Chapter 8-3

Silicon and Germanium

The conduction and valence bands of germanium are shown in Fig. 14, based on a combination of theoretical and experimental results. The valence band edge in both Si and Ge is at **k** = 0 and is derived from $p_{3/2}$ and $p_{1/2}$ states of the free atoms, as is clear from the tight-binding approximation (Chapter 9) to the wavefunctions.

The $p_{3/2}$ level is fourfold degenerate as in the atom; the four states correspond to m_J values $\pm\frac{3}{2}$ and $\pm\frac{1}{2}$. The $p_{1/2}$ level is doubly degenerate, with $m_J = \pm\frac{1}{2}$. The $p_{3/2}$ states are higher in energy than the $p_{1/2}$ states; the energy difference Δ is a measure of the spin-orbit interaction.

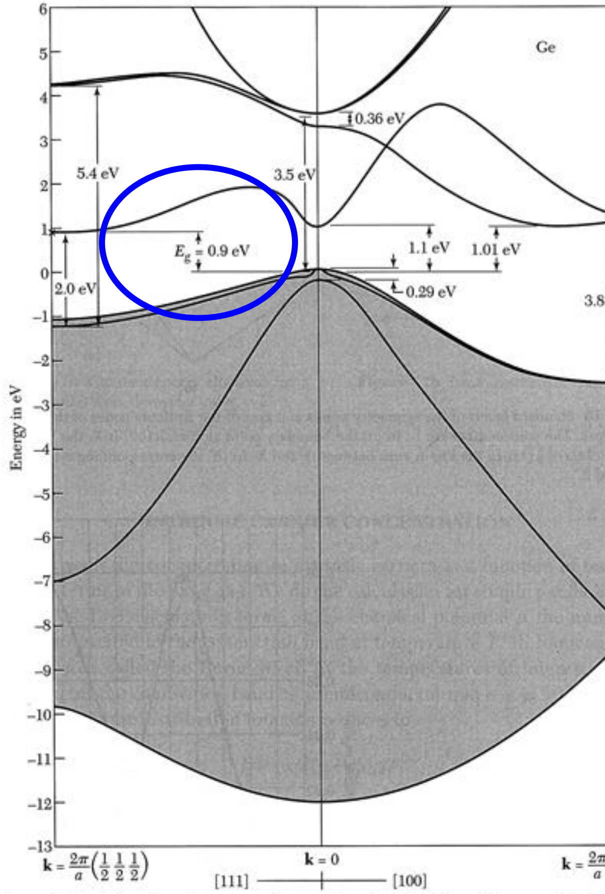


Figure 14 Calculated band structure of germanium, after C. Y. Fong. The general featur
good agreement with experiment. The four valence bands are shown in gray. The fine str

