

# Handout 6

## Semiconductors and Insulators

The most important aspect of semiconductor<sup>1</sup> bandstructure may be summarised as follows; at absolute zero the highest completely filled band (*the valence band*) is separated from the lowest empty band (*the conduction band*) by an energy gap or band gap  $E_g$  of forbidden states. Therefore the material does not conduct electricity at  $T = 0$ . At finite temperatures a variety of processes enable electrons to be excited into the conduction band and empty states to occur in the valence band, thus allowing electrical conduction. However, we shall see that the presence of the energy gap still dominates the properties of the semiconductor.

Most of the technologically-important semiconductors, such as Ge, Si, GaAs and (Hg,Cd)Te, have a face-centred-cubic lattice with a two-atom basis; this is illustrated in Figure 6.1. In the case of Si and Ge, the atoms on the A and B sites in Figure 6.1 are identical (the so-called *diamond structure*). In the case of binary semiconductors such as (for example) GaAs the A sites will have Ga atoms and the B sites As atoms; the crystal is said to have the *zinc blende structure*. As stated above, in each case, the underlying lattice is face-centred cubic and there is a two atom basis. Thus, both the group IV elements and many of the binary semiconductors such as GaAs have the same shape of first Brillouin zone, which is shown in Figure 6.1 and which will be useful for understanding the band diagrams in the following discussion.

### 6.1 Bandstructure of Si and Ge

#### 6.1.1 General points

Si and Ge were the first semiconductors to be exploited commercially, and Si continues to be very important as a technological material.<sup>2</sup> Figures 6.2 and 6.3 show calculations of the bandstructures of Si and Ge respectively. At first sight, the situation looks a complex, fearful mess. However, at the typical temperatures that will concern us ( $0 - \sim 300$  K), the only dramatic action (*i.e.* thermal excitation of electrons and holes, optical absorption edges) will occur close to the highest point in the valence band and the lowest points in the conduction band.

#### 6.1.2 Heavy and light holes

In both Si and Ge, two bands converge at the valence band maximum in the Brillouin-zone centre (the  $\Gamma$ -point). These bands are known as *the heavy- and light-hole bands*; the flatter one, with its large value of  $(d^2E/dk^2)^{-1}$ , is the heavy hole band, and the steeper one the light hole band (for obvious reasons—see Figure 5.1).

The heavy holes tend to dominate the properties of the valence-band extremum; their heavier effective mass means that their density of states will be much larger than that of the light holes (see Section 5.2.4).

---

<sup>1</sup>For brevity I shall refer to such materials collectively as “semiconductors”; as we shall see, the distinction between a semiconductor and an insulator is fairly nebulous.

<sup>2</sup>See *e.g.* *Semiconductor Physics*, by K. Seeger (Springer, Berlin 1991) Section 5.7 and references therein.

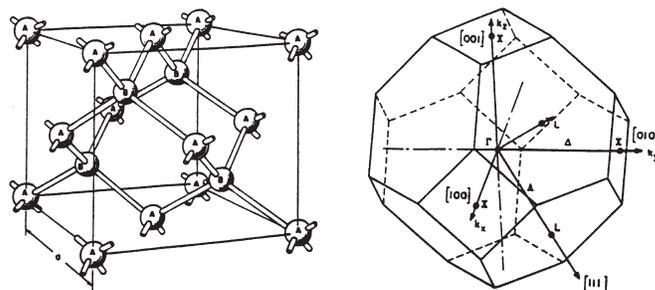


Figure 6.1: Left: an illustration of the crystal structures of the group IV elements and many of the binary semiconductors such as GaAs and CdTe. In the case of C (diamond), Si, Ge and Sn, the atoms on the A and B sites are identical (the so-called *diamond structure*). In the case of binary semiconductors such as for example GaAs, the A will be Ga and B As; the crystal is said to have the *zinc blende structure*. In each case, the underlying lattice is face-centred cubic and there is a two atom basis. Thus, both the group IV elements and the binary semiconductors have the same shape of first Brillouin zone, which is shown on the right.

