Figure 6.10   Temperature dependence of critical magnetic field for a superconductor. Reprinted, by permission, from L. Solymar and D. Walsh, *Lectures on the Electrical Properties of Materials*, 5th ed., p. 429. Copyright © 1993 by Oxford University Press.

Table 6.1   Critical Temperature and Critical Magnetic Field of a Number of Superconducting Elements

Element	T_c(K)	$H_0 \times 10^{-4}$(A/m)	Element	T_c(K)	$H_0 \times 10^{-4}$(A/m)
Al	1.19	0.8	Pb	7.18	6.5
Ga	1.09	0.4	Sn	3.72	2.5
Hg α	4.15	3.3	Ta	4.48	6.7
Hg β	3.95	2.7	Th	1.37	1.3
In	3.41	2.3	V	5.30	10.5
Nb	9.46	15.6	Zn	0.92	0.4

Source: L. Solymar, and D. Walsh, *Lectures on the Electrical Properties of Materials*, 5th ed. Copyright © 1993 by Oxford University Press.

6.1.1.4   *Intrinsic Semiconduction.*

We return now to our description of band gaps from Section 6.1.1.1 in order to elaborate upon those materials with conductivities in the range 10^{-6} to $10^4 (\Omega \cdot m)^{-1}$. At first, it may not seem important to study materials that neither readily conduct electricity nor protect against it, as do insulators. However, the development of semiconducting materials has, and continues to, revolutionize our lives.

Recall from Figure 6.2 that the gap between the valence and conduction bands called the band gap, E_g, can be used to classify materials as conductors, insulators, or semiconductors; also recall that for semiconductors the value of E_g is typically on the order of 1–2 eV. The magnitude of the band gap is characteristic of the lattice alone and varies widely for different crystals. In semiconductors, the valence and conduction bands do not overlap as in metals, but there are enough electrons in the valence band that can be "promoted" to the conduction band at a certain temperature to allow for limited electrical conduction. For example, in silicon, the energies of the valence electrons that bind the crystal together lie in the valence band. All four
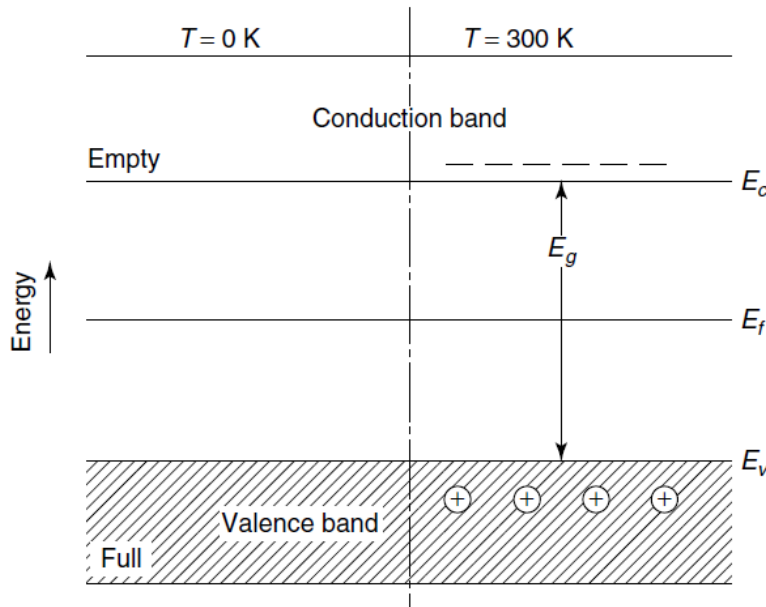
Figure 6.11   Energy bands of an intrinsic semiconductor: E_f is the Fermi energy level; E_c is the lower edge of the conduction band; E_v is the upper edge of the valence band; and E_g is the band gap. From Z. Jastrzebski, *The Nature and Properties of Engineering Materials*, 2nd ed. Copyright © 1976 by John Wiley & Sons, Inc. This material is used by permission of John Wiley & Sons, Inc.

valence electrons for each atom are tied in place, forming covalent bonds. There are no electrons in the conduction band at absolute zero, and the material is effectively an insulator (see Figure 6.11). At an elevated temperature, enough electrons have been thermally promoted to the conduction band to permit limited conduction. Promotion of electrons leaves behind positively charged "holes" in the valence band which maintain charge neutrality. The term *hole* denotes a mobile vacancy in the electronic valence structure of a semiconductor that is produced by removing one electron from a valence band. Holes, in almost all respects, can be regarded as moving positive charges through the crystal with a charge magnitude and mass the same as that of an electron.

