6 THE HALL EFFECT

Consider a conductive sheet placed in a magnetic field as shown in Figure 14-25. A voltage is applied to the sheet causing a current in the *x* direction. The current may be due to either mobile electrons (Figure 14-25a) or mobile holes (Figure 14-25b). For the case of mobile electrons drifting in the negative *x* direction, there is a magnetic force (F_m),

$$\mathbf{F}_m = -e\mathbf{v}_d \times \mathbf{B}, \quad (14.78)$$

on electrons in the negative *y* direction. This magnetic force causes an accumulation of negative charge on the lower edge of the sheet (Figure 14-25a). This charge generates an electric force (F_e) on the drifting electrons that just cancels the magnetic force. This is called the *Hall effect* after Edwin H. Hall, who first observed it in 1879. If the current is due to mobile holes (Figure 14-25b), then the magnetic force on the holes is in the negative *y* direction and positive charge accumulates on the lower edge of the sheet. The magnitudes of the forces are

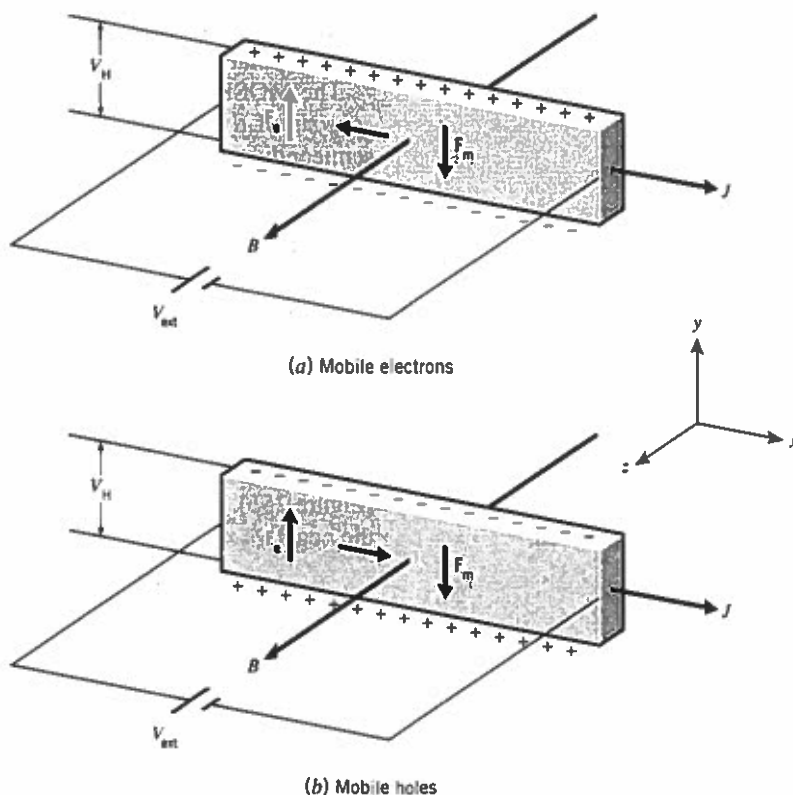
$$F_e = eE = F_m = ev_d B. \quad (14.79)$$

The Hall voltage (V_H) is defined to be the potential difference across the width of the sheet from the accumulated charges:

$$V_H = Ey = v_d By, \quad (14.80)$$

where *y* is the width of the sheet. The Hall voltage is very small ($V_H \ll 1$ V) even for large magnetic fields because the electron drift speed is small. The polarity of the Hall voltage is determined by the sign of the mobile charges (electrons or holes). Measurement of the Hall voltage provides a determination of the drift velocity. If the current density ($J = nev_d$) is also measured, then measurement of the Hall voltage provides a determination of the density of mobile charges:

$$n = \frac{J}{ev_d} = \frac{JBy}{eV_H}. \quad (14.81)$$

**FIGURE 14-25** The Hall effect.

A thin conducting sheet is placed in a uniform magnetic field (B) which is in the z direction. A voltage is applied so that a current (J) flows in the x direction. (a) The current is due to electrons moving in the negative x direction. There is a magnetic force (F_m) on the electrons in the negative y direction. Negative charges accumulate on the lower edge of the conducting sheet until the resulting electrical force (F_e) on an electron just cancels the magnetic force. (b) The current is due to holes moving in the x direction. There is a magnetic force (F_m) on the holes in the negative y direction. Positive charges accumulate on the lower edge of the conducting sheet until the resulting electrical force (F_e) on a hole just cancels the magnetic force.