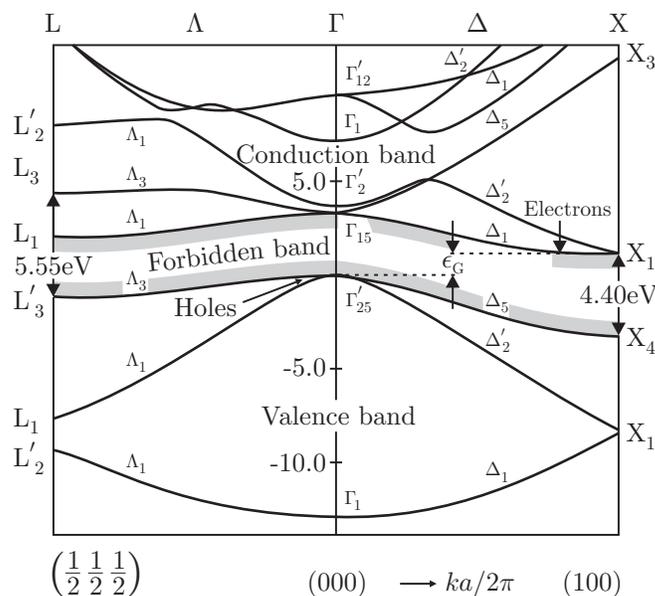


Figure 6.2: Calculated bandstructure of Si projected along the (100) and (111) directions. The shading indicates the lowest (unoccupied at  $T = 0$ ) conduction band and the highest (occupied at  $T = 0$ ) valence band, with the “forbidden band” or band gap in between. (Based on M. Cardona and F. Pollack, *Phys. Rev.* **142**, 530 (1966).)

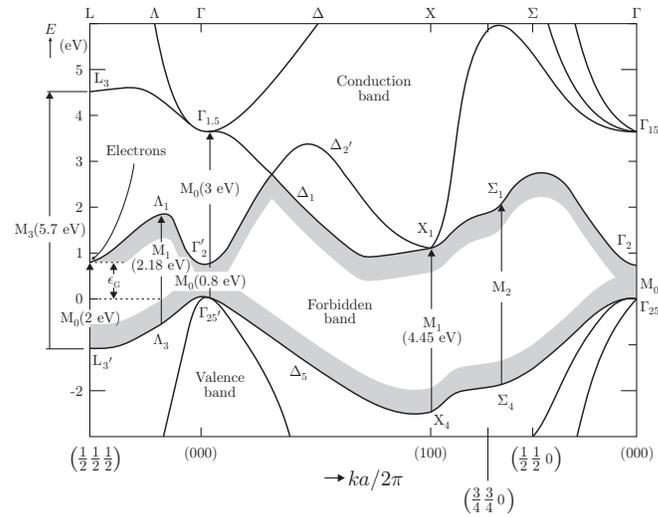


Figure 6.3: Calculation of the bandstructure of Ge along various projections. The shading indicates the lowest (unoccupied at  $T = 0$ ) conduction band and the highest occupied at  $T = 0$  valence band. (Based on J.C. Philips *et al.*, *Proc. Int. Conf. Phys. Semiconductors* (Exeter, UK) (The Institute of Physics, London, 1962) 564.)

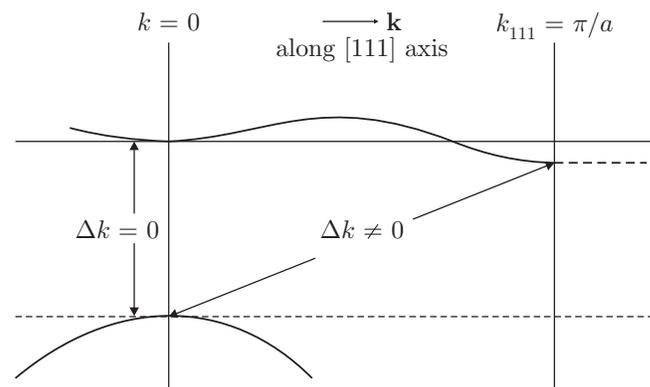


Figure 6.4: Schematic of direct and indirect optical transitions in Ge.

### 6.1.3 Optical absorption

Photons with energy  $h\nu \sim E_g \sim 0 - 2$  eV will have wavevectors which are  $\ll$  typical Brillouin-zone size (energetic X-rays ( $h\nu \gg 1$  eV) have wavevectors  $\sim$  Brillouin-zone size). This means that transitions involving the absorption of a photon to excite an electron from the valence band to the conduction band, leaving a hole behind, will be essentially vertical in  $k$ -space. The transition strengths will be greatest when the joint density of initial and final states is large, *i.e.* when conduction and valence bands are approximately parallel.

Note that Si and Ge are *indirect-gap semiconductors*; the smallest band separation (the thermodynamic band gap, which determines the thermal population of electron and hole states) is not vertical in  $k$ -space. Figure 6.4 shows a schematic representation of this situation in Ge; strong optical transitions will occur at the point labelled  $\Delta k = 0$  on the diagram, at a higher energy than the thermodynamic band gap, which is labelled  $\Delta k \neq 0$ .

It turns out that optical transitions *can* occur at energies close to the thermodynamic band gap in Si and Ge if both a phonon and a photon are involved; emission or (at higher temperatures) absorption of a phonon with the appropriate wavevector allows momentum to be conserved so that the transitions labelled  $\Delta k \neq 0$  in Figure 6.4 are possible.

