Chapter 8-4

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 at room temperature by a factor of 10^3. 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. Impurity atoms that can give up an electron are called **donors**.

P, As, Sb

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. The crystal as a whole remains neutral because the electron remains in the crystal.

The extra 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.

Si has +4 valence electrons
As has +5 valence electrons

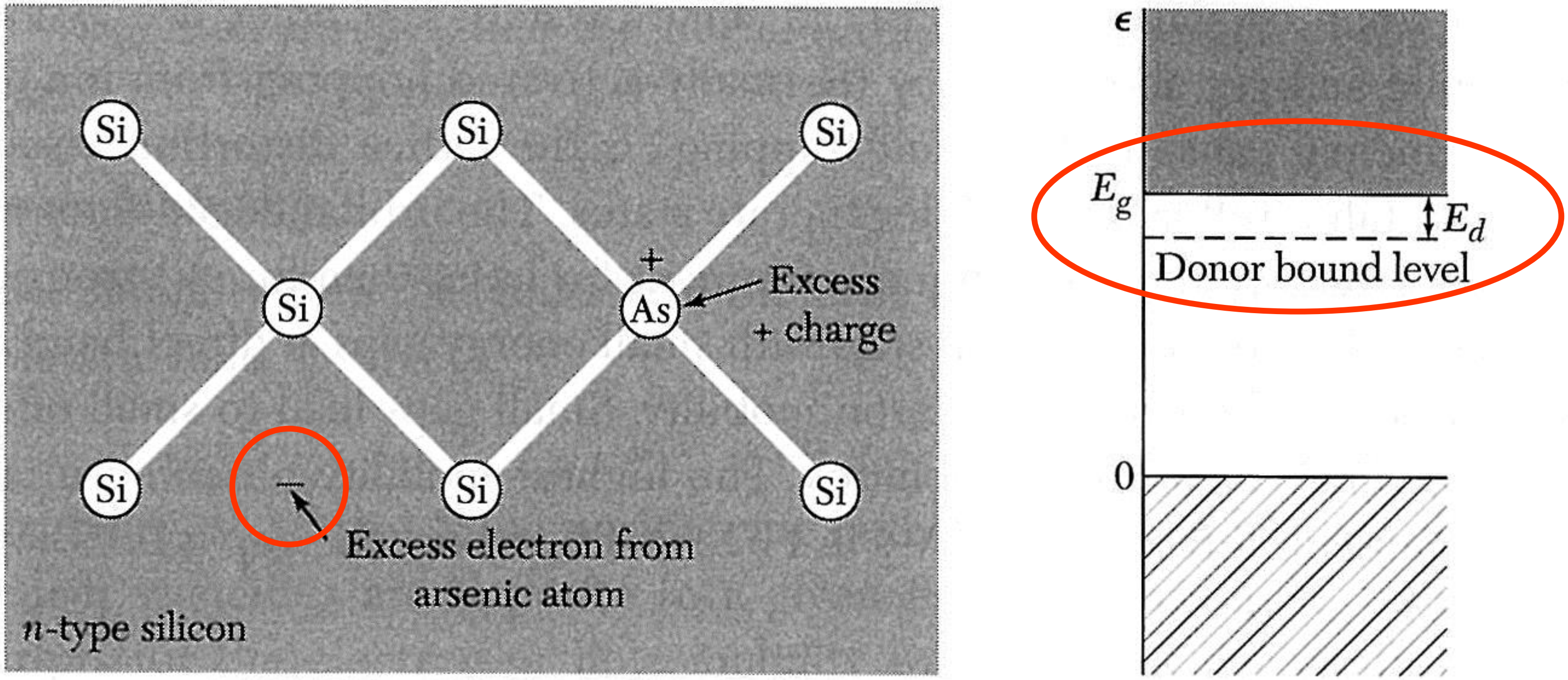


Figure 19 Charges associated with an arsenic impurity atom in silicon. Arsenic has five valence electrons, but silicon has only four valence electrons. Thus four electrons on the arsenic form tetrahedral covalent bonds similar to silicon, and the fifth electron is available for conduction. The arsenic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

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.