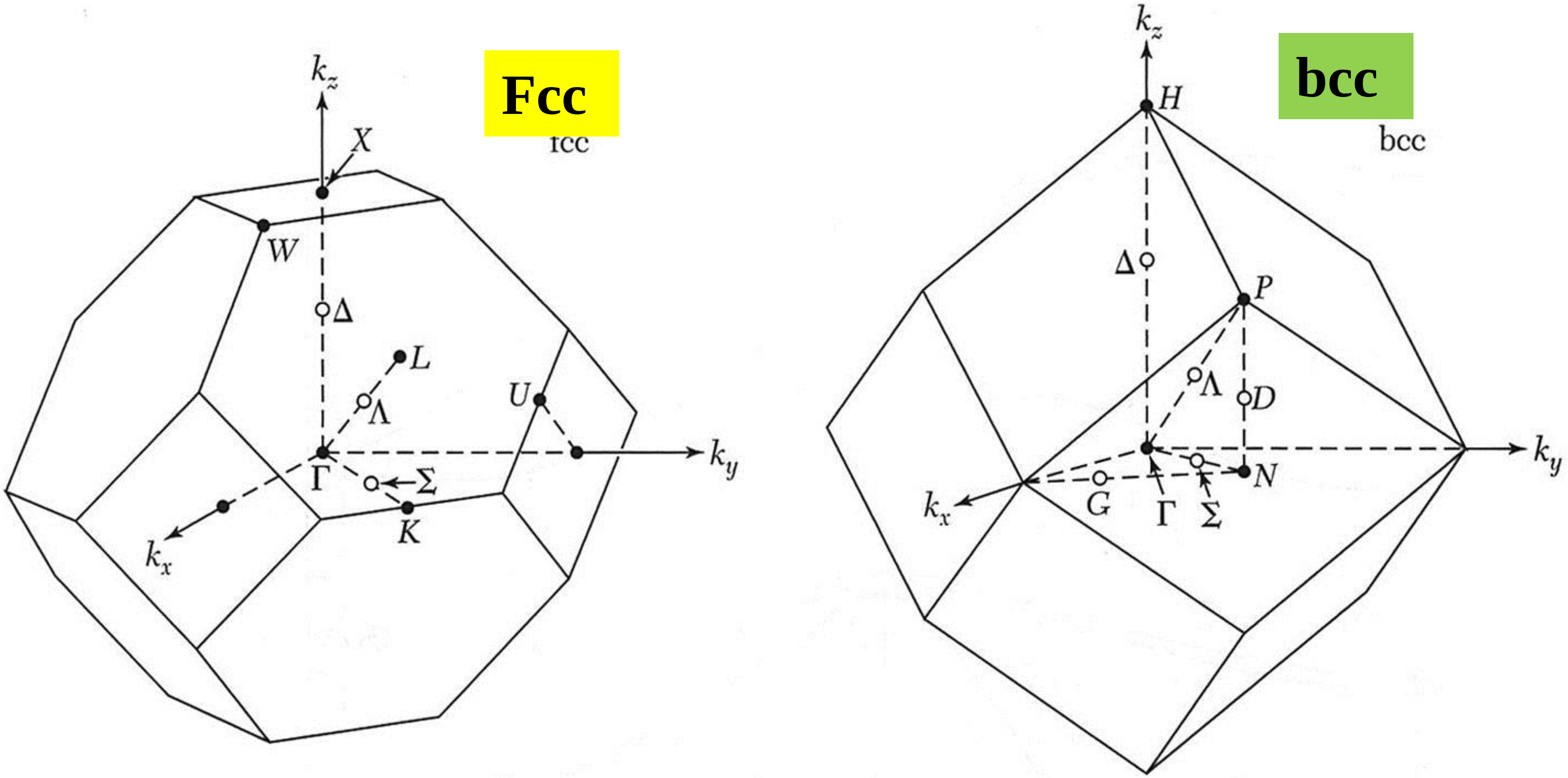
The valence band edges are not simple. Holes near the band edge are characterized by two effective masses, light and heavy. These arise from the two bands formed from the $p_{3/2}$ level of the atom. There is also a band formed from the $p_{1/2}$ level, split off from the $p_{3/2}$ level by the spin-orbit interaction. The energy surfaces are not spherical, but warped (*QTS*, p. 271):

$$\epsilon(\mathbf{k}) = Ak^2 \pm [B^2k^4 + C^2(k_x^2k_y^2 + k_y^2k_z^2 + k_z^2k_x^2)]^{1/2} \tag{33}$$

The choice of sign distinguishes the two masses. The split-off band has $\epsilon(k) = -\Delta + Ak^2$. The experiments give, in units $\hbar^2/2m$,

Si: $A = -4.29$; $|B| = 0.68$; $|C| = 4.87$; $\Delta = 0.044$ eV
Ge: $A = -13.38$; $|B| = 8.48$; $|C| = 13.15$; $\Delta = 0.29$ eV

Roughly, the light and heavy holes in germanium have masses 0.043 m and 0.34 m; in silicon 0.16 m and 0.52 m; in diamond 0.7 m and 2.12 m.



(a) (b)

Figure 15 Standard labels of the symmetry points and axes of the Brillouin zones of the fcc and bcc lattices. The zone centers are Γ. In (a) the boundary point at $(2\pi/a)(100)$ is X; the boundary point at $(2\pi/a)(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})$ is L; the line Δ runs between Γ and X. In (b) the corresponding symbols are H, P, and Δ.