Figure 6.5 shows the optical absorption coefficient of Ge at 300 K and 77 K. Both the indirect ( $\Delta k \neq 0$ ) and direct ( $\Delta k = 0$ ) transitions can be seen as absorption edges. The higher energy direct transition is some 100 times stronger than the indirect transition. In addition, the indirect transition is stronger at 300 K than at 77 K, as there is a substantial population of phonons of a suitable wavevector to take part in the transition at the higher temperature; optical transitions assisted by phonon absorption thus becomes possible in addition to those assisted by emission.

Finally, note that the energy gaps change with temperature. This is not unexpected in models of bandstructure; *e.g.* in the tight-binding model of bands, thermal expansion will influence the atomic separation and hence the transfer integrals.

### 6.1.4 Constant energy surfaces in the conduction bands of Si and Ge

The conduction band minima in Si and Ge (see Figure 6.2 and 6.3) are situated away from the Brillouin-zone centre (the  $\Gamma$  point) and are thus rather anisotropic. At energies close to (*i.e.*  $< \sim 50 - 100$  meV from) the bottom of the conduction bands, effective mass tensors with constant coefficients (as discussed in the problems) can be used to describe the conduction-band minima in Si and Ge. By choosing suitable axes, the tensors can be made diagonal. The constant energy surfaces are approximate ellipsoids of rotation about one of these axes (see Figure 6.6).

## 6.2 Bandstructure of the direct-gap III-V and II-VI semiconductors

### 6.2.1 Introduction

Compound semiconductors such as GaAs and InSb are known as *III-V semiconductors* because they combine elements from groups III and V of the Periodic Table. In a similar way, semiconductors such as (Cd,Hg)Te are known as II-VI semiconductors. Many III-V and II-VI semiconductors have technological applications, often as emitters and detectors of electromagnetic radiation. It is important that we examine their bandstructure and consequent properties, in order to see why they are used for such applications. We shall see that one of the most important points is that the minimum energy band-gaps in these materials are direct, so that optical transitions with  $\Delta k \approx 0$  can occur.

### 6.2.2 General points

Figure 6.7 shows the Brillouin zone and calculated bandstructure of GaAs, a typical direct-gap III-V semiconductor. Note that

- both heavy- and light-hole bands are present at the valence-band extremum, as before (*c.f.* Figure 6.3);

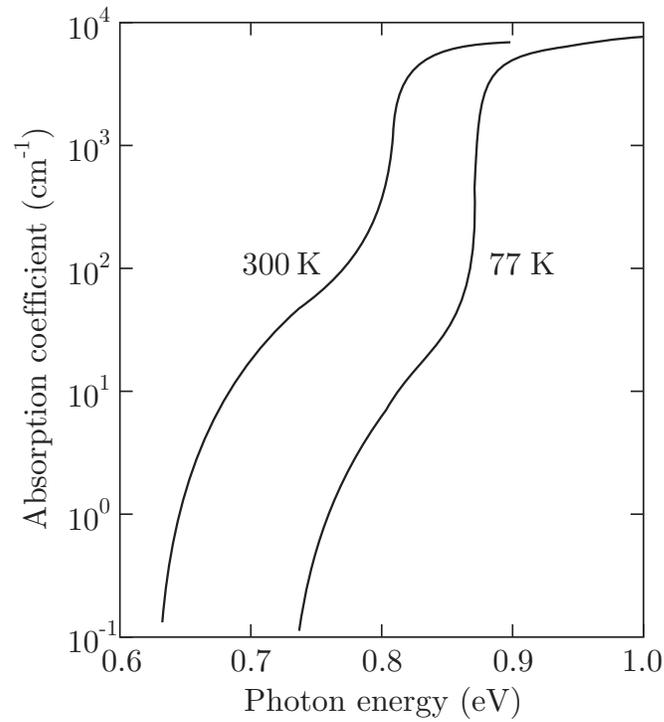


Figure 6.5: Optical absorption of Ge at 300 K and 77 K. (Data from R. Newman and W.W. Tyler, *Solid State Physics* **8**, 49 (1959).)

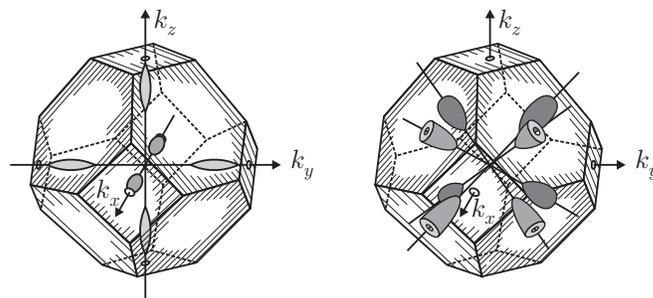


Figure 6.6: Constant energy surfaces of Si (left) and Ge (right).