If the sheet has a thickness d , we may write the current density as

$$J = \frac{I}{yd}, \quad (14.82)$$

to get

$$V_H = \frac{IB}{ned}. \quad (14.83)$$

The Hall effect provides a practical method for magnetic field measurement. If a device in which the density of mobile charges is known is placed in an unknown external magnetic field, then measurement of the current and the Hall voltage determines B . Such a device is called a *Hall probe*.

EXAMPLE 14-10

A sheet of copper with a thickness of $100\ \mu\text{m}$ carries a current of $1\ \text{A}$. What is the Hall voltage when the copper sheet is placed in an external magnetic field of $1\ \text{T}$? The density of conduction electrons in copper is $8.45 \times 10^{29}\ \text{m}^{-3}$.

SOLUTION:

The Hall voltage times the electron charge is

$$eV_H = \frac{IB}{nd} = \frac{(1\ \text{A})(1\ \text{T})}{(8.45 \times 10^{29}\ \text{m}^{-3})(10^{-4}\ \text{m})} \\ = 1.18 \times 10^{-25}\ \text{J}.$$

The Hall voltage is

$$V_H = \left(\frac{1.18 \times 10^{-25} \text{ J}}{e} \right) \left(\frac{1 \text{ eV}}{1.6 \times 10^{-19} \text{ J}} \right) \\ = 7.40 \times 10^{-7} \text{ V.}$$

The *Hall resistance* (R_H) is defined to be the Hall voltage divided by the current.

$$R_H \equiv \frac{V_H}{I} = \frac{B}{ned}. \quad (14.84)$$

Quantum Hall Effect

In 1980, a surprising discovery was made concerning the Hall effect by Klaus von Klitzing and his collaborators, Gerhard Dorda and Michael Pepper. Measurements were made of the Hall voltage in a MOSFET at low temperature (about 2 K) in a strong magnetic field (about 15 T). The geometry of their MOSFET is shown in Figure 14-26a (insert). The current in the MOSFET was kept constant at μA and the gate voltage (V_g) was varied from 0 to 25 V. Two voltages were measured, the Hall voltage (V_H) and the voltage along the strip (V_s). Figure 14-26a shows a plot of V_H and V_s versus V_g . For certain values of V_g , V_s vanishes and therefore the resistance of the strip vanishes! When $V_g = 0$, the Hall voltage is observed to have a plateau. The corresponding values of the Hall resistance are

$$R_H = \frac{h}{\nu e^2}, \quad (14.85)$$

where $\nu = 1, 2, 3, \dots$. This result is known as the *quantum Hall effect* (QHE). The Hall resistance (14.85) does not depend on the detailed properties of the material!

Figure 14-26b shows a detail of one of the voltage plateaus. These data show a plateau in the Hall resistance (14.85) at a value of $6453.3 \pm 0.1 \Omega$ corresponding to $\nu = 4$. It was immediately appreciated that the QHE allowed a very accurate determination of the electromagnetic coupling constant (α), through the relationship

$$\alpha = \frac{ke^2}{\hbar c} = \frac{2\pi k}{\nu c R_H}. \quad (14.86)$$

The value of the quantized Hall resistance for $\nu = 1$ is known as the *von Klitzing resistance* (R_K),

$$R_K = \frac{h}{e^2} = \frac{6.6262 \times 10^{-34} \text{ J} \cdot \text{s}}{(1.6022 \times 10^{-19} \text{ C})^2} \\ = 25813 \Omega. \quad (14.87)$$

