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.

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.

INTRINSIC CARRIER CONCENTRATION

We want the concentration of intrinsic carriers 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 $\epsilon - \mu \gg k_B T$, and the Fermi-Dirac distribution function reduces to

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

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

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

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

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

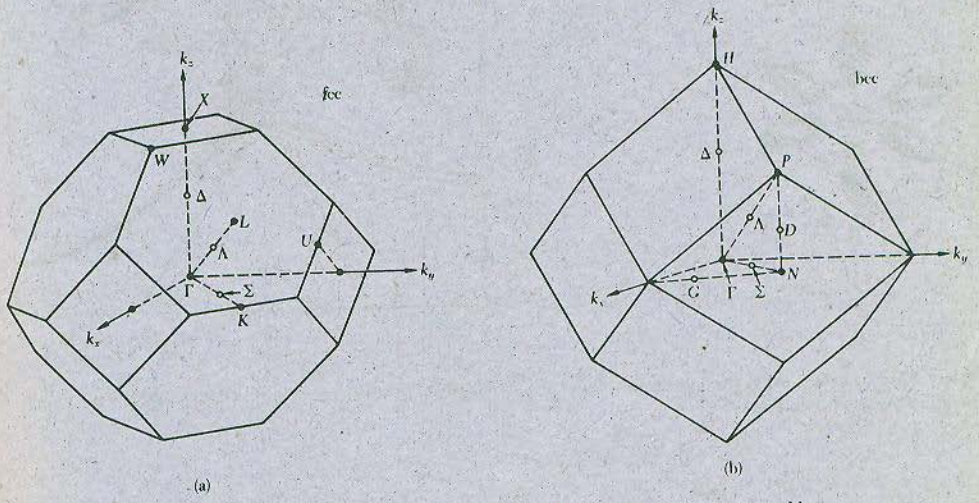


Figure 15 Standard labels of the symmetry points and axes of the Brillouin zones of the fcc and bcc lattices. The zone centers are Γ. In (a) the boundary point at $(2\pi/a)(100)$ is X; the boundary point at $(2\pi/a)(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ is L; the line Δ runs between Γ and X. In (b) the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

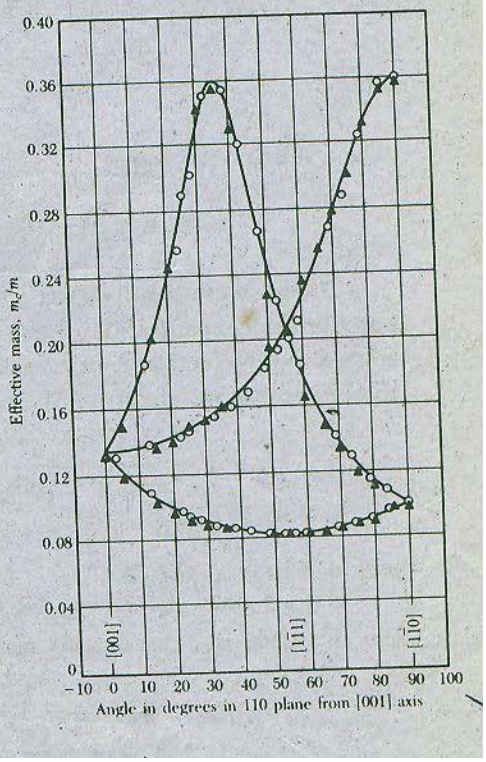
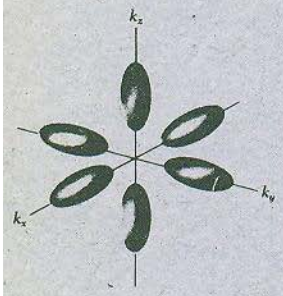
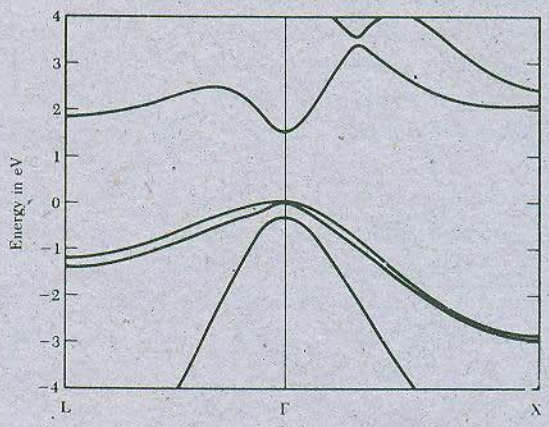