The conduction band edges in Ge are at the equivalent points L of the Brillouin zone, Fig. 15a. Each band edge has a spheroidal energy surface oriented along a $\langle 111 \rangle$ crystal axis, with a longitudinal mass $m_l = 1.59\ m$ and a transverse mass $m_t = 0.082\ m$. For a static magnetic field at an angle θ with the longitudinal axis of a spheroid, the effective cyclotron mass m_c is

$$\frac{1}{m_c^2} = \frac{\cos^2\theta}{m_t^2} + \frac{\sin^2\theta}{m_t m_l} \tag{34}$$

Results for Ge are shown in Fig. 16.

In silicon the conduction band edges are spheroids oriented along the equivalent $\langle 100 \rangle$ directions in the Brillouin zone, with mass parameters $m_l = 0.92\ m$ and $m_t = 0.19\ m$, as in Fig. 17a. The band edges lie along the lines labeled Δ in the zone of Fig. 15a, a little way in from the boundary points X.

In GaAs we have $A = -6.98$, $B = -4.5$, $|C| = 6.2$, $\Delta = 0.341$ eV. The band structure is shown in Fig. 17b. It has a direct band gap with an isotropic conduction electron mass of $0.067\ m$.

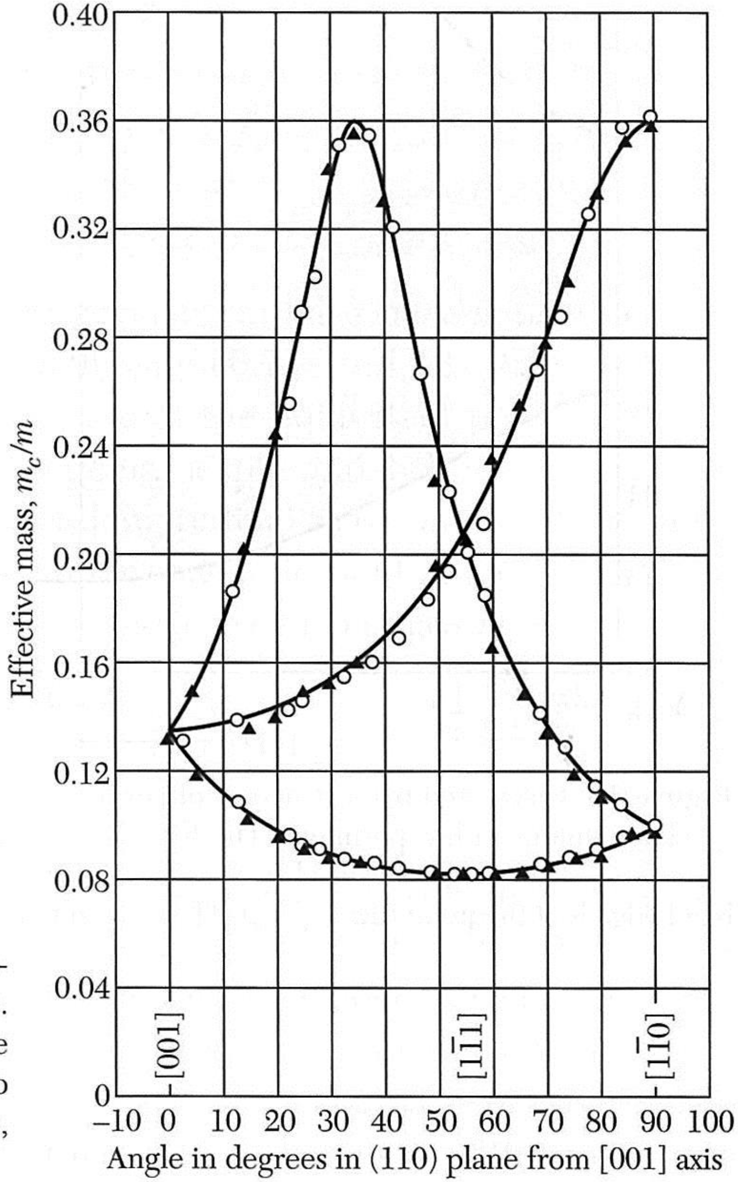
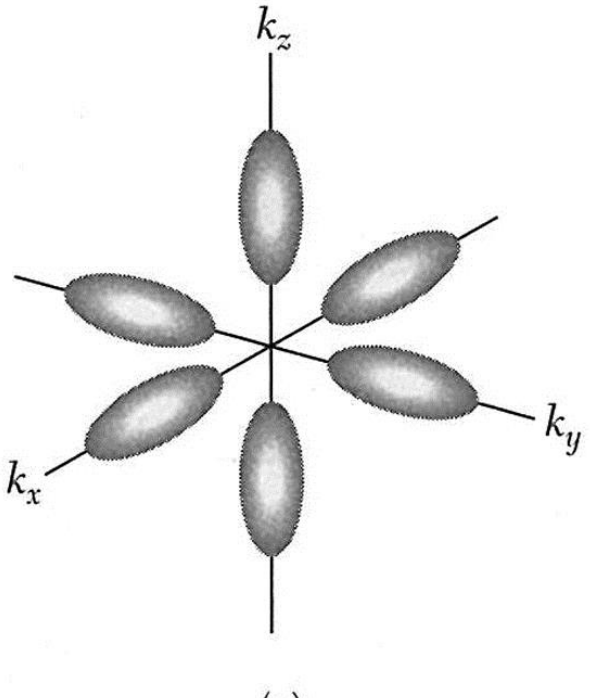