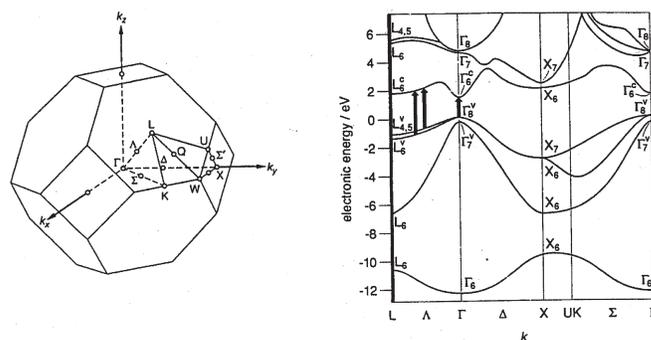


Figure 6.7: Left-hand side: Brillouin zone of GaAs. Right-hand side: bandstructure of GaAs. (After D. Long, *Energy bands in semiconductors* (Wiley, New York, 1968).)

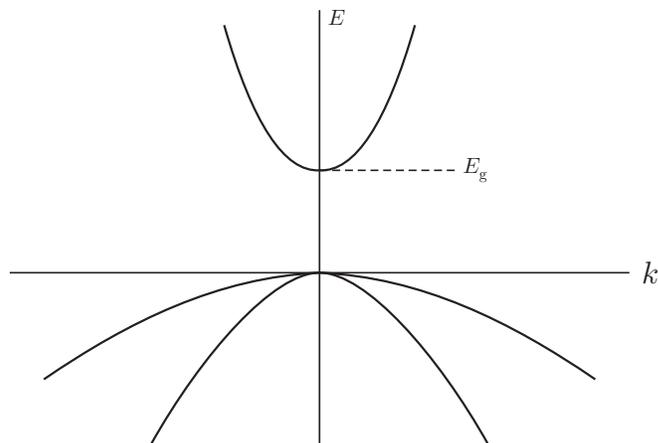


Figure 6.8: Schematic of bandstructure of GaAs close to the direct band gap. The origin of the energy scale is taken as the top of the valence band.

Material	$E_g$	$m_c^*$	$m_{lh}^*$	$m_{hh}^*$
GaAs	1.52	0.067	0.082	0.45
InAs	0.42	0.023	0.025	0.41
InSb	0.24	0.014	0.016	0.40

Table 6.1: Energy gaps (in eV), and effective masses (in units  $m_e$ ) of typical III-V semiconductors.

- the thermodynamic band gap separating the highest point of the valence band from the lowest point of the conduction band is direct;
- Just below the valence-band maximum, there is another band, known as the *spin-orbit split-off band*; this is labelled  $\Gamma_7^V$  at the Brillouin-zone centre.

For most practical purposes, we need consider only the electronic dispersion relationships close to the valence band maximum and conduction band minimum; a schematic of this region of  $k$ -space is given in Figure 6.8. In fact Figure 6.8 is a good representation of this region for many direct-gap III-V (*e.g.* InSb, InAs) and II-VI (*e.g.* CdTe, Cd<sub>0.2</sub>Hg<sub>0.8</sub>Te) semiconductors. Table 6.1 shows band-edge effective masses for three examples. Note that

- the light-hole effective mass  $m_{lh}^* \approx m_c^*$ , the electron (conduction-band) effective mass;
- $m_c^*$  and  $m_{lh}^*$  scale roughly with  $E_g$ ;
- the heavy-hole effective mass  $m_{hh}^*$  is almost material-independent.

The fact that wider band gap semiconductors have larger conduction-band and light-hole effective masses is rather a general feature of semiconductors and insulators; it will be an important factor in the discussion below.

### 6.2.3 Optical absorption

Figure 6.9 shows the optical absorption coefficient of GaAs at several temperatures. Note that the lowest energy band-gap is direct ( $\Delta k = 0$ ); in contrast to the case of Ge, there is no indirect band-gap absorption at energies below the direct gap. There is, nevertheless, one marked similarity to the case of Ge; the direct energy-gap rises as the temperature falls.

At lower temperatures, an extra peak emerges close to the onset of absorption. This is due to the formation of an *exciton*, a bound electron-heavy hole pair.<sup>3</sup> (As stated above, the heavy holes

<sup>3</sup>Excitons are also seen just below the direct band gaps of semiconductors such as Ge and Si at sufficiently low temperatures; see *e.g.* T.P. McLean, in *Progress in Semiconductors*, **5** (Wiley, 1960).