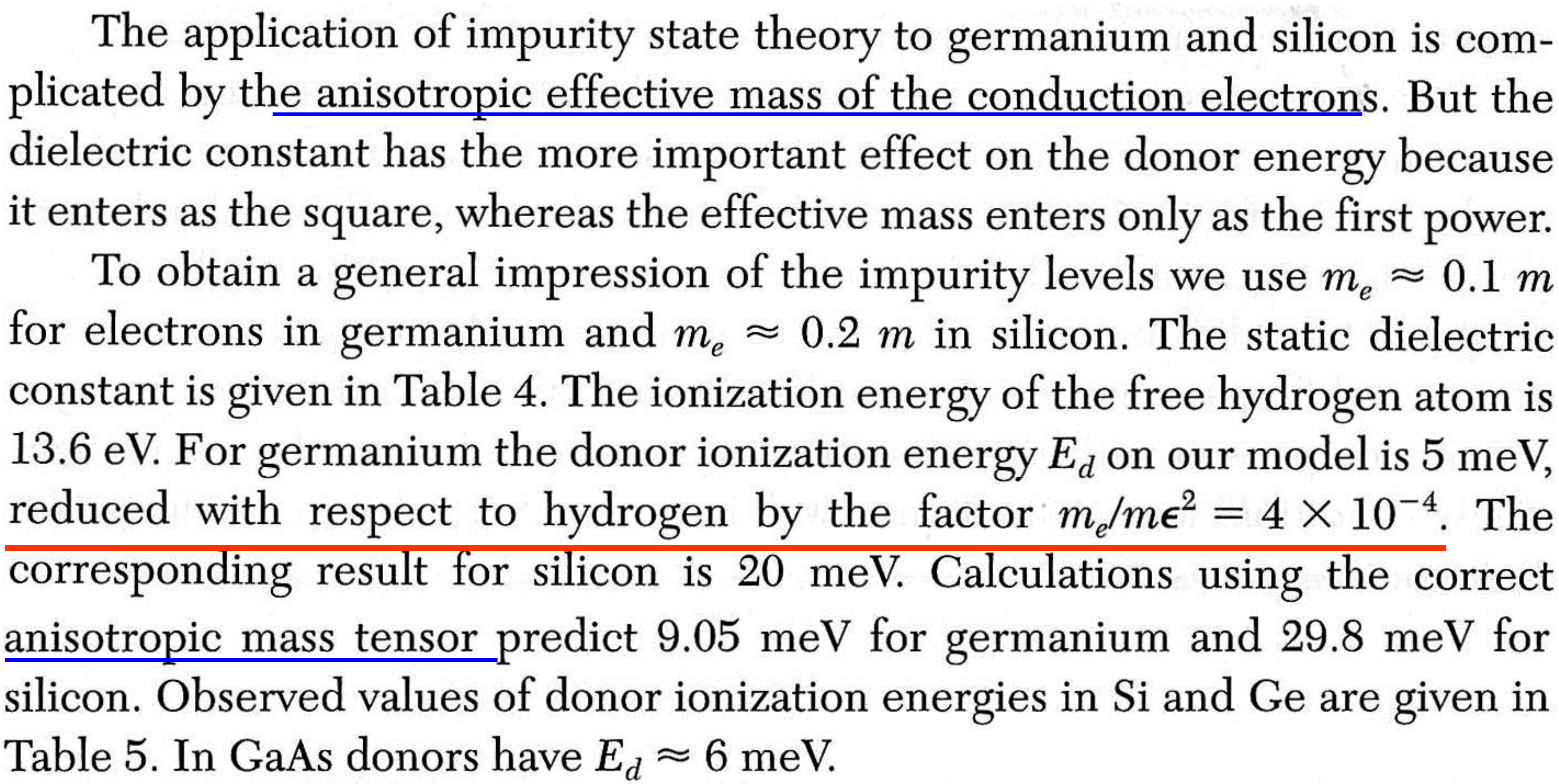
In the semiconductor with dielectric constant ϵ we replace e^2 by e^2/ϵ and m by the effective mass m_e to obtain

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

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

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



The application of impurity state theory 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. In GaAs donors have $E_d \approx 6$ meV.

Ge: $m_e/m\in^2 = 4 \times 10^{-4}$, $E_d = 5$ meV
Si: $m_e/m\in^2 = 1.6 \times 10^{-3}$, $E_d = 20$ meV

Anisotropic mass tensor	**Table 5 (Exp)**
9.05 mev	12 mev
29.8 mev	45 mev

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 + 5

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

The radius of the first Bohr orbit is increased by $\boxed{\epsilon m/m_e}$ over the value 0.53 Å for the free hydrogen atom. The corresponding radius is $(160)(0.53) \simeq 80$ Å in germanium and $(60)(0.53) \simeq 30$ 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 orbit overlap, an "impurity band" is formed from the donor states: see the discussion of the metal-insulator transition in Chapter 14.

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, in order 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.