Figure 16 Effective cyclotron mass of electrons in germanium at 4 K for magnetic field directions in a 110 plane. There are four independent mass spheroids in Ge, one along each 111 axis, but viewed in the 110 plane two spheroids always appear equivalent. (After Dresselhaus, Kip, and Kittel.)



(a)

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



(b)

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

The concentration of electrons in the conduction band is

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

which integrates to give

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

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

$$f_h = 1 - \frac{1}{\exp[(\epsilon - \mu)/k_B T] + 1} = \frac{1}{\exp[(\mu - \epsilon)/k_B T] + 1} \cong \exp[(\epsilon - \mu)/k_B T] \ , \tag{40}$$

provided $(\mu - \epsilon) \gg k_B T$.

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

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

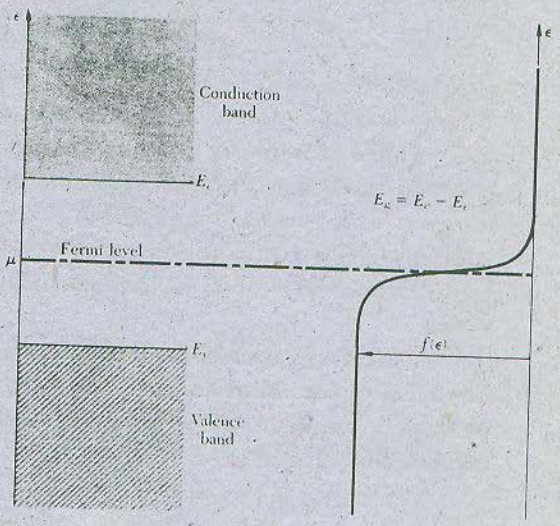


Figure 18 Energy scale for statistical calculations. The Fermi distribution function is shown on the same scale, for a temperature $k_BT \ll E_g$. The Fermi level μ is taken to lie well within the band gap, as for an intrinsic semiconductor. If $\epsilon = \mu$, then $f = \frac{1}{2}$.

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

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

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 $E_g = E_c - E_v$,

$$np = 4\left(\frac{k_B T}{2\pi\hbar^2}\right)^3 (m_e m_h)^{3/2} \exp(-E_g/k_B T) \ . \qquad (43)$$

This useful result does not involve the Fermi level μ. It is an expression of the law of mass action.

We have nowhere assumed in the derivation that the material is intrinsic: the result holds in the presence of impurities 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. 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.

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 recombi-

nation reaction $e + h =$ photon. Then

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

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 $E_g = E_c - E_v$,

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

The intrinsic carrier depends exponentially on $E_g/2k_B T$, 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,

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

$$\mu = \tfrac{1}{2}E_g + \tfrac{3}{4}k_B T \ln (m_h/m_e) \tag{47}$$

If $m_h = m_e$, then $\mu = \frac{1}{2}E_g$ and the Fermi level is in the middle of the forbidden gap. A thorough treatment of the statistical physics of semiconductors is given in *TP*, Chapter 13.

Intrinsic Mobility

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

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

The mobility is defined to be positive for both electrons and holes, although their drift velocities are opposite. By writing μ_e or μ_h 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:

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

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

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

Table 3 Carrier mobilities at room temperature, in $cm^2/V\text{-}s$

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

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.

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 (Chapter 14). The necessary orbital degeneracy 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. By (9.41) small gaps lead to light effective masses, which by (50) favor high mobilities. The highest mobility observed in a semiconductor is 5×10^6 $cm^2/V\text{-}s$ in PbTe at 4 K, where the gap is 0.19 eV.

IMPURITY CONDUCTIVITY

Certain impurities and imperfections drastically affect the electrical properties of a semiconductor. The addition of boron to silicon in the proportion of 1 boron atom to 10^5 silicon atoms increases the conductivity of pure silicon by a factor of 10^3 at room temperature. In a compound semiconductor a stoichiometric deficiency of one constituent will act as an impurity; such semiconductors

are known as **deficit semiconductors**. The deliberate addition of impurities to a semiconductor is called **doping**.