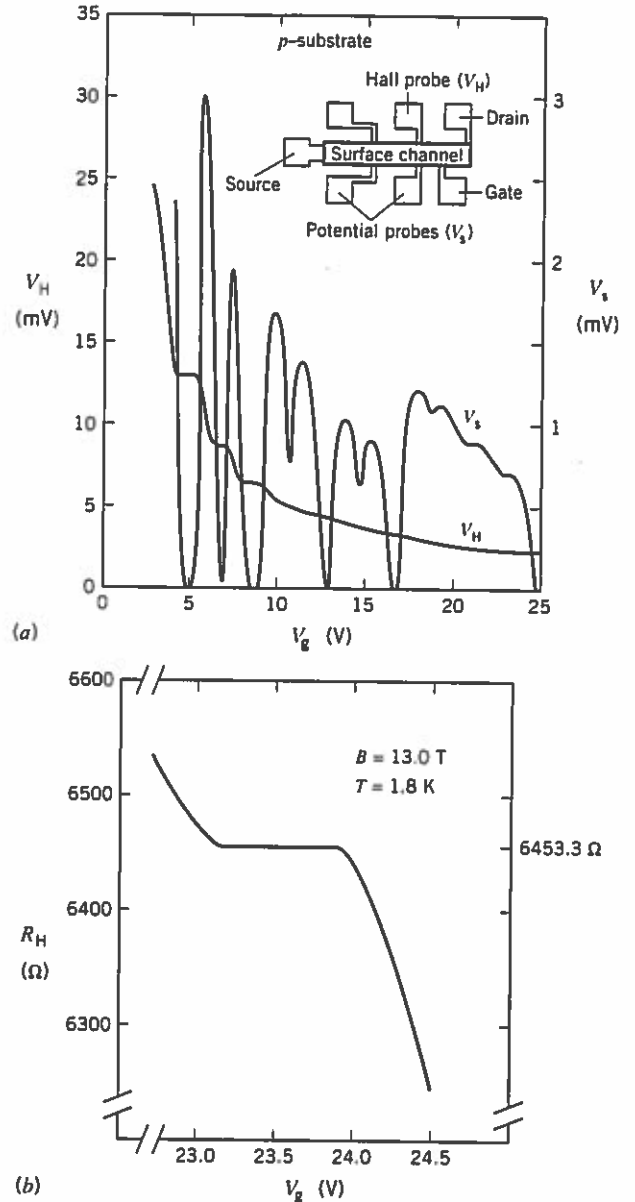


FIGURE 14-26 Discovery of the quantum Hall effect. A MOSFET (insert) is cooled with liquid helium and placed in a strong magnetic field. (a) The voltage along the strip V_s (right-hand scale) and the Hall voltage V_H (left-hand scale) are measured as a function of the gate voltage V_g . At certain values of V_g , V_s is observed to vanish and V_H is observed to have a plateau. ($T = 1.5 \text{ K}$ and $B = 18 \text{ T}$.) (b) The Hall resistance R_H is plotted as a function of V_g in the region of one of the plateaus. The data show a plateau at $R_H = h/4e^2 = 6453 \Omega$. ($T = 1.8 \text{ K}$ and $B = 13 \text{ T}$.) From K. v. Klitzing, G. Dorda and M. Pepper, "New Method for High-Accuracy Determination of the Fine-Structure Constant Based on Quantized Hall Resistance," *Phys. Rev. Lett.* **45**, 494 (1980).

The experimental technique of determining the Hall resistance is so accurate (about 1 part per billion), that in 1990 a new definition of the ohm was adopted,

$$R_K \equiv 25812.807 \, \Omega. \quad (14.88)$$

The important feature of the MOSFET relevant for the QHE is that the current is confined to a thin layer of silicon; the electrons move in two dimensions. The number of states per area (n_2 , the two-dimensional analogy of n_1) is directly proportional to the magnetic field. The magnetic field dependence of n_2 is a consequence of the fact that the electrons are constrained to move in two dimensions. The Bohr model may be used to deduce the magnetic field dependence of n_2 . The Bohr-Sommerfeld quantization condition on an electron constrained to move in a circle in a magnetic field may be written

$$\oint d\mathbf{r} \cdot \mathbf{p} = v\hbar = e\Phi, \quad (14.89)$$

where v is a positive integer and Φ is the magnetic flux through a loop of radius r . (The quantization of magnetic flux is discussed in more detail in Chapter 15.) The magnetic flux may be written

$$\Phi = \pi r^2 B = \pi \left(\frac{p}{eB} \right)^2 B = \frac{\pi p^2}{e^2 B}, \quad (14.90)$$

where we have used the relationship $p = e r B$. The number of states per area is

$$n_2 = \frac{\pi p^2}{h^2}, \quad (14.91)$$

which gives

$$n_2 = \frac{v e B}{h}. \quad (14.92)$$

The number of states per area is an integer multiple of eB/h . The integer v is called the *filling factor*.