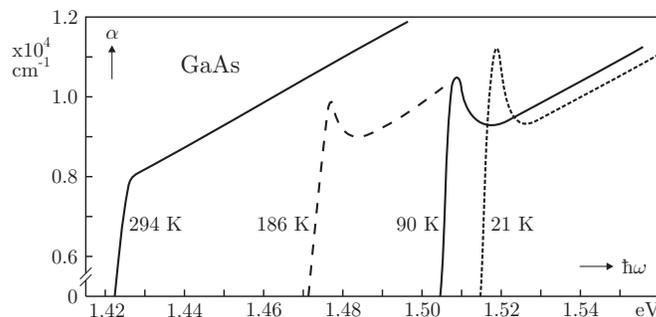


Figure 6.9: Optical absorption coefficient of GaAs at several different temperatures. Note that the joint density of states of the electrons and holes might be expected to give an absorption coefficient which is initially proportional to  $(\hbar\omega - E_g)^{1/2}$  (see Section 5.2.4), as the conduction and valence bands are almost parabolic close to the band edges. However, this is masked by the contribution of the exciton to the joint density of states. (Data from M.D. Sturge, *Phys. Rev.* **127**, 768 (1962).)

dominate the spectra because of their large density of states.) Excitons and the optical properties of semiconductors will be covered in the *Optical Properties of Solids* part of the course.

### 6.2.4 Constant energy surfaces in direct-gap III-V semiconductors

Figure 6.7 shows that the conduction-band minimum and valence-band maximum of GaAs are at the Brillouin-zone centre (the  $\Gamma$  point), a point of very high symmetry. Close to these points, the bands are quite isotropic (especially the conduction band); for many purposes, each band can therefore be treated using a single, constant effective mass (see Table 6.1) to a reasonable degree of accuracy, as long as the carrier energies do not exceed a few tens of meV.

## 6.3 Thermal population of bands in semiconductors

### 6.3.1 The law of Mass-Action

The most notable thing about semiconductors (compared to metals) is the fact that the number of mobile charge carriers varies with temperature. We shall now derive the equation governing this behaviour. The number density of electrons  $dn$  with energy between  $E$  and  $E + dE$  will be given by

$$dn = f_D(E, T)g(E)dE, \quad (6.1)$$

where  $f_D$  is the Fermi-Dirac distribution function

$$f_D = \frac{1}{e^{\frac{(E-\mu)}{k_B T}} + 1} \quad (6.2)$$

$g(E)$  is the density of states and  $\mu$  is the chemical potential.<sup>4</sup>

**Distribution functions for electrons and holes** Now let us consider the case that  $\mu$  is within the band gap, such that the chance of occupancy of a conduction-band state is  $\ll 1$ . This implies that  $(E - \mu) \gg k_B T$ , so that the Fermi-Dirac distribution function  $f_{DC}$  for an electron in the conduction band can be approximated as

$$f_{DC} \approx \frac{1}{e^{\frac{(E-\mu)}{k_B T}}} = e^{-\frac{(E-\mu)}{k_B T}}. \quad (6.3)$$

<sup>4</sup>In the next bit of the derivation we are going to make a distinction between the Fermi-Dirac distribution function in the valence and conduction bands, as though it becomes two different functions. Of course it does not; however, differing approximations can be made for the two bands, so that some sort of short-hand labelling which distinguishes the two is desirable.

The chance of finding a hole in the valence band will be  $1 - f_{\text{DV}}$ , where  $f_{\text{DV}}$  is the Fermi-Dirac distribution function within the valence band. Under similar conditions to those used in the derivation of Equation 6.3,  $(E - \mu)$  will be negative and  $|E - \mu| \gg k_{\text{B}}T$ . Therefore the approximation

$$1 - f_{\text{DV}} = 1 - \left(1 + e^{\frac{(E-\mu)}{k_{\text{B}}T}}\right)^{-1} \approx 1 - \left(1 - e^{\frac{(E-\mu)}{k_{\text{B}}T}}\right) = e^{-\frac{(\mu-E)}{k_{\text{B}}T}} \quad (6.4)$$

can be made.