We consider the effect of impurities in silicon and germanium. These elements crystallize in the diamond structure. Each atom forms four covalent bonds, one with each of its nearest neighbors, corresponding to the chemical valence four. If an impurity atom of valence five, such as phosphorus, arsenic, or antimony, is substituted in the lattice in place of a normal atom, there will be one valence electron from the impurity atom left over after the four covalent bonds are established with the nearest neighbors, that is, after the impurity atom has been accommodated in the structure with as little disturbance as possible.

Donor States. The structure in Fig. 19 has a positive charge on the impurity atom (which has lost one electron). Lattice constant studies have verified that the pentavalent impurities enter the lattice by substitution for normal atoms, and not in interstitial positions. Impurity atoms that can give up an electron are called **donors**. The crystal as a whole remains neutral because the electron remains in the crystal.

The electron moves in the coulomb potential $e/\epsilon r$ of the impurity ion, where ϵ in a covalent crystal is the static dielectric constant of the medium. The factor $1/\epsilon$ takes account of the reduction in the coulomb force between charges caused by the electronic polarization of the medium. This treatment is valid for orbits large in comparison with the distance between atoms, and for slow motions of the electron such that the orbital frequency is low in comparison with the frequency ω_g corresponding to the energy gap. These conditions are satisfied quite well in Ge and Si by the donor electron of P, As, or Sb.

We estimate the ionization energy of the donor impurity. The Bohr theory of the hydrogen atom may be modified to take into account the dielectric constant of the medium and the effective mass of an electron in the periodic potential of the crystal. The ionization energy of atomic hydrogen is $-e^4m/2\hbar^2$ in CGS and $-e^4m/2(4\pi\epsilon_0\hbar)^2$ in SI.

In the semiconductor we replace e^2 by e^2/ϵ and m by the effective mass m_e to obtain

$$\text{(CGS)}\quad E_d = \frac{e^4 m_e}{2\epsilon^2\hbar^2} = \left(\frac{13.6}{\epsilon^2}\,\frac{m_e}{m}\right)\text{eV}\ ; \qquad \text{(SI)}\quad E_d = \frac{e^4 m_e}{2(4\pi\epsilon\epsilon_0\hbar)^2}\ , \tag{51}$$

as the donor ionization energy of the semiconductor.

The Bohr radius of the ground state of hydrogen is $\hbar^2/me^2$ in CGS or $4\pi\epsilon_0\hbar^2/me^2$ in SI. Thus the Bohr radius of the donor is

$$\text{(CGS)}\quad a_d = \frac{\epsilon\hbar^2}{m_e e^2} = \left(\frac{0.53\epsilon}{m_e/m}\right)\text{Å}\ ; \qquad \text{(SI)}\quad a_d = \frac{4\pi\epsilon\epsilon_0\hbar^2}{m_e e^2}\ . \tag{52}$$

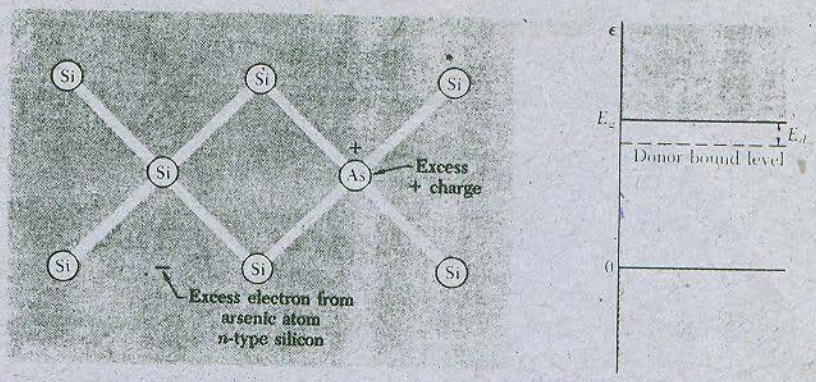


Figure 19 Charges associated with an arsenic impurity atom in silicon. Arsenic has five valence electrons, but silicon has only four valence electrons. Thus four electrons on the arsenic form tetrahedral covalent bonds similar to silicon, and the fifth electron is available for conduction. The arsenic atom is called a **donor** because when ionized it donates an electron to the conduction band.