For fixed magnetic field, the Hall resistance (14.84) for the two dimensional strip is

$$R_H = \frac{B}{n_2 e}. \quad (14.93)$$

The quantization condition on n_2 (14.92) gives the quantized Hall resistance (14.85) discovered by von Klitzing et al.

The energy levels of electrons whose motion is confined to two dimensions are called *Landau levels*. The electrons that are free to move in the silicon strip occupy

energy levels called *extended levels*. Above and below each extended energy level are *localized levels* caused by impurities. Electrons that occupy the localized levels are not free to move. The Landau levels in a MOSFET depend on both gate voltage (V_g) and the magnetic field. Figure 14-27 shows Landau levels in a fixed magnetic field as a function of V_g . An increase in V_g causes a decrease in the Fermi energy. When the Fermi energy resides in the region of localized energy levels, electrical conduction occurs normally; electrons with energies near the Fermi energy can move into nearby empty states and the motion of electrons causes a transfer of energy to phonons resulting in resistance. When the Fermi energy resides in the region of localized energy levels, however, the electrons cannot move and the resistance along the strip vanishes. It is important to note that the resistance vanishes because the extended Landau level is completely full. This is possible because the localized levels constitute a reservoir of electrons. The charge reservoir of the localized states is large enough to keep the extended Landau level full for small changes in the Fermi energy, hence a vanishing strip resistance coincides with a plateau in the Hall resistance. The ratio of Hall resistances (14.93) at any two plateaus is the ratio of integers because n_2 (14.92) depends on the number of filled extended Landau levels. The plateaus occur when $n_2 h / eB$ is an integer.

The QHE can also be observed by keeping the Hall voltage fixed and varying the magnetic field. (The Hall voltage can be controlled with V_g , see Figure 14-26a.) Since the density of states increases with increasing B , the Fermi level decreases with increasing B . The QHE occurs when the Fermi energy resides in the region of localized energy levels.

Fractional Quantum Hall Effect

In 1982, Daniel T. Tsui, Horst L. Störmer, and Arthur C. Gossard discovered a second remarkable phenomenon in the Hall effect. Tsui et al. were studying the quantum Hall effect in a *heterojunction*, an interface of two semiconducting crystals. The junction studied was GaAs–AlGaAs. The GaAs semiconductor was doped with silicon atoms resulting in mobile electrons with a density of $1.23 \times 10^{15} \text{ m}^{-2}$, and an electron mobility of $9 \text{ m}^2/\text{V}\cdot\text{s}$. The device current was kept constant at $1 \, \mu\text{A}$. The data of Tsui, Störmer, and Gossard are shown in Figure 14-28, which shows the Hall resistance and the strip resistivity as a function of the magnetic field strength. A plateau in the Hall resistance is expected from the quantized Hall effect when