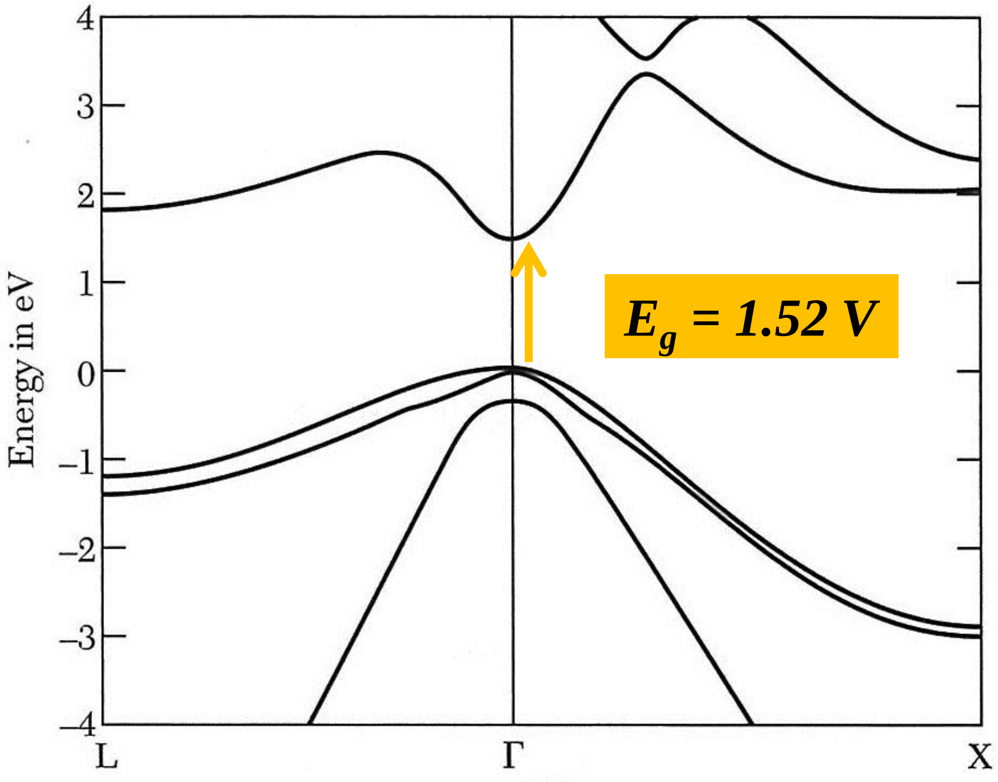
Figure 16 Effective cyclotron mass of electrons in germanium at 4 K for magnetic field directions in a (110) plane. There are four independent mass spheroids in Ge, one along each [111] axis, but viewed in the (110) plane two spheroids always appear equivalent. (After Dresselhaus, Kip, and Kittel.)

