Chapter 41

Conduction of Electricity in Solids

Metals: How Many Conduction Electrons Are There?

$$n = \frac{\text{number of conduction electrons in sample}}{\text{sample volume } V}.$$

$$\begin{pmatrix}\text{number of conduction}\\ \text{electrons in sample}\end{pmatrix} = \begin{pmatrix}\text{number of atoms}\\ \text{in sample}\end{pmatrix}\begin{pmatrix}\text{number of valence}\\ \text{electrons per atom}\end{pmatrix}.$$

$$\begin{aligned}\begin{pmatrix}\text{number of atoms}\\ \text{in sample}\end{pmatrix} &= \frac{\text{sample mass } M_{\text{sam}}}{\text{atomic mass}} = \frac{\text{sample mass } M_{\text{sam}}}{(\text{molar mass } M)/N_{\text{A}}}\\ &= \frac{(\text{material's density})(\text{sample volume } V)}{(\text{molar mass } M)/N_{\text{A}}},\end{aligned}$$

where the molar mass M is the mass of one mole of the material in the sample and N_{A} is Avogadro's number ($6.02 \times 10^{23}\ \text{mol}^{-1}$).

Sample Problem 41.02 Number of conduction electrons in a metal

How many conduction electrons are in a cube of magnesium of volume $2.00 \times 10^{-6}\ \text{m}^3$? Magnesium atoms are bivalent.

KEY IDEAS

1. Because magnesium atoms are bivalent, each magnesium atom contributes two conduction electrons.
2. The cube's number of conduction electrons is related to its number of magnesium atoms by Eq. 41-2.
3. We can find the number of atoms with Eq. 41-4 and known data about the cube's volume and magnesium's properties.

Calculations: We can write Eq. 41-4 as

$$\begin{pmatrix}\text{number}\\ \text{of atoms}\\ \text{in sample}\end{pmatrix} = \frac{(\text{density})(\text{sample volume } V)N_A}{\text{molar mass } M}.$$

Magnesium has density $1.738\ \text{g/cm}^3$ $(= 1.738 \times 10^3\ \text{kg/m}^3)$ and molar mass $24.312\ \text{g/mol}$ $(= 24.312 \times 10^{-3}\ \text{kg/mol})$ (see Appendix F). The numerator gives us

$$(1.738 \times 10^3\ \text{kg/m}^3)(2.00 \times 10^{-6}\ \text{m}^3) \times (6.02 \times 10^{23}\ \text{atoms/mol}) = 2.0926 \times 10^{21}\ \text{kg/mol}.$$

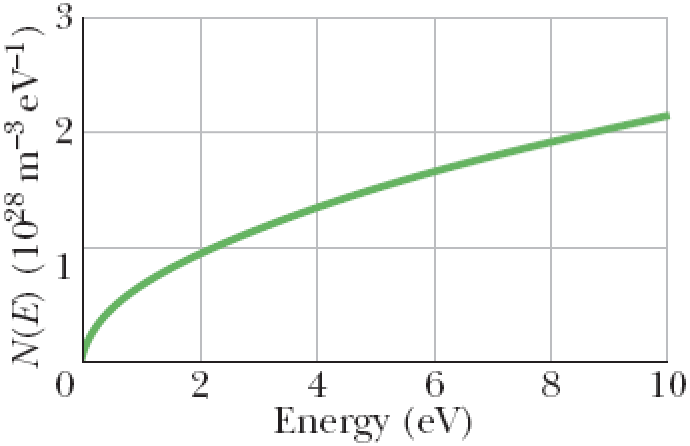
Thus,

$$\begin{pmatrix}\text{number of atoms}\\ \text{in sample}\end{pmatrix} = \frac{2.0926 \times 10^{21}\ \text{kg/mol}}{24.312 \times 10^{-3}\ \text{kg/mol}} = 8.61 \times 10^{22}.$$

Using this result and the fact that magnesium atoms are bivalent, we find that Eq. 41-2 yields

$$\begin{pmatrix}\text{number of}\\ \text{conduction electrons}\\ \text{in sample}\end{pmatrix} = (8.61 \times 10^{22}\ \text{atoms})\left(2\,\frac{\text{electrons}}{\text{atom}}\right) = 1.72 \times 10^{23}\ \text{electrons}. \qquad \text{(Answer)}$$

How Many Quantum States Are There?