**Density of states** We assume that the conduction and valence bands near the band edges are parabolic, each characterised by a single effective mass. (Even though there are both heavy and light holes, this is not a bad approximation, as the heavy holes have a much bigger effective mass and hence density of states; the light holes can be neglected.) The densities of states for the conduction band ( $g_{\text{c}}$ ) and valence band ( $g_{\text{v}}$ ) are therefore

$$g_{\text{c}} = C m_{\text{c}}^{*\frac{3}{2}} (E - E_{\text{c}})^{\frac{1}{2}} \quad (6.5)$$

and

$$g_{\text{v}} = C m_{\text{hh}}^{*\frac{3}{2}} (E_{\text{v}} - E)^{\frac{1}{2}} \quad (6.6)$$

respectively, where  $m_{\text{c}}^*$  and  $m_{\text{hh}}^*$  are the electron and heavy hole effective masses respectively,  $E_{\text{c}}$  and  $E_{\text{v}}$  are the energies of the conduction and valence band edges respectively and  $C = (1/2\pi^2)(2/\hbar^2)^{3/2}$  (see Section 5.2.4).

Combining Equations 6.1, 6.3 and 6.5, the number of electrons in the conduction band per unit volume is

$$n = \int_{E_{\text{c}}}^{\infty} f_{\text{DC}} g_{\text{c}} dE \approx C m_{\text{c}}^{*\frac{3}{2}} \int_{E_{\text{c}}}^{\infty} (E - E_{\text{c}})^{\frac{1}{2}} e^{-\frac{(E-\mu)}{k_{\text{B}}T}} dE. \quad (6.7)$$

Making the substitution  $y = (E - E_{\text{c}})/(k_{\text{B}}T)$  gives

$$n \approx C (m_{\text{c}}^* k_{\text{B}}T)^{\frac{3}{2}} e^{-\frac{(E_{\text{c}}-\mu)}{k_{\text{B}}T}} \int_0^{\infty} y^{\frac{1}{2}} e^{-y} dy, \quad (6.8)$$

leading to

$$n = 2 \frac{(2\pi m_{\text{c}}^* k_{\text{B}}T)^{\frac{3}{2}}}{h^3} e^{-\frac{(E_{\text{c}}-\mu)}{k_{\text{B}}T}} = N_{\text{c}} e^{-\frac{(E_{\text{c}}-\mu)}{k_{\text{B}}T}}. \quad (6.9)$$

Here  $N_{\text{c}}$  is the effective number density of *accessible* states at the conduction band bottom.

Similarly, combining Equations 6.1, 6.4 and 6.6,  $p$ , the number of holes in the valence band per unit volume is

$$p = \int_{-\infty}^{E_{\text{v}}} (1 - f_{\text{DV}}) g_{\text{v}} dE \approx C m_{\text{hh}}^{*\frac{3}{2}} \int_{-\infty}^{E_{\text{v}}} (E_{\text{v}} - E)^{\frac{1}{2}} e^{-\frac{(\mu-E)}{k_{\text{B}}T}} dE. \quad (6.10)$$

The same type of substitution as in the case of the electrons leads to

$$p \approx 2 \frac{(2\pi m_{\text{hh}}^* k_{\text{B}}T)^{\frac{3}{2}}}{h^3} e^{-\frac{(\mu-E_{\text{v}})}{k_{\text{B}}T}} = N_{\text{v}} e^{-\frac{(\mu-E_{\text{v}})}{k_{\text{B}}T}}, \quad (6.11)$$

where  $N_{\text{v}}$  is the effective number density of *accessible* states at the valence band top.

Combining Equations 6.9 and 6.11 gives

$$np \approx N_{\text{c}} N_{\text{v}} e^{-\frac{E_{\text{g}}}{k_{\text{B}}T}} = WT^3 e^{-\frac{E_{\text{g}}}{k_{\text{B}}T}}, \quad (6.12)$$

where the energy gap  $E_{\text{g}} = E_{\text{c}} - E_{\text{v}}$ , and  $W$  is a constant depending on the details of the valence and conduction-band extrema. This is known as the *Law of Mass-Action*. The exponential dependence of  $np$  on the temperature is the chief mechanism determining the temperature dependence of the electrical conductivity of semiconductors.

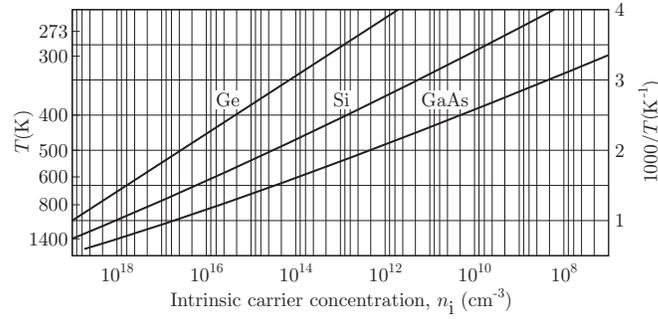


Figure 6.10: Calculated intrinsic carrier densities  $n_i$  versus temperature in Ge ( $E_g = 0.74$  eV), Si ( $E_g = 1.17$  eV) and GaAs ( $E_g = 1.52$  eV).