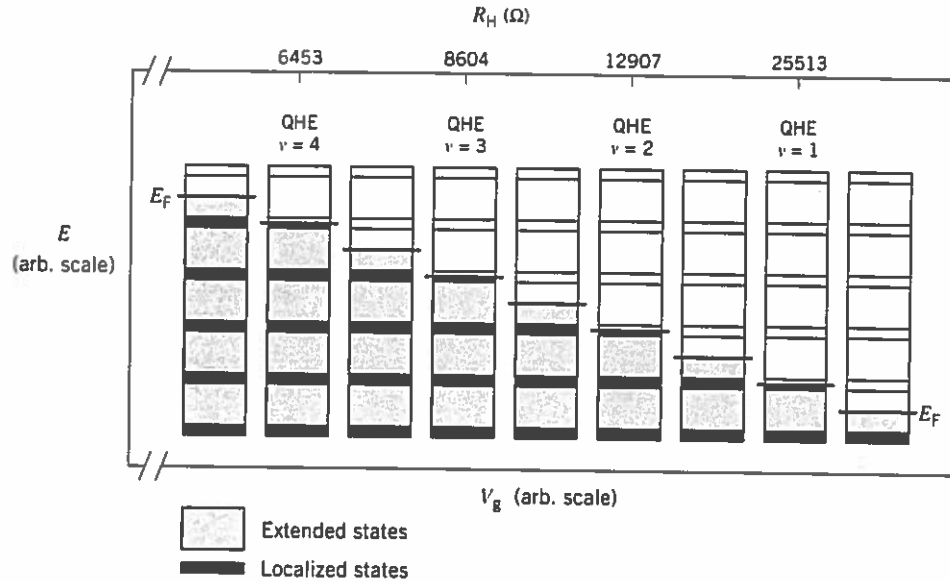


FIGURE 14-27 Band diagram of Landau levels in a MOSFET.

Electrons that are free to move occupy extended states. Localized states, which are caused by impurities, are occupied by electrons that cannot move. For fixed magnetic field, the Fermi energy increases with increasing gate voltage V_g . When the Fermi energy lies in a band of extended states, normal conduction occurs. When the Fermi energy coincides with a band of localized states, the resistance along the strip vanishes and the QHE occurs. The quantized Hall resistance is inversely proportional to the number of filled extended bands.

$$B = \frac{n_2 h}{e v}, \quad (14.94)$$

where $v = 1, 2, 3, \dots$. These plateaus are observed. An additional plateau is observed at

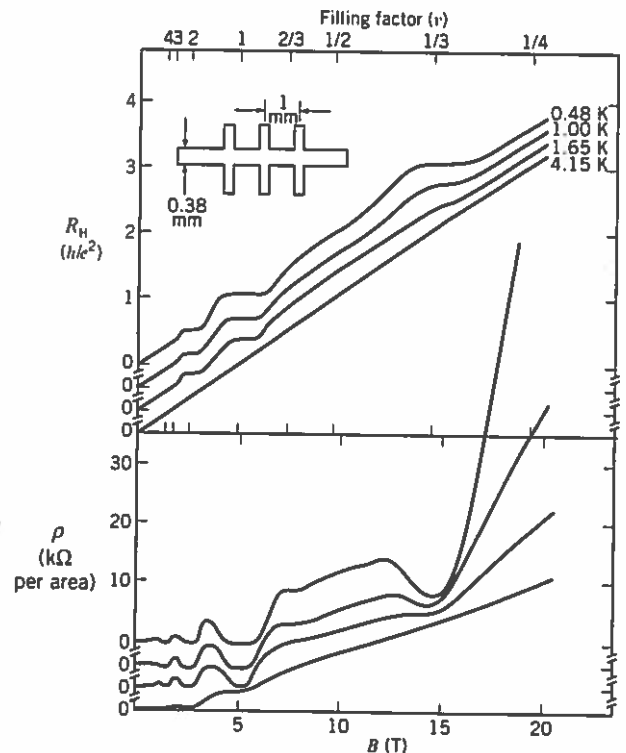
$$B = \frac{3 n_2 h}{e}, \quad (14.95)$$

and

$$R_H = \frac{3 h}{e^2}, \quad (14.96)$$

FIGURE 14-28 Discovery of the fractional quantum Hall effect.

An GaAs-AlGaAs heterojunction is cooled with liquid helium placed in a strong magnetic field. The Hall resistance R_H and longitudinal resistivity ρ are measured as a function of the magnetic field at temperatures from 0.48 to 4.15 K. The QHE is observed at integer values of the filling factor v . An additional plateau in R_H and a corresponding drop in ρ is observed when $v = 1/3$. From D. C. Tsui, H. L. Stormer and A. C. Gossard, "Two-Dimensional Magnetotransport in the Extreme Quantum Limit," *Phys. Rev. Lett.* 48, 1559 (1982).



corresponding to a filling factor of

$$\nu = \frac{1}{3}. \quad (14.97)$$

This unpredicted phenomenon is called the *fractional quantized Hall effect* (FQHE). The FQHE has also been observed at other values of the filling factor (for example, $\nu = 2/3, 2/5, 3/5, 4/5$, and $2/7$).