The density of energy levels increases upward in a band.

Fig. 41-6 The density of states $N(E)$—that is, the number of electron energy levels per unit energy interval per unit volume—plotted as a function of electron energy. The density of states function simply counts the available states; it says nothing about whether these states are occupied by electrons.

$$N(E) = \frac{8\sqrt{2}\pi m^{3/2}}{h^3} E^{1/2} \qquad \text{(density of states, m}^{-3}\text{ J}^{-1}\text{)},$$

☑ Checkpoint 1

Is the spacing between adjacent energy levels at $E = 4$ eV in copper larger than, the same as, or smaller than the spacing at $E = 6$ eV?

larger

Sample Problem 41.03 **Number of states per electron volt in a metal**

(a) Using the data of Fig. 41-6, determine the number of states per electron-volt at 7 eV in a metal sample with a volume V of 2×10^{-9} m^3.

KEY IDEA

We can obtain the number of states per electron-volt at a given energy by using the density of states $N(E)$ at that energy and the sample's volume V.

Calculations: At an energy of 7 eV, we write

$$\begin{pmatrix}\text{number of states}\\ \text{per eV at 7 eV}\end{pmatrix} = \begin{pmatrix}\text{density of states}\\ N(E)\text{ at 7 eV}\end{pmatrix}\begin{pmatrix}\text{volume } V\\ \text{of sample}\end{pmatrix}.$$

From Fig. 41-6, we see that at an energy E of 7 eV, the density of states is about $1.8 \times 10^{28}\ \text{m}^{-3}\ \text{eV}^{-1}$. Thus,

$$\begin{aligned}\begin{pmatrix}\text{number of states}\\ \text{per eV at 7 eV}\end{pmatrix} &= (1.8 \times 10^{28}\ \text{m}^{-3}\ \text{eV}^{-1})(2 \times 10^{-9}\ \text{m}^3)\\ &= 3.6 \times 10^{19}\ \text{eV}^{-1}\\ &\approx 4 \times 10^{19}\ \text{eV}^{-1}. \qquad \text{(Answer)}\end{aligned}$$

(b) Next, determine the number of states N in the sample within a *small* energy range ΔE of 0.003 eV centered at 7 eV (the range is small relative to the energy level in the band).

Calculation: From Eq. 41-5 and Fig. 41-6, we know that the density of states is a function of energy E. However, for an energy range ΔE that is small relative to E, we can approximate the density of states (and thus the number of states per electron-volt) to be constant. Thus, at an energy of 7 eV, we find the number of states N in the energy range ΔE of 0.003 eV as

$$\begin{pmatrix}\text{number of states } N\\ \text{in range } \Delta E \text{ at 7 eV}\end{pmatrix} = \begin{pmatrix}\text{number of states}\\ \text{per eV at 7 eV}\end{pmatrix}\begin{pmatrix}\text{energy}\\ \text{range } \Delta E\end{pmatrix}$$

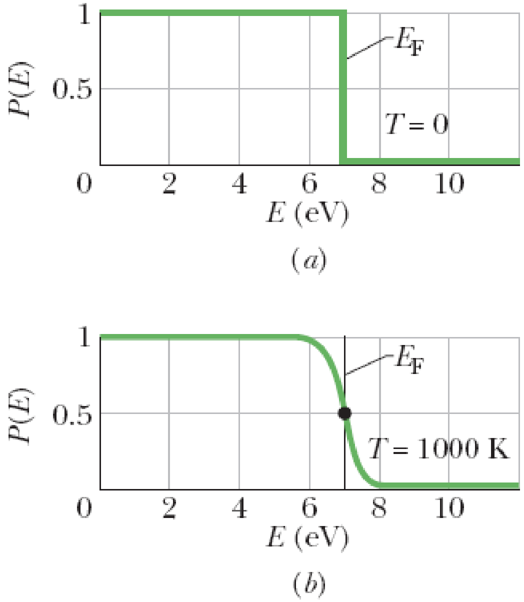
or

$$\begin{aligned}N &= (3.6 \times 10^{19}\ \text{eV}^{-1})(0.003\ \text{eV})\\ &= 1.1 \times 10^{17} \approx 1 \times 10^{17}. \qquad \text{(Answer)}\end{aligned}$$

(When you are asked for the number of states in a certain energy range, first see if that range is small enough to allow this type of approximation.)