Table 6 Acceptor ionization energies E_a of trivalent impurities in germanium and silicon, in meV +3

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

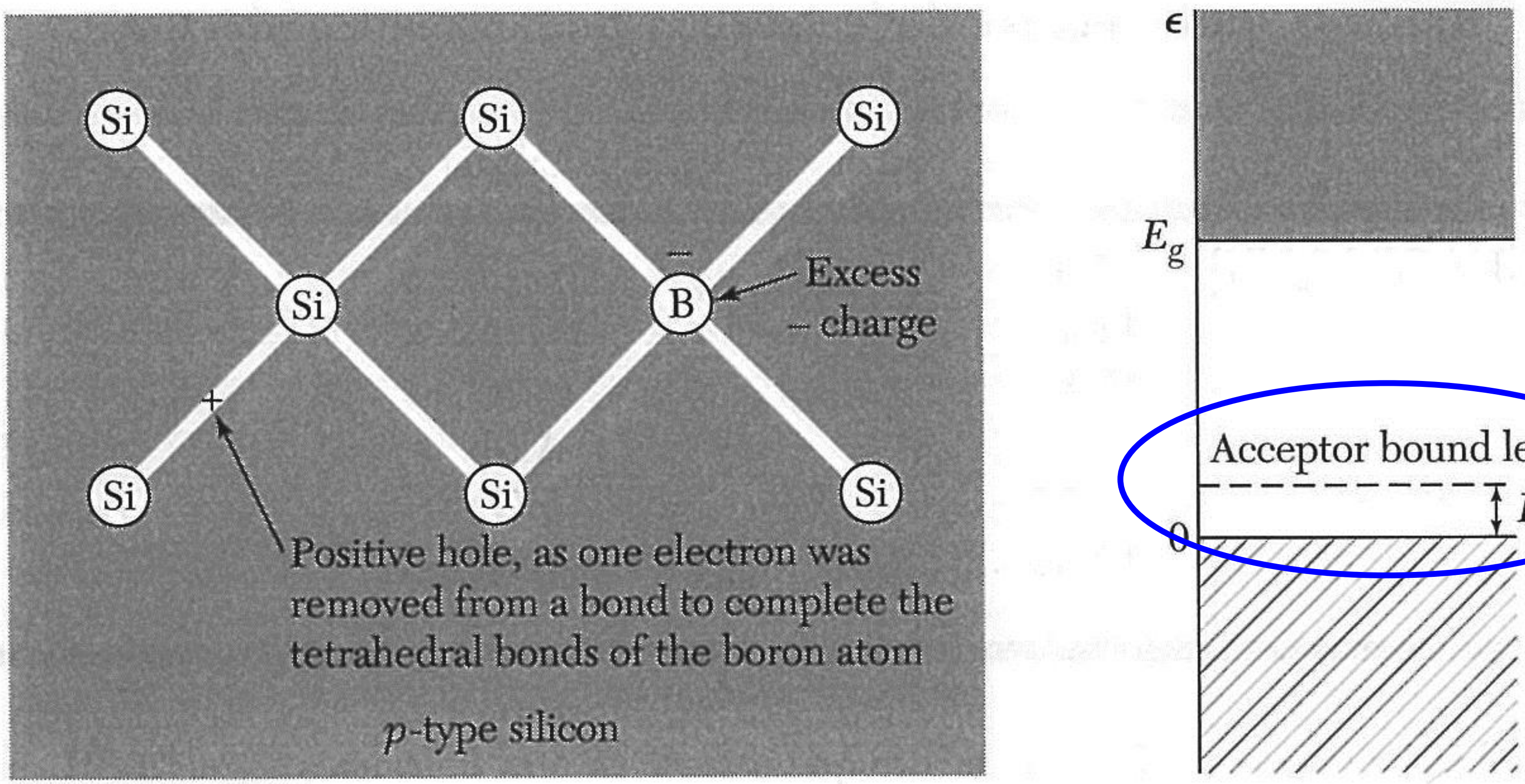


Figure 20 Boron has only three valence electrons; it can complete its tetrahedral bonds only by taking an electron from a Si-Si bond, leaving behind a hole in the silicon valence band. The positive hole is then available for conduction. The boron atom is called an **acceptor** because when ionized it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

The tables show that donor and acceptor ionization energies in Si are comparable with $k_B T$ 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* type. The sign of the Hall voltage (6.53) 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. 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}. There are impurities (H, O, 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.