### 6.3.2 The motion of the chemical potential

We now consider what happens to the chemical potential as a function of  $T$ . Setting  $n = p$  and equating Equations 6.9 and 6.11 gives

$$\frac{N_c}{N_v} = e^{\frac{(2\mu - E_c - E_v)}{k_B T}}. \quad (6.13)$$

Now  $(N_c/N_v) = (m_c^*/m_{hh}^*)^{3/2}$  (see Section 5.2.4), so that the chemical potential is given by

$$\mu = \frac{1}{2}(E_c + E_v) + \frac{3}{4}k_B T \ln \left( \frac{m_{hh}^*}{m_c^*} \right). \quad (6.14)$$

Therefore  $\mu$  starts off in the middle of the bandgap (*i.e.* exactly half way between the empty and full states) at  $T = 0$ ; as  $m_{hh}^*$  is bigger than  $m_c^*$  in most semiconductors,  $\mu$  usually moves up as  $T$  rises.

### 6.3.3 Intrinsic carrier density

Let us first assume that the only source of electrons in the conduction band and holes in the valence band is the thermal excitation of electrons across the band gap (*i.e.* there are no impurities; see Section 6.3.4 below); such electrons and holes are known as *intrinsic* carriers. In this case (see Equation 6.12)

$$n_i = n = p = T^{\frac{3}{2}} W^{\frac{1}{2}} e^{-\frac{E_g}{2k_B T}}, \quad (6.15)$$

where  $n_i$  is the *intrinsic carrier density*. Note that the exponential contains  $E_g/2$  and *not*  $E_g$ ; this is because the creation of each electron in the conduction band automatically makes a hole in the valence band.

Figure 6.10 shows  $n_i$  for Ge, Si and GaAs as a function of  $T$ ; the exponential dependence on  $E_g$  means that relatively small differences in band gap result in  $n_i$ s which are several orders of magnitude apart.

### 6.3.4 Impurities and extrinsic carriers

For virtually all practical applications (*i.e.* those at room temperature), the conductivity of semiconductors such as GaAs, Ge and Si is dominated by *extrinsic carriers*, those provided by doping the semiconductor with impurities.

Two types of impurity will concern us, *donors*, which donate electrons, and *acceptors*, which provide holes.

- **Donors** An atom of the semiconductor with valence  $\mathcal{V}$  is replaced by a donor atom, with valence  $\mathcal{V} + 1$ . After the donor has bonded into the host lattice, it will still have one electron left over. Examples of donors include P in Si or Ge, Si on a Ga site in GaAs, and Te on an As site in GaAs.

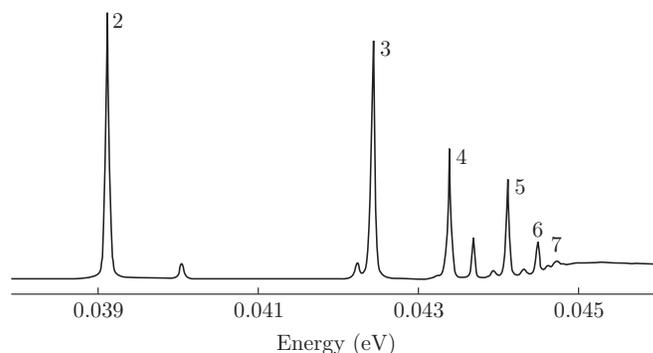


Figure 6.11: Far-infrared absorption due to P impurities (donors) in Si. Hydrogen-like transitions between the  $n = 1$  groundstate and higher levels can clearly be seen. (Data courtesy of Prof. R.A. Stradling.)

- **Acceptors** An atom of the semiconductor with valence  $\mathcal{V}$  is replaced by an acceptor atom, with valence  $\mathcal{V} - 1$ . Bonding into the lattice will therefore leave the acceptor short of one electron, *i.e.* with a surplus hole. Typical acceptors include Al and Ga in Si and Ge, Be on a Ga site in GaAs and Si on an As site in GaAs.

The surplus carrier (electron or hole) will orbit the (positively or negatively) charged ionic core of the impurity; again (see Section ??) the situation is analogous to Hydrogen, with the following alterations (*c.f.* Section ??)

- the free-electron mass  $m_e$  in the Hydrogen is replaced by the effective mass of the carrier;
- the carrier moves through a medium of relative permittivity  $\epsilon_r$ .

Thus, the energy levels of *e.g.* a donor are given by

$$E(n) = \frac{m_c^*}{m_e} \frac{1}{\epsilon_r^2} \times \frac{13.6 \text{ eV}}{n^2}, \quad (6.16)$$

with  $n$  an integer (see Figure 6.11 for a graphic illustration of these energy levels).<sup>5</sup>

As in the exciton model,  $n = 1$  represents the ground state (the 1s state) of the donor, and  $n = \infty$  represents a free electron in the conduction band (the “ionisation” of the donor). Similar considerations hold for acceptors.