GaAs



(a)

Figure 17a Constant energy ellipsoids for electrons in silicon, drawn for $m_l/m_t = 5$.



E_g = 1.52 V

(b)

Figure 17b Band structure of GaAs, after S. G. Louie.

INTRINSIC CARRIER CONCENTRATION

We want the concentration of intrinsic carriers as a function of temperature, in terms of the band gap. We do the calculation for simple parabolic band edges. We first calculate in terms of the chemical potential μ the number of electrons excited to the conduction band at temperature T. In semiconductor physics μ is called the Fermi level. At the temperatures of interest we may suppose for the conduction band of a semiconductor that $\epsilon - \mu \gg k_BT$, so that the Fermi-Dirac distribution function reduces to

$$f_e \simeq \exp[(\mu - \epsilon)/k_BT] \quad . \tag{35}$$

This is the probability that a conduction electron orbital is occupied, in an approximation valid when $f_e \ll 1$.

The energy of an electron in the conduction band is

$$\epsilon_k = E_c + \hbar^2 k^2/2m_e \quad , \tag{36}$$

where E_c is the energy at the conduction band edge, as in Fig. 18. Here m_e is the effective mass of an electron. Thus from (6.20) the density of states at ϵ is

$$D_e(\epsilon) = \frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2}(\epsilon - E_c)^{1/2} \quad . \tag{37}$$

The concentration of electrons in the conduction band is

$$\begin{aligned} n = \int_{E_c}^{\infty} D_e(\epsilon) f_e(\epsilon) d\epsilon = \frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2} \exp(\mu/k_BT) \times \\ \int_{E_c}^{\infty} (\epsilon - E_c)^{1/2} \exp(-\epsilon/k_BT) d\epsilon \ , \end{aligned} \tag{38}$$

which integrates to give

$$\boxed{n = 2\left(\frac{m_e k_B T}{2\pi\hbar^2}\right)^{3/2} \exp[(\mu - E_c)/k_BT] \ .} \tag{39}$$

The problem is solved for n when μ is known. It is useful to calculate the equilibrium concentration of holes p. The distribution function f_h for holes is related to the electron distribution function f_e by $f_h = 1 - f_e$, because a hole is the absence of an electron. We have

$$\begin{aligned} f_h = 1 - \frac{1}{\exp[(\epsilon - \mu)/k_BT] + 1} = \frac{1}{\exp[(\mu - \epsilon)/k_BT] + 1} \\ \cong \exp[(\epsilon - \mu)/k_BT] \ , \end{aligned} \tag{40}$$

provided $(\mu - \epsilon) \gg k_BT$.

If the holes near the top of the valence band behave as particles with effective mass m_h, the density of hole states is given by

$$D_h(\epsilon) = \frac{1}{2\pi^2}\left(\frac{2m_h}{\hbar^2}\right)^{3/2}(E_v - \epsilon)^{1/2} \quad , \tag{41}$$

where E_v is the energy at the valence band edge. Proceeding as in (38) we obtain