Metals: The Occupancy Probability P(E):

The Fermi energy of a given material is the energy of a quantum state that has the probability 0.5 of being occupied by an electron.



The occupancy probability is high below the Fermi level.

Fig. 41-7 The occupancy probability $P(E)$ is the probability that an energy level will be occupied by an electron. (*a*) At $T =$ 0 K, $P(E)$ is unity for levels with energies E up to the Fermi energy E_F and zero for levels with higher energies. (*b*) At $T = 1000$ K, a few electrons whose energies were slightly less than the Fermi energy at $T = 0$ K move up to states with energies slightly greater than the Fermi energy. The dot on the curve shows that, for $E = E_F$, $P(E) = 0.5$.

$$P(E) = \frac{1}{e^{(E-E_F)/kT} + 1} \qquad \text{(occupancy probability),}$$

For $E < E_F$, the exponential term in Eq. 41-6 is $e^{-\infty}$, or zero; so $P(E) = 1$, in agreement with Fig. 41-7*a*.

For $E > E_F$, the exponential term is $e^{+\infty}$; so $P(E) = 0$, again in agreement with Fig. 41-7*a*.

Sample Problem 41.04 Probability of occupancy of an energy state in a metal

(a) What is the probability that a quantum state whose energy is 0.10 eV above the Fermi energy will be occupied? Assume a sample temperature of 800 K.

KEY IDEA

The occupancy probability of any state in a metal can be found from Fermi–Dirac statistics according to Eq. 41-6.

Calculations: Let's start with the exponent in Eq. 41-6:

$$\frac{E - E_{\mathrm{F}}}{kT} = \frac{0.10\ \mathrm{eV}}{(8.62 \times 10^{-5}\ \mathrm{eV/K})(800\ \mathrm{K})} = 1.45.$$

Inserting this exponent into Eq. 41-6 yields

$$P(E) = \frac{1}{e^{1.45} + 1} = 0.19 \text{ or } 19\%. \qquad \text{(Answer)}$$

(b) What is the probability of occupancy for a state that is 0.10 eV *below* the Fermi energy?

Calculation: The Key Idea of part (a) applies here also except that now the state has an energy *below* the Fermi energy. Thus, the exponent in Eq. 41-6 has the same magnitude we found in part (a) but is negative, and that makes the denominator smaller. Equation 41-6 now yields