CHAPTER 14: PHYSICS SUMMARY

- Electron energy levels in a solid form bands. In a conductor, the highest energy electronic band is partially filled. In an insulator, there is an energy gap of several electronvolts between the highest energy band, which is filled, and the next available band, which is empty. The band structure of an intrinsic semiconductor is similar to that of an insulator except that the energy gap is typically about 1 electronvolt.
- Metals are good electrical conductors because they contain a large number of electrons, roughly 10^{29} m^{-3} , that are easily displaced when an electric field is applied.
- In a metal, the current density (J) and electric field are related by Ohm's law,

$$J = \sigma E.$$

Ohm's law holds because the electric field accelerates electrons for a characteristic time,

$$\tau = \frac{d}{v_F},$$

where d is the mean free path between collisions and v_F is the Fermi speed.

- Metals are good thermal conductors and have low electronic heat capacities. When energy is supplied to the metal in the form of heat, only those electrons with energies near the Fermi energy can gain kinetic energy.
- The properties of semiconductors are greatly enhanced by the addition of impurity atoms. If the dopants have an excess of electrons, then an n -type semiconductor is created. If the dopants have fewer electrons, then a p -type semiconductor is created. A

semiconductor diode is made by joining p -type and n -type materials. At the semiconductor junction, diffusion of charges creates a contact potential difference across a thin region that is depleted of mobile charges. If an external voltage is applied with a polarity that increases the contact potential (reverse bias), then essentially no current flows. If an external voltage is applied with a polarity that decreases the contact potential (forward bias), then the current increases exponentially with the voltage.

- A transistor is made with a p - n - p or an n - p - n junction. The three terminals are called the collector, base, and emitter. The base-emitter junction is forward biased and the base-collector junction is reverse biased. A small current through the base (I_b) controls a large current in the collector (I_c). Typically, $I_c/I_b \approx 100$.
- When a voltage is applied to a conducting sheet, the magnetic force on the moving charges causes an accumulation of charge on the edge of the sheet that creates a potential difference called the Hall voltage. The resulting electric force on the moving charges balances the magnetic force. The Hall resistance is defined to be the Hall voltage divided by the current.
- In semiconductors at low temperatures, it was discovered that the Hall resistance has a plateau at

$$R_H = \frac{h}{ve^2},$$

where

$$\nu = 1, 2, 3, \dots$$

This result is known as the quantum Hall effect. Measurement of the Hall resistance allows a very accurate determination of α through the relationship,

$$\alpha = \frac{ke^2}{\hbar c} = \frac{2\pi k}{vcR_H}.$$

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QUESTIONS AND PROBLEMS

Electronic energy bands

1. Why are most of the elements (about three-fourths) metals?

Fermi energy

2. What is the relationship between the work function and the Fermi energy of a metal?
3. In 1 gram of copper, how many conduction electrons have kinetic energies in the interval 1–2 eV?
4. Determine the energy E_m where one-half of the conduction electrons in copper have an energy greater than E_m .
5. The Fermi energy for zinc is 9.39 eV. Calculate the density of conduction electrons. How many conduction electrons are there per atom?
6. The density of calcium ($Z = 20$) is 1.8 times the density of potassium ($Z = 19$). The Fermi energy in potassium is 2.1 eV. Estimate the Fermi energy in calcium.
7. Copper is an excellent conductor with one valence electron per atom and a Fermi energy of about 7 eV. Make an estimate of the fraction of conduction electrons that have energies larger than E_F at room temperature.
8. One gram of gold is cooled to liquid helium temperature. Calculate the total kinetic energy of the conduction electrons.

Heat capacity

9. The Fermi energy of aluminum is 11.6 eV. Calculate (a) the Fermi speed and (b) the electronic heat capacity of 1 gram of aluminum at room temperature.
10. Determine the temperature where the contribution to the heat capacity from electrons is equal to that from phonons in copper. The Fermi energy of copper is 7.0 eV and the Debye temperature is 343 K.
11. An accelerator is capable of delivering 10^{12} protons each with a kinetic energy of 1 GeV in a pulse of short duration. The protons are directed into a copper target (initially at room temperature) having a volume of 10^{-3} m^3 where they deposit all their kinetic

energy. Estimate the number of pulses needed to raise the temperature of the copper target by 10 kelvin. You may neglect the cooling of the target between pulses.