Conduction that arises from thermally or optically excited electrons is called *intrinsic semiconduction*. The conduction of intrinsic semiconductors usually takes place at elevated temperatures, since sufficient thermal agitation is necessary to transfer a reasonable number of electrons from the valence band to the conduction band. The elements that are capable of intrinsic semiconduction are relatively limited and are shown in Figure 6.12. The most important of these are silicon and germanium.

In intrinsic semiconductors, the number of holes equals the number of mobile electrons. The resulting electrical conductivity is the sum of the conductivities of the valence band and conduction band charge carriers, which are holes and electrons, respectively. In this case, the conductivity can be expressed by modifying Eq. (6.9) to account for both charge carriers:

$$\sigma = n_e q_e \mu_e + n_h q_h \mu_h \tag{6.20}$$

where n_h, q_h, and μ_h are now the number, charge, and mobility of the holes, respectively, and contribute to the overall conductivity in addition to the corresponding

Figure 6.12 The intrinsic semiconducting elements. Reprinted, by permission, from I. Amato, *Stuff*, p. 68. Copyright © 1997 by Ivan Amato.

quantities for the electrons, indicated by the subscript e. The charge of the holes has the same numerical value as that of the electron, and since one hole is created for every electron that is promoted to the conduction band, $n_e = n_h$, such that Eq. (6.20) simplifies to

$$\sigma = n_e q_e (\mu_e + \mu_h) \tag{6.21}$$

The mobilities of holes are always less than those of electrons; that is $\mu_h < \mu_e$. In silicon and germanium, the ratio μ_e/μ_h is approximately three and two, respectively (see Table 6.2). Since the mobilities change only slightly as compared to the change of the charge carrier densities with temperature, the temperature variation of conductivity for an intrinsic semiconductor is similar to that of charge carrier density.

It can be shown from quantum mechanics that the effective density of states for the conduction and valence bands, N_c and N_v, respectively, are

$$N_c = 2 \left(\frac{2\pi m_e^* k_B T}{h^2} \right)^{3/2} \tag{6.22}$$

Table 6.2 Some Room-Temperature Electronic Properties of Group IV Elements

Element	E_g(eV)	σ(ohm$^{-1} \cdot$ m^{-1})	μ_e(m^2/V $\cdot$ s)	μ_h(m^2/V $\cdot$ s)
C (diamond)	~7	10^{-14}	0.18	0.14
Silicon	1.21	4.3×10^{-4}	0.14	0.05
Germanium	0.785	2.2	0.39	0.19
Gray tin	0.09	3×10^5	0.25	0.24
White tin	0	10^7	—	—
Lead	0	5×10^6	—	—

Source: K. M. Ralls, T. H. Courtney, and J. Wulff, *Introduction to Materials Science and Engineering.* Copyright © 1976 by John Wiley & Sons, Inc.

and

$$N_v = 2 \left(\frac{2\pi m_h^* k_B T}{h^2} \right)^{3/2} \tag{6.23}$$

where m_e^* and m_h^* are the effective mass of electrons and holes, respectively, k_B is Boltzmann's constant, T is absolute temperature, and h is Planck's constant. If we multiply these densities of state by the distribution of Eq. (6.11), in which we replace the energy, E, with the respective energy of the conduction and valence bands (E_v is lower in energy than the Fermi energy, E_f, and E_c is higher), we can obtain the number of mobile charge carriers in each band:

$$n_e = N_c \exp \left[\frac{-(E_c - E_f)}{k_B T} \right] \tag{6.24}$$

and

$$n_h = N_v \exp \left[\frac{-(E_f - E_v)}{k_B T} \right] \tag{6.25}$$

The product of the mobile positive and negative charge carriers is then obtained by multiplication of Eqs. (6.24) and (6.25), and recalling that $n_e = n_h$ we obtain

$$n_h \cdot n_e = n_e^2 = N_c N_v \exp \left[\frac{-(E_c - E_v)}{k_B T} \right] \tag{6.26}$$

and since $E_c - E_v = E_g$, the band gap energy is

$$n_e = (N_v N_c)^{1/2} \exp \left[\frac{-E_g}{2k_B T} \right] \tag{6.27}$$

Equation (6.27) illustrates that the product of charge carriers, $n_e n_h$, is independent of the position of the Fermi level and depends on the energy gap. It is a further result of this relationship that

$$E_f = \frac{E_c + E_v}{2} \tag{6.28}$$

Thus, the Fermi level is halfway between the conduction and valence bands.