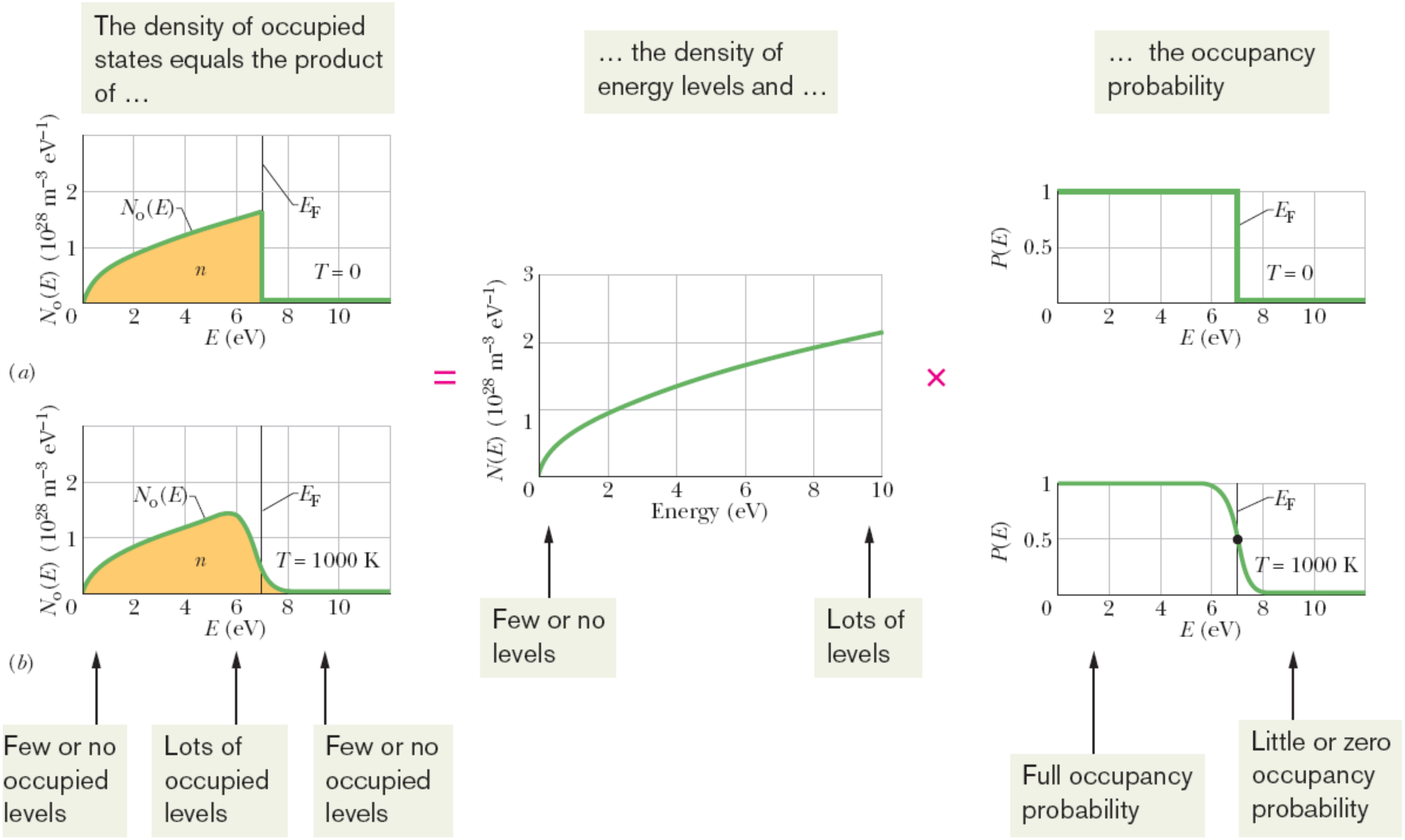
$$P(E) = \frac{1}{e^{-1.45} + 1} = 0.81 \text{ or } 81\%. \qquad \text{(Answer)}$$

For states below the Fermi energy, we are often more interested in the probability that the state is *not* occupied. This probability is just $1 - P(E)$, or 19%. Note that it is the same as the probability of occupancy in (a).

$$\begin{pmatrix}\text{density of occupied states}\\ N_o(E)\text{ at energy }E\end{pmatrix} = \begin{pmatrix}\text{density of states}\\ N(E)\text{ at energy }E\end{pmatrix}\begin{pmatrix}\text{occupancy probability}\\ P(E)\text{ at energy }E\end{pmatrix}$$

or

$$N_o(E) = N(E)\,P(E) \quad \text{(density of occupied states).} \tag{41-7}$$



The density of occupied states equals the product of …

… the density of energy levels and …

… the occupancy probability

Few or no levels

Lots of levels

Few or no occupied levels

Lots of occupied levels

Few or no occupied levels

Full occupancy probability

Little or zero occupancy probability

Fig. 41-8 (a) The density of occupied states $N_o(E)$ for copper at absolute zero. The area under the curve is the number density of electrons n. Note that all states with energies up to the Fermi energy $E_F = 7$ eV are occupied, and all those with energies above the Fermi energy are vacant. (b) The same for copper at $T = 1000$ K. Note that only electrons with energies near the Fermi energy have been affected and redistributed.