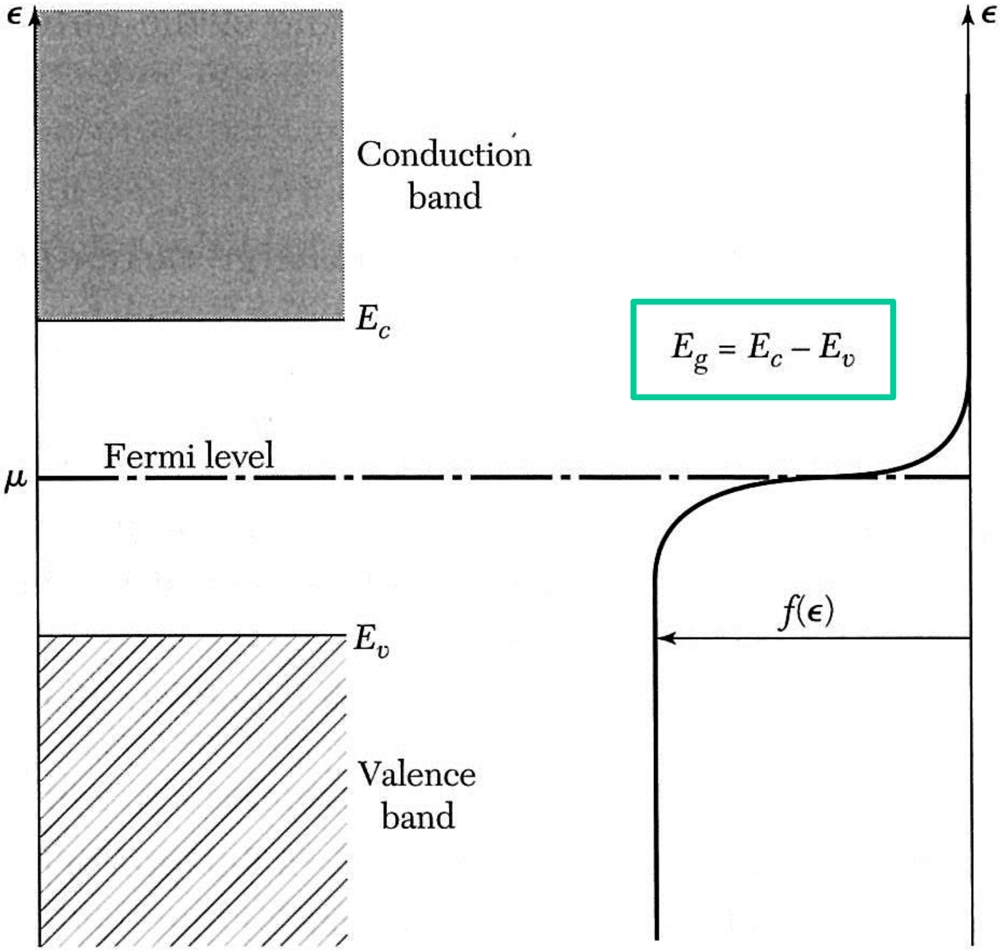
$$\boxed{p = \int_{-\infty}^{\overset{E_v}{E_c}} D_h(\epsilon)f_h(\epsilon)d\epsilon = 2\left(\frac{m_h k_B T}{2\pi\hbar^2}\right)^{3/2} \exp[(\overset{E_v}{E_c} - \mu)/k_B T]} \tag{42}$$

for the concentration p of holes in the valence band.

We multiply together the expressions for n and p to obtain the equilibrium relation, with the energy gap $E_g = E_c - E_v$ as in Fig. 18,

$$\boxed{np = 4\left(\frac{k_B T}{2\pi\hbar^2}\right)^3 (\overset{\overset{m_e}{\downarrow}}{m_c} m_h)^{3/2} \exp(-E_g/k_B T) \quad .} \tag{43}$$

This useful result does not involve the Fermi level μ. At 300 K the value of np is 2.10×10^{19} cm^{-6}, 2.89×10^{26} cm^{-6}, and 6.55×10^{12} cm^{-6}, for the actual band structures of Si, Ge, and GaAs, respectively.



$$\boxed{E_g = E_c - E_v}$$

Figure 18 Energy scale for statistical calculations. The Fermi distribution function is shown on the same scale, for a temperature $k_BT \ll E_g$. The Fermi level μ is taken to lie well within the band gap, as for an intrinsic semiconductor. If $\epsilon = \mu$, then $f = \frac{1}{2}$.

We have nowhere assumed in the derivation that the material is intrinsic: the result holds for impurity ionization as well. The only assumption made is that the distance of the Fermi level from the edge of both bands is large in comparison with k_BT.

A simple kinetic argument shows why the product np is constant at a given temperature. Suppose that the equilibrium population of electrons and holes is maintained by black-body photon radiation at temperature T. The photons generate electron-hole pairs at a rate $A(T)$, while $B(T)np$ is the rate of the recombination reaction $e + h =$ photon. Then

$$dn/dt = A(T) - B(T)np = dp/dt \quad . \tag{44}$$

In equilibrium $dn/dt = 0$, $dp/dt = 0$, whence $np = A(T)/B(T)$.