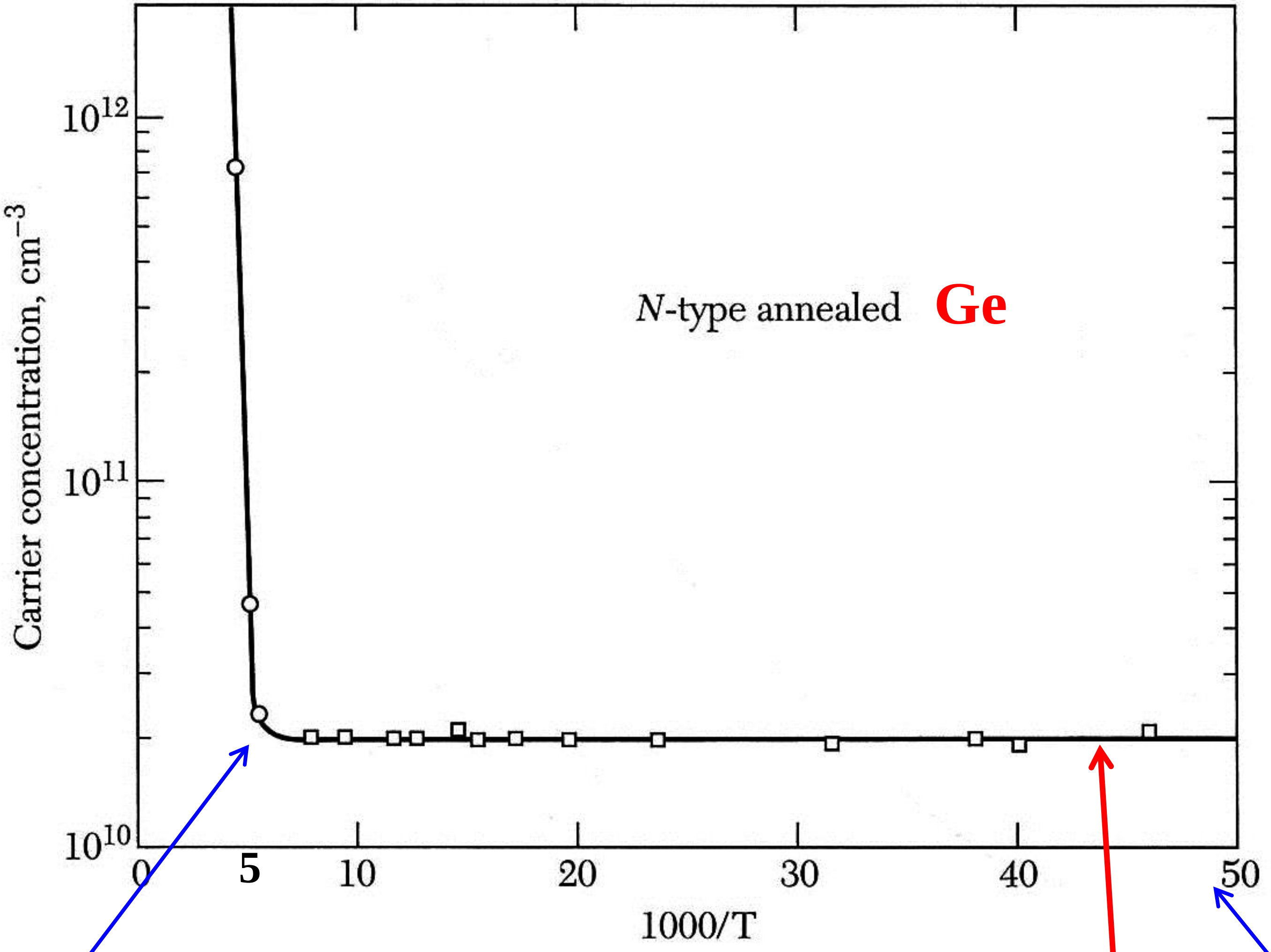


Figure 21 Temperature dependence of the free carrier concentration in ultrapure Ge, after R. N. Hall. The net concentration of electrically active impurities is 2×10^{10} cm^{-3}, as determined by Hall coefficient measurements. The rapid onset of intrinsic excitation as the temperature is increased is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

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 $k_BT \ll E_d$ is

The donors are at $\boldsymbol{E_d}$ energy level just below $\boldsymbol{E_c}$.

$$\boxed{n \cong (n_0N_d)^{1/2}\exp(-E_d/2k_BT)\ ,} \qquad (53)$$

From eq. 45

with $n_0 \equiv 2(m_ek_BT/2\pi\hbar^2)^{3/2}$; 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.