Sample Problem 41.05 Number of occupied states in an energy range in a metal

A lump of copper (Fermi energy = 7.0 eV) has volume $2 \times 10^{-9}\ \mathrm{m}^3$. How many occupied states per eV lie in a narrow energy range around 7.0 eV?

KEY IDEAS

(1) First we want the density of occupied states $N_o(E)$ as given by Eq. 41-7 ($N_o(E) = N(E)\,P(E)$). (2) Because we want to evaluate quantities for a narrow energy range around 7.0 eV (the Fermi energy for copper), the occupancy probability $P(E)$ is 0.50.

Calculations: From Fig. 41-6, we see that the density of states at 7 eV is about $1.8 \times 10^{28}\ \mathrm{m}^{-3}\,\mathrm{eV}^{-1}$. Thus, Eq. 41-7 tells us that the density of occupied states is

$$\begin{aligned} N_o(E) = N(E)\,P(E) &= (1.8 \times 10^{28}\ \mathrm{m}^{-3}\,\mathrm{eV}^{-1})(0.50) \\ &= 0.9 \times 10^{28}\ \mathrm{m}^{-3}\,\mathrm{eV}^{-1}. \end{aligned}$$

Next, we write

$$\begin{pmatrix}\text{number of } \textit{occupied} \\ \text{states per eV at 7 eV}\end{pmatrix} = \begin{pmatrix}\text{density of } \textit{occupied} \\ \text{states } N_o(E) \text{ at 7 eV}\end{pmatrix} \times \begin{pmatrix}\text{volume } V \\ \text{of sample}\end{pmatrix}.$$

Substituting for $N_o(E)$ and V gives us

$$\begin{aligned} \begin{pmatrix}\text{number of occupied} \\ \text{states per eV} \\ \text{at 7 eV}\end{pmatrix} &= (0.9 \times 10^{28}\ \mathrm{m}^{-3}\,\mathrm{eV}^{-1})(2 \times 10^{-9}\ \mathrm{m}^3) \\ &= 1.8 \times 10^{19}\ \mathrm{eV}^{-1} \\ &\approx 2 \times 10^{19}\ \mathrm{eV}^{-1}. \qquad \text{(Answer)} \end{aligned}$$

Metals: Calculating the Fermi Energy:

$$n = \int_0^{E_F} N_0(E)\, dE.$$

(The number of occupied states per unit volume at *T = 0 K* for all energies between $E=0$ and $E=E_F$).

$$n = \frac{8\sqrt{2}\pi m^{3/2}}{h^3} \int_0^{E_F} E^{1/2}\, dE$$

(Here *m* is the electron mass)

$$= \frac{8\sqrt{2}\pi m^{3/2}}{h^3} \frac{2E_F^{3/2}}{3},$$

$$E_F = \left(\frac{3}{16\sqrt{2}\pi}\right)^{2/3} \frac{h^2}{m} n^{2/3} = \frac{0.121h^2}{m} n^{2/3}.$$

41.2: Semiconductors and Doping:

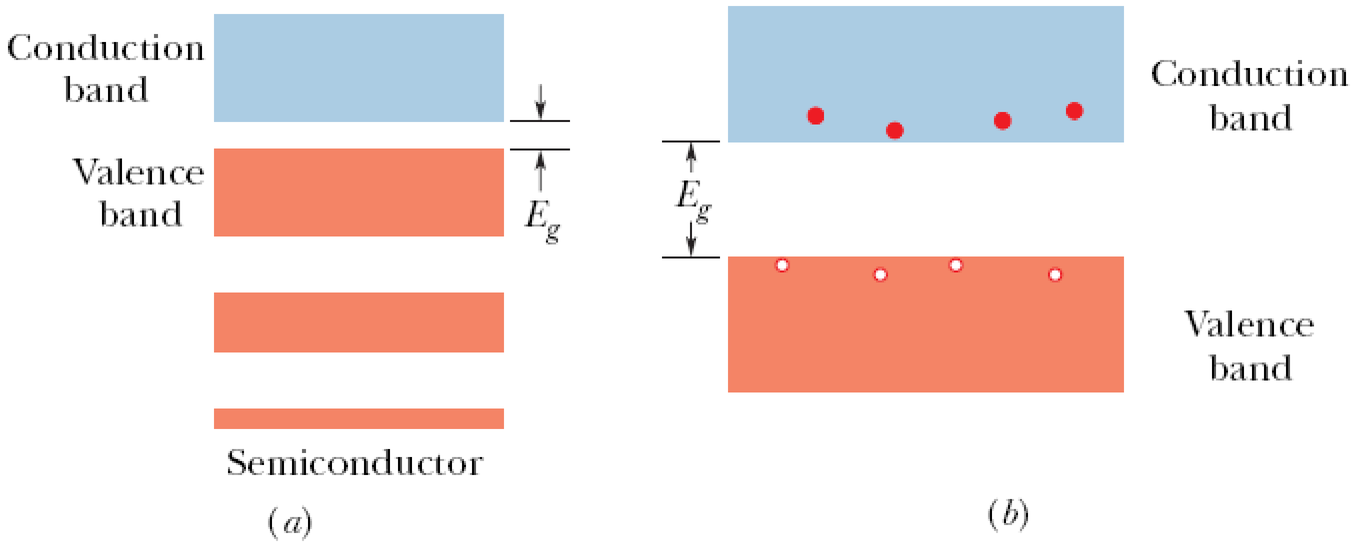


Fig. 41-9 (a) The band–gap pattern for a semiconductor. It resembles that of an insulator except that here the energy gap E_g is much smaller; thus electrons, because of their thermal agitation, have some reasonable probability of being able to jump the gap. (b) Thermal agitation has caused a few electrons to jump the gap from the valence band to the conduction band, leaving an equal number of holes in the valence band.

Semiconductors: Temperature Coefficient of Resistivity:

$$\alpha = \frac{1}{\rho}\frac{d\rho}{dT}.$$ (Here ρ is the resistivity)

The resistivity of copper increases with temperature (that is, $d\rho/dT > 0$) because collisions of copper's charge carriers occur more frequently at higher temperatures. This makes α positive for copper. The collision frequency also increases with temperature for silicon.

In contrast, the resistivity of silicon actually decreases with temperature $(d\rho/dT < 0)$ since the number of charge carriers n (electrons in the conduction band and holes in the valence band) increases so rapidly with temperature. (More electrons jump the gap from the valence band to the conduction band.) Thus, the fractional change α is negative for silicon.

Doped Semiconductors:

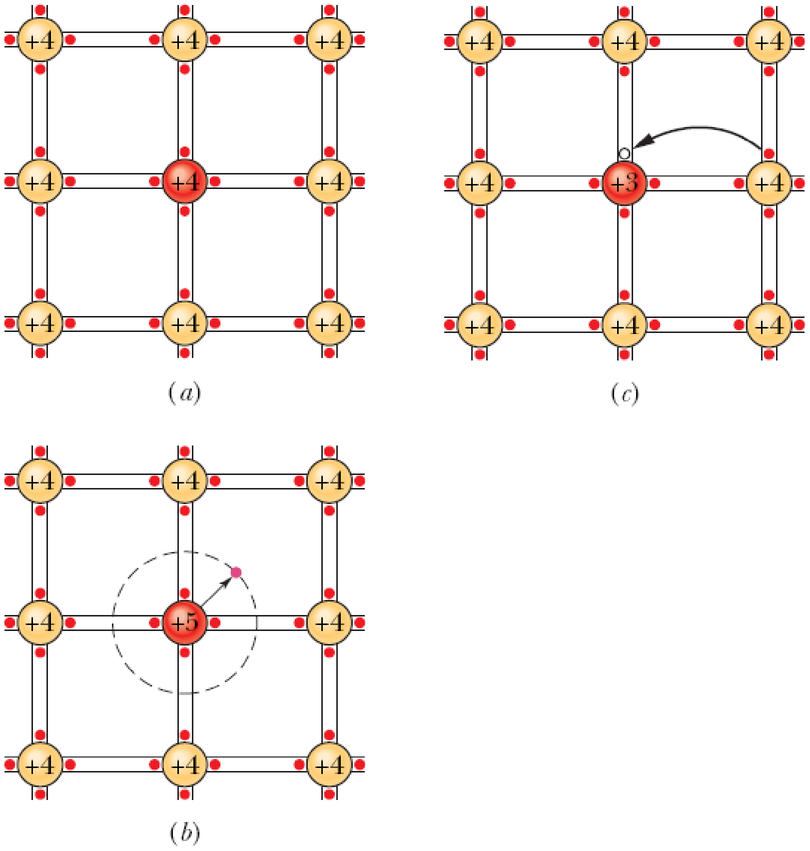
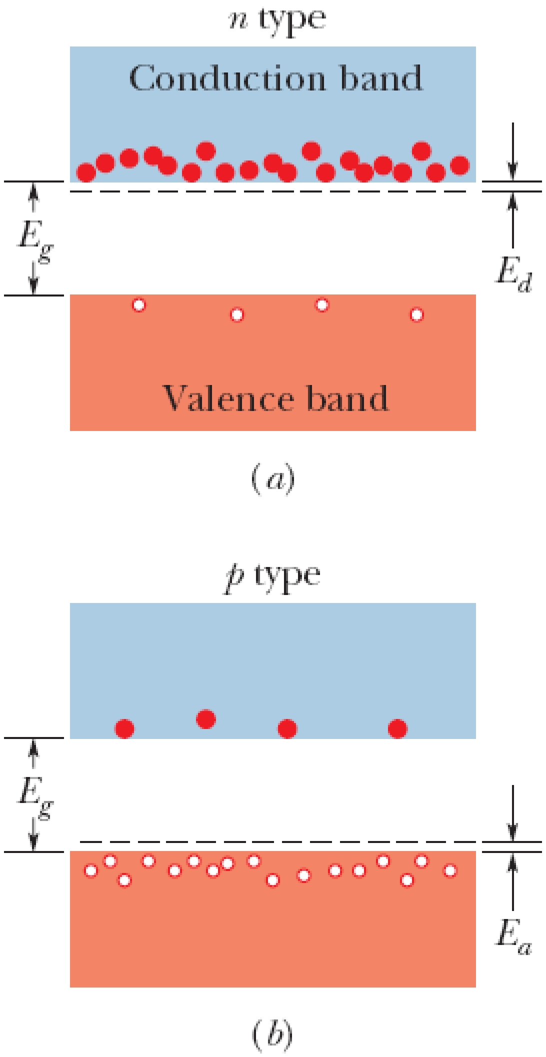


Fig. 41-10 (*a*) A flattened-out representation of the lattice structure of pure silicon. Each silicon ion is coupled to its four nearest neighbors by a two-electron covalent bond (represented by a pair of red dots between two parallel black lines). The electrons belong to the bond—not to the individual atoms—and form the valence band of the sample. (*b*) One silicon atom is replaced by a phosphorus atom (valence = 5). The "extra" electron is only loosely bound to its ion core and may easily be elevated to the conduction band, where it is free to wander through the volume of the lattice. (*c*) One silicon atom is replaced by an aluminum atom (valence = 3). There is now a hole in one of the covalent bonds and thus in the valence band of the sample. The hole can easily migrate through the lattice as electrons from neighboring bonds move in to fill it. Here the hole migrates rightward.

Fig. 41-11 (*a*) In a doped *n*-type semiconductor, the energy levels of donor electrons lie a small interval E_d below the bottom of the conduction band. Because donor electrons can be easily excited to the conduction band, there are now many more electrons in that band. The valence band contains the same small number of holes as before the dopant was added. (*b*) In a doped *p*-type semiconductor, the acceptor levels lie a small energy interval E_a above the top of the valence band. There are now many more holes in the valence band. The conduction band contains the same small number of electrons as before the dopant was added. The ratio of majority carriers to minority carriers in both (*a*) and (*b*) is very much greater than is suggested by these diagrams.



Electrons jump up from donors at the dashed level.