Because the product of the electron and hole concentrations is a constant independent of impurity concentration at a given temperature, the introduction of a small proportion of a suitable impurity to increase n, say, must decrease p. This result is important in practice—we can reduce the total carrier concentration $n + p$ in an impure crystal, sometimes enormously, by the controlled introduction of suitable impurities. Such a reduction is called **compensation**.

In an intrinsic semiconductor the number of electrons is equal to the number of holes, because the thermal excitation of an electron leaves behind a hole in the valence band. Thus from (43) we have, letting the subscript i denote intrinsic and $E_g = E_c - E_v$,

$$\boxed{n_i = p_i = 2\left(\frac{k_B T}{2\pi\hbar^2}\right)^{3/2} (m_e m_h)^{3/4} \exp(-E_g/2k_B T) \ .} \qquad (45)$$

The intrinsic carrier concentration depends exponentially on $E_g/2k_BT$, where E_g is the energy gap. We set (39) equal to (42) to obtain, for the Fermi level as measured from the top of the valence band,

$$\exp(2\mu/k_BT) = (m_h/m_e)^{3/2} \exp(E_g/k_BT) \;; \tag{46}$$

$$\boxed{\mu = \tfrac{1}{2} E_g + \tfrac{3}{4} k_BT \ln{(m_h/m_e)} \;.} \tag{47}$$

If $m_h = m_e$, then $\mu = \frac{1}{2} E_g$ and the Fermi level is in the middle of the forbidden gap.

Intrinsic Mobility

The mobility is the magnitude of the drift velocity of a charge carrier per unit electric field:

$$\boxed{\mu = |v|/E \ .} \tag{48}$$

The mobility is defined to be positive for both electrons and holes, although their drift velocities are opposite in a given field. By writing μ_e or μ_h with subscripts for the electron or hole mobility we can avoid any confusion between μ as the chemical potential and as the mobility.

The electrical conductivity is the sum of the electron and hole contributions:

$J = \sigma E = n\ e\ \upsilon$

$\sigma = n\ e\ \upsilon / E = n\ e\ \mu$

$$\boxed{\sigma = (ne\mu_e + pe\mu_h) \ ,} \tag{49}$$

where n and p are the concentrations of electrons and holes. In Chapter 6 the drift velocity of a charge q was found to be $v = q\tau E/m$, whence

$$\boxed{\mu_e = e\tau_e/m_e \ ; \qquad \mu_h = e\tau_h/m_h \ ,} \tag{50}$$

where τ is the collision time.

The mobilities depend on temperature as a modest power law. The temperature dependence of the conductivity in the intrinsic region will be dominated by the exponential dependence $\exp(-E_g/2k_BT)$ of the carrier concentration, Eq. (45).

Table 3 gives experimental values of the mobility at room temperature. The mobility in SI units is expressed in $m^2/V\text{-}s$ and is 10^{-4} of the mobility in practical units. For most substances the values quoted are limited by the scattering of carriers by thermal phonons. The hole mobilities typically are smaller than the electron mobilities because of the occurrence of band degeneracy at the valence band edge at the zone center, thereby making possible interband scattering processes that reduce the mobility considerably.