See Ashroft & Mermin , p. 581-584

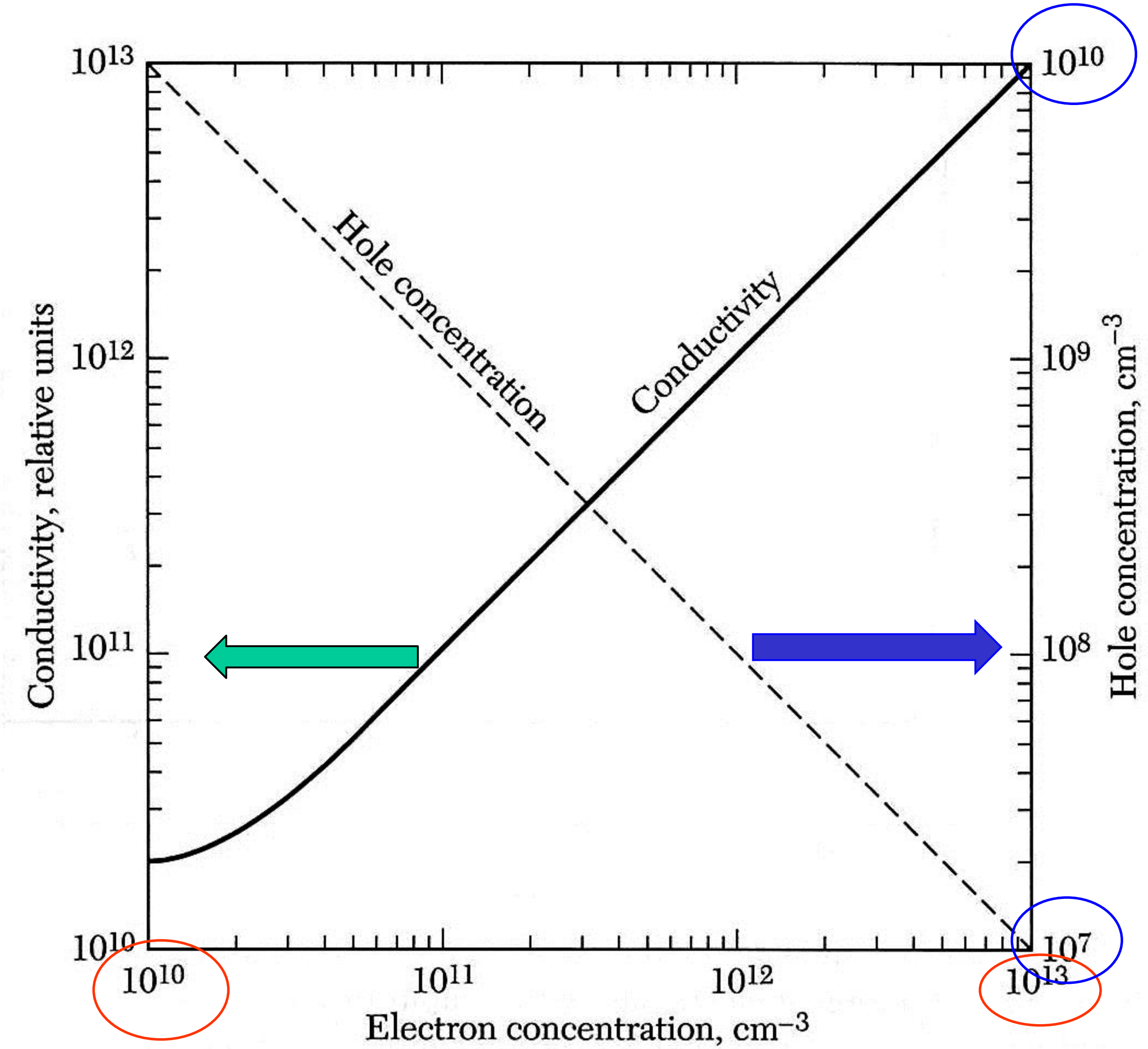


Figure 22 Electrical conductivity and hole concentration p calculated as a function of electron concentration n for a semiconductor at a temperature such that $np = 10^{20}$ cm^{-6}. The conductivity is symmetrical about $n = 10^{10}$ cm^{-3}. For $n > 10^{10}$, the specimen is n type; for $n < 10^{10}$,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

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

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

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

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

$$J_u = n\,\Delta U\,\upsilon \qquad j_U = n(E_c - \mu + \tfrac{3}{2}k_B T)(-\mu_e)E \ . \tag{55}$$