Electrons jump up to acceptors at the dashed level, leaving holes.

Table 41-2

Properties of Two Doped Semiconductors

Property	Type of Semiconductor	
	n	*p*
Matrix material	Silicon	Silicon
Matrix nuclear charge	$+14e$	$+14e$
Matrix energy gap	1.2 eV	1.2 eV
Dopant	Phosphorus	Aluminum
Type of dopant	Donor	Acceptor
Majority carriers	Electrons	Holes
Minority carriers	Holes	Electrons
Dopant energy gap	$E_d = 0.045$ eV	$E_a = 0.067$ eV
Dopant valence	5	3
Dopant nuclear charge	$+15e$	$+13e$
Dopant net ion charge	$+e$	$-e$

Sample Problem 41.06 Doping silicon with phosphorus

The number density n_0 of conduction electrons in pure silicon at room temperature is about $10^{16}\ \mathrm{m^{-3}}$. Assume that, by doping the silicon lattice with phosphorus, we want to increase this number by a factor of a million (10^6). What fraction of silicon atoms must we replace with phosphorus atoms? (Recall that at room temperature, thermal agitation is so effective that essentially every phosphorus atom donates its "extra" electron to the conduction band.)

Number of phosphorus atoms: Because each phosphorus atom contributes one conduction electron and because we want the total number density of conduction electrons to be $10^6 n_0$, the number density of phosphorus atoms n_P must be given by

$$10^6 n_0 = n_0 + n_P.$$

Then

$$\begin{aligned} n_P &= 10^6 n_0 - n_0 \approx 10^6 n_0 \\ &= (10^6)(10^{16}\ \mathrm{m^{-3}}) = 10^{22}\ \mathrm{m^{-3}}. \end{aligned}$$

This tells us that we must add 10^{22} atoms of phosphorus per cubic meter of silicon.

Fraction of silicon atoms: We can find the number density n_{Si} of silicon atoms in pure silicon (before the doping) from Eq. 41-4, which we can write as

$$\begin{pmatrix}\text{number of atoms}\\ \text{in sample}\end{pmatrix} = \frac{(\text{silicon density})(\text{sample volume } V)}{(\text{silicon molar mass } M_{Si})/N_A}.$$

Dividing both sides by the sample volume V to get the number density of silicon atoms n_{Si} on the left, we then have

$$n_{Si} = \frac{(\text{silicon density})N_A}{M_{Si}}.$$

Appendix F tells us that the density of silicon is $2.33\ \mathrm{g/cm^3}$ ($= 2330\ \mathrm{kg/m^3}$) and the molar mass of silicon is $28.1\ \mathrm{g/mol}$ ($= 0.0281\ \mathrm{kg/mol}$). Thus, we have

$$\begin{aligned} n_{Si} &= \frac{(2330\ \mathrm{kg/m^3})(6.02 \times 10^{23}\ \mathrm{atoms/mol})}{0.0281\ \mathrm{kg/mol}} \\ &= 5 \times 10^{28}\ \mathrm{atoms/m^3} = 5 \times 10^{28}\ \mathrm{m^{-3}}. \end{aligned}$$

The fraction we seek is approximately

$$\frac{n_P}{n_{Si}} = \frac{10^{22}\ \mathrm{m^{-3}}}{5 \times 10^{28}\ \mathrm{m^{-3}}} = \frac{1}{5 \times 10^6}. \qquad \text{(Answer)}$$

If we replace only *one silicon atom in five million* with a phosphorus atom, the number of electrons in the conduction band will be increased by a factor of a million.

How can such a tiny admixture of phosphorus have what seems to be such a big effect? The answer is that, although the effect is very significant, it is not "big." The number density of conduction electrons was $10^{16}\ \mathrm{m^{-3}}$ before doping and $10^{22}\ \mathrm{m^{-3}}$ after doping. For copper, however, the conduction-electron number density (given in Table 41-1) is about $10^{29}\ \mathrm{m^{-3}}$. Thus, even after doping, the number density of conduction electrons in silicon remains much less than that of a typical metal, such as copper, by a factor of about 10^7.