The application to germanium and silicon is complicated by the anisotropic effective mass of the conduction electrons. But the dielectric constant has the more important effect on the donor energy because it enters as the square, whereas the effective mass enters only as the first power.

To obtain a general impression of the impurity levels we use $m_e \approx 0.1\ m$ for electrons in germanium and $m_e \approx 0.2\ m$ in silicon. The static dielectric constant is given in Table 4. The ionization energy of the free hydrogen atom is 13.6 eV. For germanium the donor ionization energy E_d on our model is 5 meV, reduced with respect to hydrogen by the factor $m_e/m\epsilon^2 = 4 \times 10^{-4}$. The corresponding result for silicon is 20 meV. Calculations using the correct anisotropic mass tensor predict 9.05 meV for germanium and 29.8 meV for silicon. Observed values of donor ionization energies in Si and Ge are given in Table 5. Recall that 1 meV $\equiv 10^{-3}$ eV. In GaAs donors have $E_d \approx 6$ meV.

The radius of the first Bohr orbit is increased by $\epsilon m/m_e$ over the value

Table 4 Static relative dielectric constant of semiconductors

Crystal	ϵ	Crystal	ϵ
Diamond	5.5	GaSb	15.69
Si	11.7	GaAs	13.13
Ge	15.8	AlAs	10.1
InSb	17.88	AlSb	10.3
InAs	14.55	SiC	10.2
InP	12.37	Cu_2O	7.1

Table 5 Donor ionization energies E_d of pentavalent impurities in germanium and silicon, in meV

	P	As	Sb
Si	45.	49.	39.
Ge	12.0	12.7	9.6

0.53 Å for the free hydrogen atom. The corresponding radius is (160)(0.53) ≃ 80 Å in germanium and (60)(0.53) ≃ 30 Å in silicon. These are large radii, so that donor orbits overlap at relatively low donor concentrations, compared to the number of host atoms. With appreciable overlap, an "impurity band" is formed from the donor states: see the discussion of the metal-insulator transition in Chapter 10.

The semiconductor can conduct in the impurity band by electrons hopping from donor to donor. The process of impurity band conduction sets in at lower donor concentration levels if there are also some acceptor atoms present, so that some of the donors are always ionized. It is easier for a donor electron to hop to an ionized (unoccupied) donor than to an occupied donor atom, so that two electrons will not have to occupy the same site during charge transport.

Acceptor States. A hole may be bound to a trivalent impurity in germanium or silicon (Fig. 20), just as an electron is bound to a pentavalent impurity. Trivalent impurities such as B, Al, Ga, and In are called acceptors because they accept electrons from the valence band in order to complete the covalent bonds with neighbor atoms, leaving holes in the band.

When an acceptor is ionized a hole is freed, which requires an input of energy. On the usual energy band diagram, an electron rises when it gains energy, whereas a hole sinks in gaining energy.

Experimental ionization energies of acceptors in germanium and silicon are given in Table 6. The Bohr model applies qualitatively for holes just as for electrons, but the degeneracy at the top of the valence band complicates the effective mass problem.

The tables show that donor and acceptor ionization energies in Si are comparable with k_BT at room temperature (26 meV), so that the thermal ionization of donors and acceptors is important in the electrical conductivity of silicon at room temperature. If donor atoms are present in considerably greater numbers than acceptors, the thermal ionization of donors will release electrons into the conduction band. The conductivity of the specimen then will be controlled by electrons (negative charges), and the material is said to be n type.