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

eq. 55 divided by eq.54

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

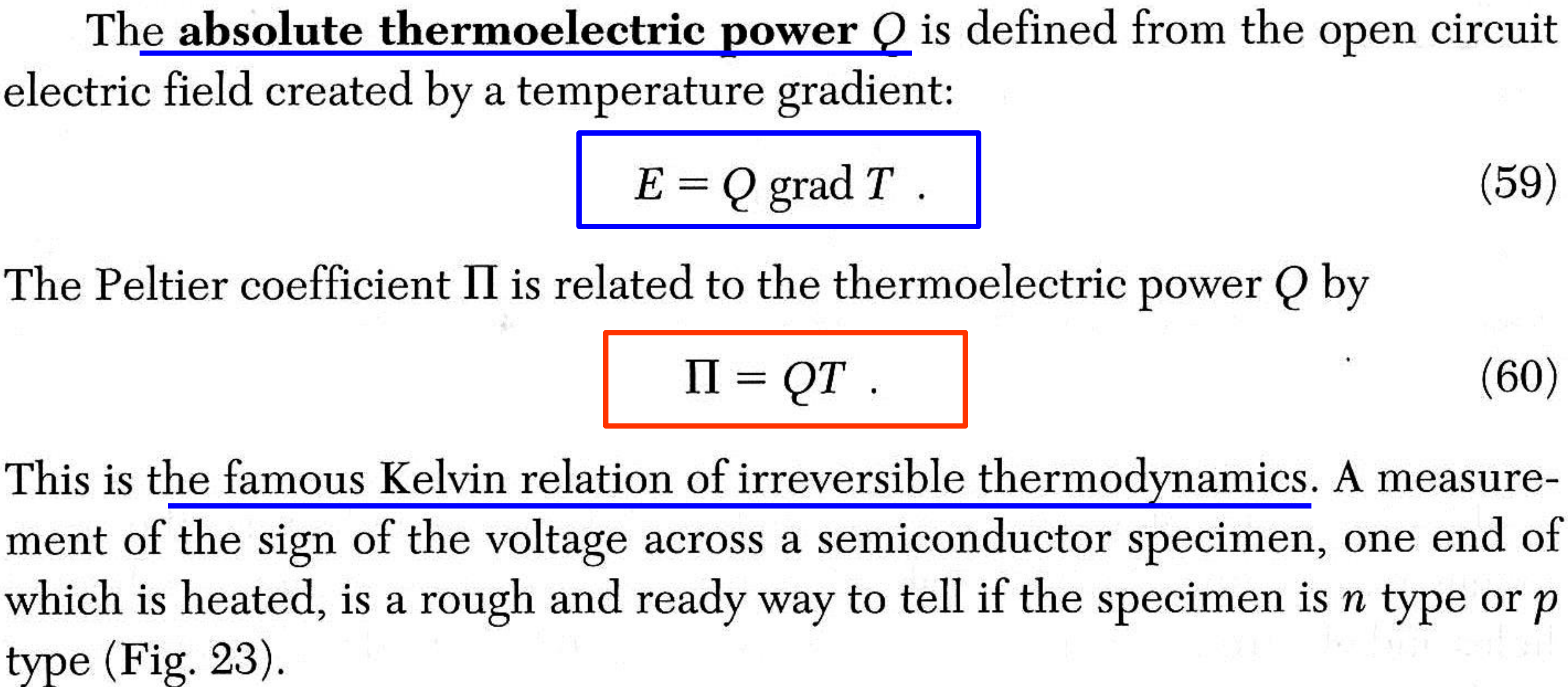
and is negative because the energy flux is opposite to the charge flux. For holes

$$j_q = pe\mu_hE \; ; \qquad j_U = p(\mu - E_v + \tfrac{3}{2}k_BT)\mu_hE \;, \tag{57}$$

where E_v is the energy at the valence band edge. Thus

$$\boxed{\Pi_h = (\mu - E_v + \tfrac{3}{2}k_BT)/e} \tag{58}$$

and is positive. Equations (56) and (58) are the result of our simple drift velocity theory; a treatment by the Boltzmann transport equation gives minor numerical differences.[2]



The **absolute thermoelectric power** Q is defined from the open circuit electric field created by a temperature gradient:

$$\boxed{E = Q \operatorname{grad} T \quad .} \tag{59}$$

The Peltier coefficient Π is related to the thermoelectric power Q by

$$\boxed{\Pi = QT \quad .} \tag{60}$$

This is the famous Kelvin relation of irreversible thermodynamics. A measurement of the sign of the voltage across a semiconductor specimen, one end of which is heated, is a rough and ready way to tell if the specimen is n type or p type (Fig. 23).