12. What is the typical energy of a phonon in a copper crystal at room temperature? What is the typical energy of a conduction electron?
13. Aluminum has a melting point of 934 kelvin and a density of $2.7 \times 10^3 \text{ kg/m}^3$. Use the data of Figure 14-10 to estimate the Debye temperature of aluminum.

Ohm's law

14. The mean free path of electrons in a very pure sample of copper at 4 kelvin is about 3 millimeters. Calculate the resistivity of the sample.
15. Calculate the mobility of electrons in copper at room temperature. Take the conductivity to be $5.9 \times 10^7 \Omega^{-1} \cdot \text{m}^{-1}$. Compare the mobility of copper with that of diamond at room temperature (see Figure 14-13).
16. Make a rough sketch of the current density (14.70) as a function of electric field in an insulator. Indicate the region where Ohm's law holds and the effect of a saturating drift speed. Assume that at some very large value of electric field that the number of conduction electrons grows exponentially.
17. Use the measured mobility in diamond (Figure 14-13b) to calculate the relaxation time at room temperature.
18. The mobility of silicon at room temperature is measured to be $0.19 \text{ m}^2/\text{V} \cdot \text{s}$. (a) Calculate the relaxation time. (b) Determine the drift speed when an electric field of 10^3 V/m is applied.

Semiconductors

19. The next element after tin in Group IV of the periodic table is lead. Why is lead not an intrinsic semiconductor?
20. Estimate the temperature where the density of conduction electrons in undoped germanium is 10^{15} per cubic meter.
21. Why doesn't Ohm's law hold for conduction in a diode?
22. Why is diamond transparent to visible light whereas a silicon crystal is not?
23. When a germanium crystal is doped with indium, what type of semiconductor results?
24. Calculate the ratio of forward to reverse current in a diode at room temperature for an applied voltage of plus or minus 1 volt.

25. Draw an energy level diagram similar to Figure 14-23 for a p - n - p transistor that is (a) unbiased and (b) biased for operation as an amplifier.
26. The conductivity of a sample of germanium is measured to be $2 \Omega^{-1} \cdot \text{m}^{-1}$ at room temperature. Give an expression for the conductivity as a function of temperature (T) for $T > 300 \text{ K}$. What is the conductivity at $T = 1000 \text{ K}$?

The Hall effect

27. Why do you think it took 101 years from the time the Hall effect was discovered until the quantized Hall effect was discovered?
28. Why was the discovery of the quantized Hall effect made at low temperature?
29. Silver has a density of $1.05 \times 10^4 \text{ kg/m}^3$ and an atomic number of 108. (a) Calculate the density of conduction electrons. (b) A current density of 10^6 A/m^2 flows in a thin sheet of width 10^{-2} m . Determine the strength of magnetic field needed to generate a Hall voltage of $1 \mu\text{V}$.
30. Von Klitzing, Dorda, and Pepper (*Phys. Rev. Lett.* **45**, 494, 1980) measured the $n = 4$ quantized Hall resistance with high accuracy and obtained a value of $R_H = 6453.17 \pm 0.02 \Omega$. With what accuracy did they determine the electromagnetic coupling constant, α ?
31. Tsui, Störmer, and Gossard (*Phys. Rev. Lett.* **48**, 1559, 1982) discovered the fractional quantum Hall effect for filling factors of $\nu = 1/3$ and $2/3$ in a device that had a density of charge carriers equal to $1.23 \times 10^{17} \text{ m}^{-2}$. Calculate the values of magnetic field where the FQHE was observed.
32. (a) Prove that the filling factor is dimensionless. (b) A quantum Hall device is designed to have a filling factor of one at $B = 10$ tesla. What is the charge carrier concentration?

Additional problems

33. Calculate the average energy of a conduction electron in gold.
34. What type of semiconductor (p or n) is obtained when silicon is doped with (a) antimony, (b) phosphorous, (c) aluminum, and (d) indium?
35. The longest wavelength that a certain semiconductor can absorb is $1.85 \mu\text{m}$. Calculate the energy gap of the semiconductor.
36. The Fermi temperature (T_F) is defined by

$$E_F \equiv kT_F.$$

Calculate the Fermi temperature for silver ($E_F = 5.48$ eV). What is the physical significance of the Fermi temperature?