If acceptors are dominant, holes will be released into the valence band and the conductivity will be controlled by holes (positive charges): the material is p

Table 6 Acceptor ionization energies E_a of trivalent impurities in germanium and silicon, in meV

	B	Al	Ga	In
Si	45.	57.	65.	157.
Ge	10.4	10.2	10.8	11.2

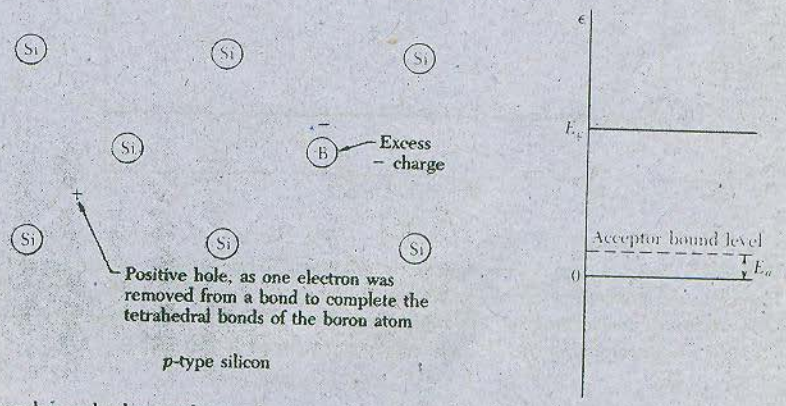


Figure 20 Boron has only three valence electrons; it can complete its tetrahedral bonds only by taking an electron from a Si-Si bond, leaving behind a hole in the silicon valence band. The positive hole is then available for conduction. The boron atom is called an **acceptor** because when ionized it accepts an electron from the valence band. At 0 K the hole is bound: remember that holes float.

type. The sign of the Hall voltage is a rough test for n or p type. Another handy laboratory test is the sign of the thermoelectric potential, discussed below.

The numbers of holes and electrons are equal in the intrinsic regime. The intrinsic electron concentration n_i at 300 K is 1.7×10^{13} cm^{-3} in germanium and 4.6×10^9 cm^{-3} in silicon. The electrical resistivity of intrinsic material is 43 ohm-cm for germanium and 2.6×10^5 ohm-cm for silicon.

Germanium has 4.42×10^{22} atoms per cm^3. The purification of Ge has been carried further than any other element.[2] The concentration of the common electrically active impurities—the shallow donor and acceptor impurities—has been reduced below 1 impurity atom in 10^{11} Ge atoms (Fig. 21). For example, the concentration of P in Ge can be reduced below 4×10^{10} cm^{-3}. The experimental sensitivity for detection of these impurities is 10^7 cm^{-3} by the method of photothermal ionization spectroscopy.[3] There are impurities (H, O,

[2]E. E. Haller, W. L. Hansen, and F. S. Goulding, "Physics of ultra-pure germanium," Adv. Phys. 30, 93–138 (1981).

[3]S. M. Kogan and T. M. Lifshits, Phys. Status Solidi (a) 39, 11 (1977).

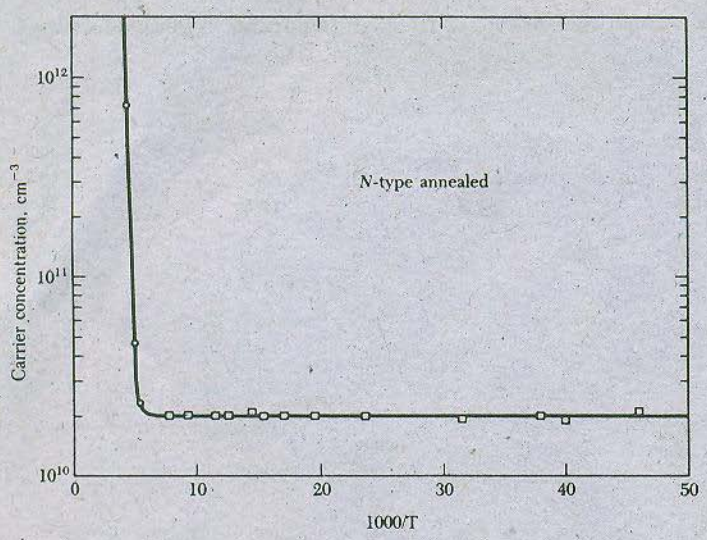


Figure 21 Temperature dependence of the free carrier concentration in ultrapure Ge, after R. N. Hall. The net concentration of electrically active impurities is 2×10^{10} cm^{-3}, as determined by Hall coefficient measurements. The rapid onset of intrinsic excitation is evident at low values of $1/T$. The carrier concentration is closely constant between 20 K and 200 K.