from eq. 59 for ***E***

$$\boxed{\Pi = J_u/J_q = \Delta U/e = (Q \operatorname{grad} T\,) \bullet \Delta x = QT} \tag{60}$$

$$= E \bullet \Delta x$$

***n*- and *p*- Si**

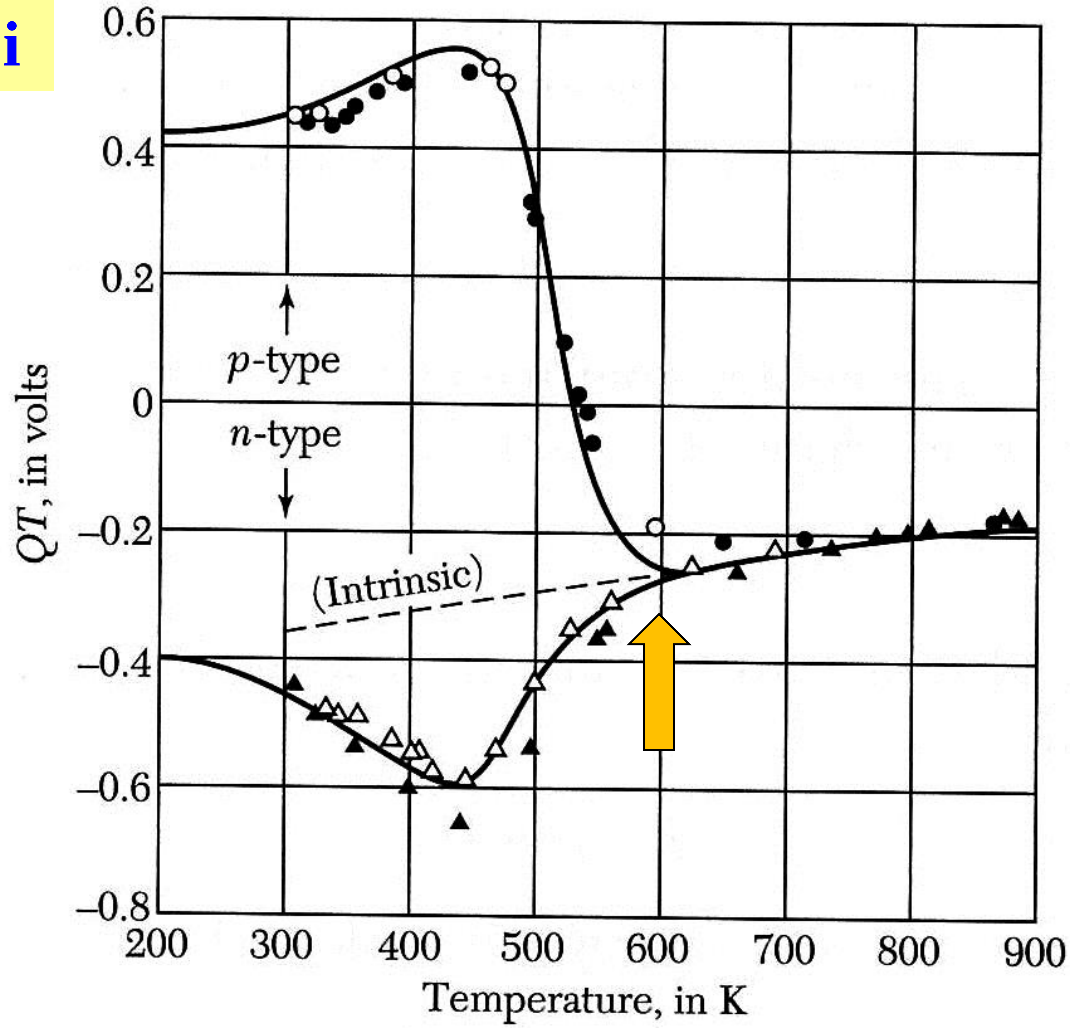


Figure 23 Peltier coefficient of *n* and *p* silicon as a function of temperature. Above 600 K the specimens act as intrinsic semiconductors. The curves are calculated and the points are experimental. (After T. H. Geballe and G. W. Hull.)

SEMIMETALS

In semimetals the conduction band edge is very slightly lower in energy than the valence band edge. A small overlap in energy of the conduction and valence bands leads to small concentration of holes in the valence band and of electrons in the conduction band (Table 7). Three of the semimetals, arsenic, antimony, and bismuth, are in group V of the periodic table.

Their atoms associate in pairs in the crystal lattice, with two ions and ten valence electrons per primitive cell. The even number of valence electrons could allow these elements to be insulators. Like semiconductors, the semimetals may be doped with suitable impurities to vary the relative numbers of holes and electrons. Their concentrations may also be varied with pressure, for the band edge overlap varies with pressure.