37. (a) For what approximate value of the electron density does the nonrelativistic expression for the Fermi energy break down? (b) Derive an expression for the Fermi energy of a gas of relativistic electrons, in terms of the electron density. (c) A star of mass 2×10^{30} kg collapses to a radius of 10^4 m. Estimate the Fermi energy of the electrons in the collapsed star.

38. *Thermal conductivity and the Wiedemann-Franz law.* (a) Consider the flow of charge q in a metal rod of gradient cross-sectional area A when a voltage V is applied. Show that Ohm's law may be written

$$\frac{dq}{dt} = \sigma A \frac{dV}{dx}.$$

(b) The heat flow in the rod is described with a similar equation. If energy in the form of heat (Q) is supplied at one end of the rod, there will be a temperature gradient (dT/dx) along the length of the rod. The rate at which energy is transferred to the other end of the rod (dQ/dt) may be written

$$\frac{dQ}{dt} = \kappa A \frac{dT}{dx},$$

where the constant of proportionality (κ) is called the *thermal conductivity*. Show that for an ideal gas the thermal conductivity may be written

$$\kappa = \frac{C_V \langle v \rangle d}{3V},$$

where $\langle v \rangle$ is the average speed of a gas molecule, d is the mean free path and V is the volume. (c) Calculate κ for a metal by treating the electrons as a gas and show that

$$\frac{\kappa}{\sigma T} = \frac{\pi^2 k^2}{3e^2} = 2.45 \times 10^{-8} \text{ W} \cdot \Omega / \text{K}^2.$$

39. *Light-emitting diode (LED).* Consider a heavily doped p - n junction that is forward biased so that a large number of electrons and holes diffuse into the junction region. Electrons can combine with the holes. (a)

How much energy is released when an electron falls into a hole? (b) In some semiconductors, such as cadmium selenide, the electron-hole combining process occurs with the emission of a photon. Calculate the wavelength of the photons that are emitted if the band gap in CdSe is 1.8 eV. (c) In other semiconductors, such as silicon and germanium, the energy from the electron-hole combining process does not produce photons. What happens to the energy?

- *40. *The photovoltaic effect.* When light is incident on a p - n junction, photons can create electron-hole pairs. The electrons are able to move a distance d_e and holes are able to move a distance d_h before recombining. (a) Photons incident on the junction create electron-hole pairs at a rate R . Calculate the current density in a forward-biased junction. (b) Calculate the current density in a reverse-biased junction as a function of R . (c) For illumination of an open-circuit diode, a voltage will build up between the terminals. Calculate the voltage as a function of R . (d) What is the maximum possible voltage? (e) Gallium arsenide, which has a band gap of 1.4 eV, is well suited for conversion of solar energy to electrical energy. Why is GaAs better than germanium for solar power conversion?

- *41. *The Richardson-Dushman equation.* Consider the escape of electrons from the surface of a metal. Let the x direction be normal to the surface. (a) Show that the condition for electrons to escape is that the x component of momentum be greater than some critical value (p_c) given by

$$p_c = \sqrt{2m(E_F + \phi)},$$

where ϕ is the work function of the metal. (b) Writing the current density (J) in terms of the number of electrons per volume (n) and making use of the density of states for electrons in a metal, show that

$$J = \frac{2e}{h^3 m} \int_{p_c}^{\infty} dp_x p_x \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z \times \frac{1}{e^{(p_x^2 + p_y^2 + p_z^2)/2m kT - E_F/2m kT} + 1}.$$

- (c) Use the fact that $\phi \gg kT$ to show that

$$J \approx \left(\frac{4\pi m e}{h^3} \right) (kT)^2 e^{-\phi/kT}.$$

42. (a) Show that the pressure (P) of the conduction electrons in a metal is

$$P = \frac{2}{5}nE_F,$$

where n is the density of conduction electrons and E_F is the Fermi energy. (b) Evaluate the electron pressure

for copper and compare your answer to atmospheric pressure.

43. The heat capacity per volume of NaCl is $1.9 \times 10^6 \text{ J}\cdot\text{m}^{-3}\cdot\text{K}^{-1}$. Treating the phonons as an ideal gas (see problem 38) with an average speed of 500 m/s and a mean free path of 2.3 nm, calculate the thermal conductivity.