Si, C) whose concentrations in Ge cannot usually be reduced below 10^{12}–10^{14} cm^{-3}, but these do not affect electrical measurements and therefore may be hard to detect.

Thermal Ionization of Donors and Acceptors

The calculation of the equilibrium concentration of conduction electrons from ionized donors is identical with the standard calculation in statistical mechanics of the thermal ionization of hydrogen atoms (*TP*, p. 369). If there are no acceptors present, the result in the low temperature limit $k_B T \ll E_d$ is

$$\boxed{n \cong (n_0 N_d)^{1/2} \exp(-E_d/2k_B T)\ ,} \tag{53}$$

with $n_0 \equiv 2(m_e k_B T/2\pi\hbar^2)^{3/2}$; here N_d is the concentration of donors. To obtain (53) we apply the laws of chemical equilibria to the concentration ratio $[e][N_d^+]/[N_d]$, and then set $[N_d^+] = [e] = n$. Identical results hold for acceptors, under the assumption of no donor atoms.

If the donor and acceptor concentrations are comparable, affairs are complicated and the equations are solved by numerical methods. However, the law of mass action (43) requires the np product to be constant at a given temperature. An excess of donors will increase the electron concentration and decrease the hole concentration; the sum $n + p$ will increase. The conductivity will increase as $n + p$ if the mobilities are equal, as in Fig. 22.

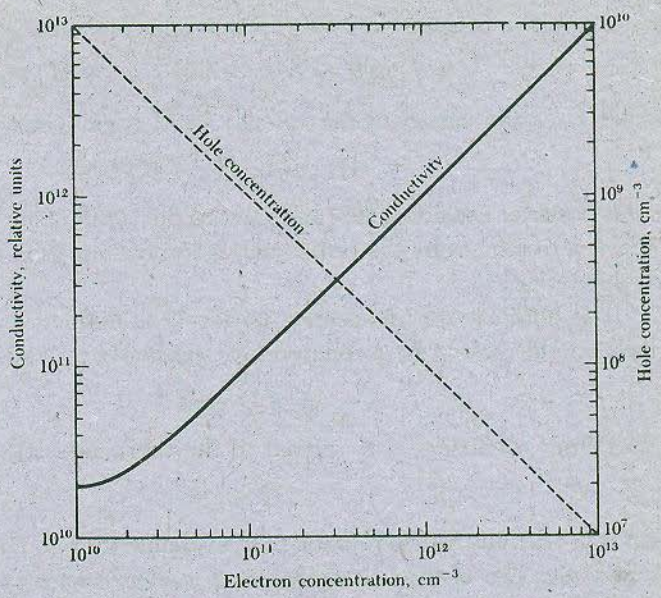


Figure 22 Electrical conductivity and hole concentration p calculated as a function of electron concentration n for a semiconductor at a temperature such that $np = 10^{20}$ cm^{-6}. The conductivity is symmetrical about $n = 10^{10}$ cm^{-3}. For $n > 10^{10}$ the specimen is n type; for $n < 10^{10}$, it is p type. We have taken $\mu_e = \mu_h$, for the mobilities.

THERMOELECTRIC EFFECTS

Consider a semiconductor maintained at a constant temperature while an electric field drives through it an electric current density j_q. If the current is carried only by electrons, the charge flux is

$$j_q = n(-e)(-\mu_e)E = ne\mu_e E \ , \tag{54}$$

where μ_e is the electron mobility. The average energy transported by an electron is, referred to the Fermi level μ,

$$(E_c - \mu) + \tfrac{3}{2}k_B T \ ,$$

where E_c is the energy at the conduction band edge. We refer the energy to the Fermi level because different conductors in contact have the same Fermi level. The energy flux that accompanies the charge flux is

$$j_U = n(E_c - \mu + \tfrac{3}{2}k_B T)(-\mu_e)E \ . \tag{55}$$

The **Peltier coefficient** Π is defined by the relation $j_U = \Pi j_q$; it is the energy carried per unit charge. For electrons,

$$\Pi_e = -(E_c - \mu + \tfrac{3}{2}k_B T)/e \tag{56}$$