Table 7 Electron and hole concentrations in semimetals

Semimetal	n_e, in cm^{-3}	n_h, in cm^{-3}
Arsenic	$(2.12 \pm 0.01) \times 10^{20}$	$(2.12 \pm 0.01) \times 10^{20}$
Antimony	$(5.54 \pm 0.05) \times 10^{19}$	$(5.49 \pm 0.03) \times 10^{19}$
Bismuth	2.88×10^{17}	3.00×10^{17}
Graphite	2.72×10^{18}	2.04×10^{18}

SUPERLATTICES

Consider a multilayer crystal of alternating thin layers of different compositions. Coherent layers on a nanometer thickness scale may be deposited by molecular-beam epitaxy or metal-organic vapor deposition, thus building up a superperiodic structure on a large scale. Systems of alternate layers of GaAs and GaAlAs have been studied to 50 periods or more, with lattice spacing A of perhaps 5 nm (50 Å). A superperiodic crystal potential arises from the superperiodic structure and acts on the conduction electrons and holes to create new (small) Brillouin zones and mini energy bands superposed on the band structures of the constituent layers. Here we treat the motion of an electron in a superlattice in an applied electric field.

Bloch Oscillator

For electron motion in K space

Consider a collisionless electron in a periodic lattice in one dimension, with motion normal to the planes of the superlattice. The equation of motion in a constant electric field parallel to k is $\hbar dk/dt = -eE$ or, for motion across a Brillouin zone with reciprocal lattice vector $G = 2\pi/A$, we have $\hbar G = \hbar 2\pi/A = eET$, where T is the period of the motion. The **Bloch frequency** of the motion is $\boxed{\omega_B = 2\pi/T = eEA/\hbar.}$ The electron accelerates from $k = 0$ toward the zone boundary; when it reaches $k = \pi/A$ it reappears (as by an Umklapp process) at the zone boundary at the identical point $-\pi/A$, using the argument of Chapter 2.

Electron oscillates!

We consider the motion in a model system in real space. We suppose that the electron lies in a simple energy band of width ϵ_0:

$$\epsilon = \epsilon_0(1 - \cos kA)\ . \tag{61}$$

The velocity in k-space (momentum space) is

$dk = (-eE/\hbar)dt$

$$v = \hbar^{-1} d\epsilon/dk = (A\epsilon_0/\hbar) \sin kA \,, \tag{62}$$

and the position of the electron in real space, with the initial condition $z = 0$ at $t = 0$, is given by

For electron motion in real space

$$\begin{aligned} z = \int v\, dt = \int dk\, v(k)(dt/dk) &= (A\epsilon_0/\hbar) \int dk(-\hbar/eE) \sin kA \\ &= (-\epsilon_0/eE)(\cos kA - 1) = (-\epsilon_0/eE)(\cos(-eEAt/\hbar) - 1) \;. \end{aligned} \tag{63}$$

This confirms that the Bloch oscillation frequency in real space is $\omega_B = eEA/\hbar$. The motion in the periodic lattice is quite different from the motion in free space, for which the acceleration is constant.

Zener Tunneling

Thus far we have considered the effect of the electrostatic potential $-eEz$ (or $-eEnA$) on one energy band; the potential tilts the whole band. Higher bands will also be tilted similarly, creating the possibility of crossing between ladder levels of different bands. The interaction between different band levels at the same energy opens the possibility for an electron in one band at n to cross to another band at n'. This field-induced interband tunneling is an example of **Zener breakdown**, met most often at a single junction as in the Zener diode.

SUMMARY

- The motion of a wave packet centered at wavevector $\mathbf{k}$ is described by $\mathbf{F} = \hbar d\mathbf{k}/dt$, where $\mathbf{F}$ is the applied force. The motion in real space is obtained from the group velocity $\mathbf{v}_g = \hbar^{-1}\nabla_{\mathbf{k}}\epsilon(\mathbf{k})$.
- The smaller the energy gap, the smaller is the effective mass $|m^*|$ near the gap.
- A crystal with one hole has one empty electron state in an otherwise filled band. The properties of the hole are those of the $N - 1$ electrons in this band.
  (a) If the electron is missing from the state of wavevector $\mathbf{k}_e$, then the wavevector of the hole is $\mathbf{k}_h = -\mathbf{k}_e$.
  (b) The rate of change of $\mathbf{k}_h$ in an applied field requires the assignment of a positive charge to the hole: $e_h = e = -e_e$.
  (c) If $\boldsymbol{v}_e$ is the velocity an electron would have in the state $\mathbf{k}_e$, then the velocity to be ascribed to the hole of wavevector $\mathbf{k}_h = -\mathbf{k}_e$ is $\boldsymbol{v}_h = \boldsymbol{v}_e$.
  (d) The energy of the hole referred to zero for a filled band is positive and is $\epsilon_h(\mathbf{k}_h) = -\epsilon(\mathbf{k}_e)$.
  (e) The effective mass of a hole is opposite to the effective mass of an electron at the same point on the energy band: $m_h = -m_e$.