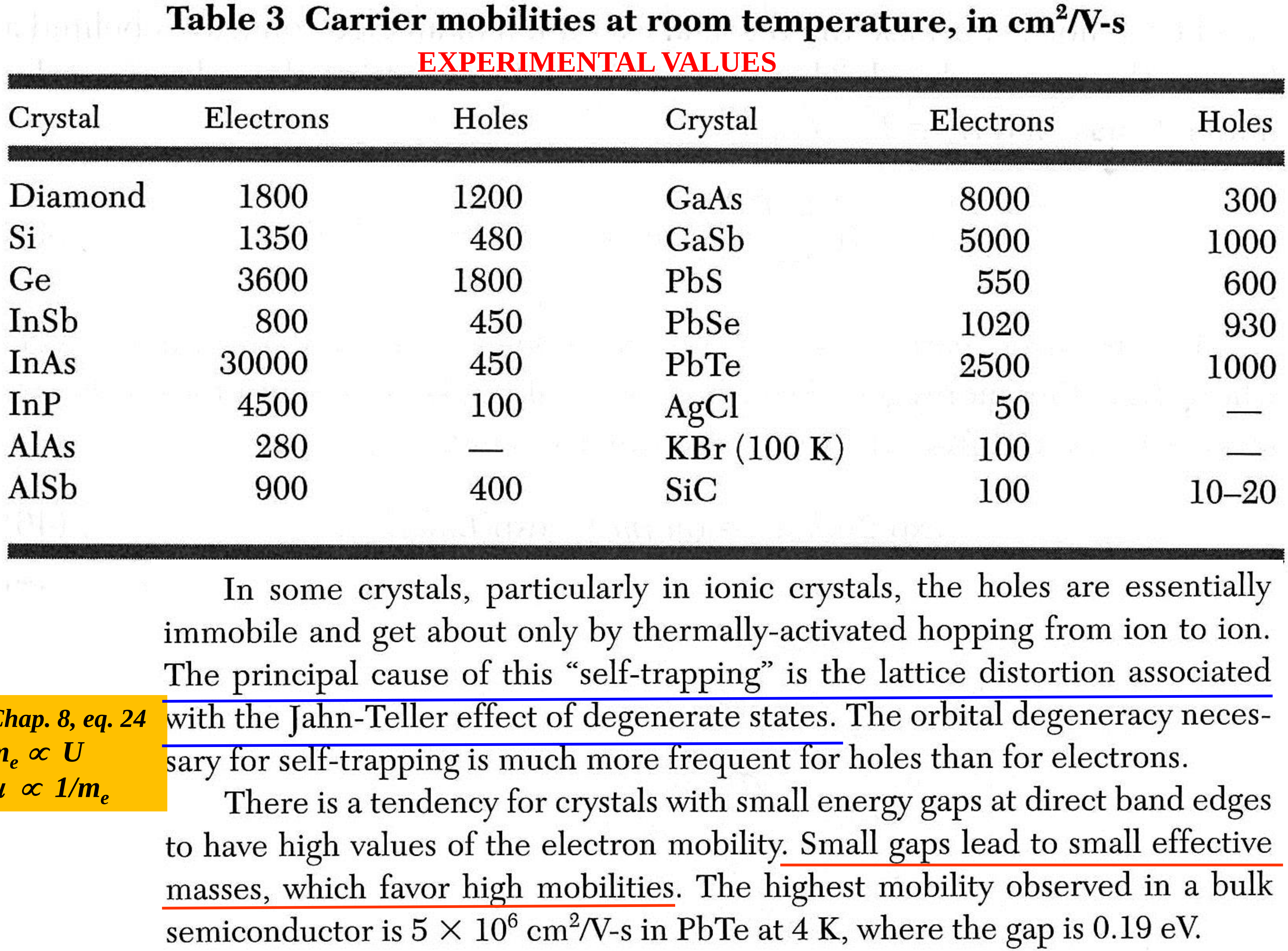


Table 3 Carrier mobilities at room temperature, in cm^2/V-s

EXPERIMENTAL VALUES

Crystal	Electrons	Holes	Crystal	Electrons	Holes
Diamond	1800	1200	GaAs	8000	300
Si	1350	480	GaSb	5000	1000
Ge	3600	1800	PbS	550	600
InSb	800	450	PbSe	1020	930
InAs	30000	450	PbTe	2500	1000
InP	4500	100	AgCl	50	—
AlAs	280	—	KBr (100 K)	100	—
AlSb	900	400	SiC	100	10–20

In some crystals, particularly in ionic crystals, the holes are essentially immobile and get about only by thermally-activated hopping from ion to ion. The principal cause of this "self-trapping" is the lattice distortion associated with the Jahn-Teller effect of degenerate states. The orbital degeneracy necessary for self-trapping is much more frequent for holes than for electrons.

There is a tendency for crystals with small energy gaps at direct band edges to have high values of the electron mobility. Small gaps lead to small effective masses, which favor high mobilities. The highest mobility observed in a bulk semiconductor is 5 × 10^6 cm^2/V-s in PbTe at 4 K, where the gap is 0.19 eV.

Chap. 8, eq. 24

$m_e \propto U$

$\mu \propto 1/m_e$