The term $(N_v N_c)^{1/2}$ in Eq. (6.27) depends on the band structure of the semiconductor and is usually a constant for a specific material, outside of its temperature dependence. Thus, we can remove the temperature dependence of N_v and N_c from Eqs. (6.22) and (6.23) and simplify Eq. (6.27) to

$$n_e = CT^{3/2} \exp \left[\frac{-E_g}{2k_B T} \right] \tag{6.29}$$

where C is a constant. Substitution of Eq. (6.29) into Eq. (6.21) gives

$$\sigma = CT^{3/2} q_e (\mu_e + \mu_h) \exp \left[\frac{-E_g}{2k_B T} \right] \tag{6.30}$$

Neglecting the variation of the $T^{3/2}$ term, which is negligible compared to the variation with temperature in the exponential term, and recalling that the mobilities are less sensitive to temperature than are the charge carrier densities, Eq. (6.30) can be rewritten as

$$\sigma = \sigma_0 \exp\left(\frac{-E_g}{2k_B T}\right) \tag{6.31}$$

where σ_0 is the overall constant.

Equation (6.31) indicates that the conductivity of intrinsic semiconductors drops nearly exponentially with increasing temperature. At still higher temperatures, the concentration of thermally excited electrons in the conduction band may become so high that the semiconductor behaves more like a metal.

6.1.1.5 Extrinsic Semiconduction. The charge carrier density can also be increased through impurities of either higher or lower valence. For example, if pentavalent substitutional atoms such as P, As, or Sb are placed into a covalently bonded tetravalent material such as Si or Ge, in a process known as *doping*, only four of their five valence electrons are required to participate in covalent bonding. Since the fifth electron remains weakly bound to the impurity or *donor* atom, it is not entirely free in the crystal. Nevertheless, the binding energy, which is of the order 0.01 eV, is much less than that of a covalently bonded electron. This "extra" electron can be easily detached from the impurity or donor atom. The energy state of this electron is indicated by E_d, since it is the donor level, and the energy required to excite it to the conduction band can be represented by the band model shown in Figure 6.13. Notice that the energy gap between the donor and conducting bands is much smaller than that between the valence and conduction bands, or the normal band gap, E_g. Thermal agitation, even at room temperature, is sufficient to transfer this electron to the conduction band, leaving behind a positively charged hole in the donor
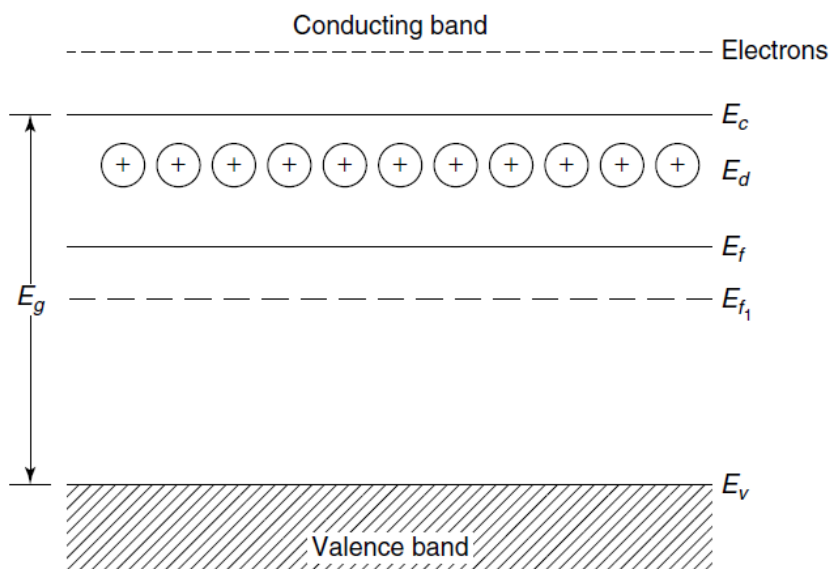

Figure 6.13   Schematic illustration of energy bands in an *n*-type, extrinsic semiconductor. From Z. Jastrzebski, *The Nature and Properties of Engineering Materials*, 2nd ed. Copyright © 1976 by John Wiley & Sons, Inc. This material is used by permission of John Wiley & Sons, Inc.