Substituting typical values for  $\epsilon_r$  ( $\epsilon_r \sim 10 - 15$  for many semiconductors) and  $m_c^*$  (*e.g.*  $m_c^* \approx 0.07m_e$  in GaAs) into Equation 6.16 gives an impurity binding energy  $E(1) \approx 5 \text{ meV}$ . Semiconductors with wide band gaps will tend to have electrons and light holes with heavier effective masses, resulting in larger impurity binding energies, whilst narrow-gap semiconductors will tend to have small impurity binding energies (see Section 6.2.2).

The hydrogen-like approach also yields an effective Bohr radius  $a_B^* \sim 10 \text{ nm}$ . The large Bohr radius of the donor implies that the donated electron will spend very little time close to its “parent” ionic core. Therefore the impurity binding energy of a donor will be almost entirely determined by the host semiconductor rather than the parent ion.

### 6.3.5 Extrinsic carrier density

As long as the numbers of donors and/or acceptors are small enough such that the chemical potential remains in the bandgap (*i.e.* the chance of occupancy of an electron state in the conduction band or a

<sup>5</sup>The perceptive reader will notice that the transitions are *not quite* at the energies predicted by the simple model of Hydrogen. In Ge and Si, a further complication arises from the multi-valley nature of the conduction bands; in Si, for example, there are six impurity states from six minima. These interact so that the final pattern of levels observed is not precisely hydrogenic (the situation in direct-gap semiconductors with a single, zone-centre conduction-band minimum (*e.g.* GaAs) is rather closer to the hydrogenic model). Similarly, the degeneracy of the valence band modifies the simple hydrogenic acceptor levels.

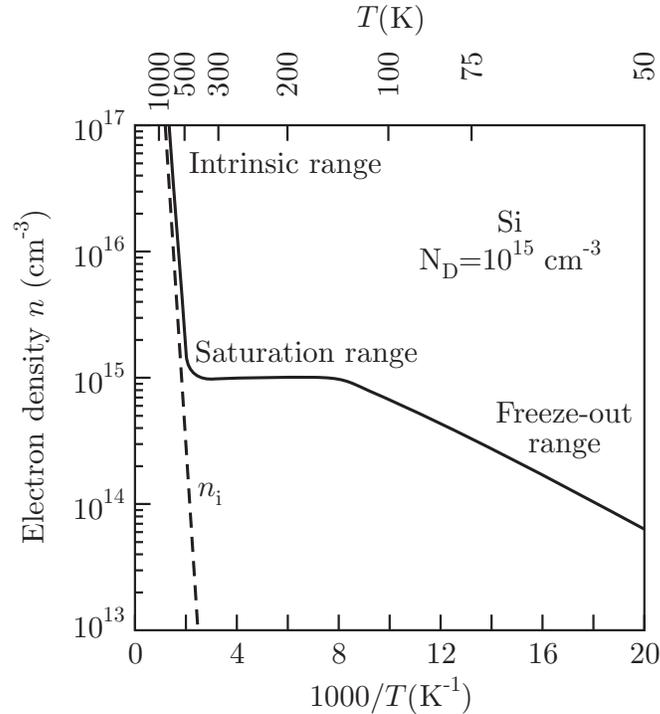


Figure 6.12: Temperature dependence of the electron density in Si with a net donor density of  $N_D - N_A = 10^{15} \text{ cm}^{-3}$ .

hole state in the valence band is much less than 1), the derivation of Section 6.3.1 will be applicable, so that the Law of Mass Action will still hold.

In order to find  $n$  and  $p$  when impurities are present we therefore use Equation 6.12

$$np = T^3 W e^{-\frac{E_g}{k_B T}}$$

combined with the conservation law

$$n - p = N_D - N_A, \quad (6.17)$$

where  $N_D$  is the density of donors and  $N_A$  is the density of acceptors (both are assumed to only provide one carrier each). The right-hand side of Equation 6.17 shows that the presence of donors can be *compensated* by acceptors; this is known (surprise, surprise!) as *compensation*.

Binding energies of order 5 – 10 meV imply that most impurities in semiconductors such as GaAs and Si will be ionised at room temperature.<sup>6</sup> Figure 6.12 shows the temperature dependence of the electron density in the conduction band of Si with a net donor density of  $N_D - N_A = 10^{15} \text{ cm}^{-3}$ . At cryogenic temperatures the extrinsic electrons *freeze out* onto the donors; however above about 200 K, all of the donors are ionised (the saturation range) and  $n$  is relatively constant. At  $\sim 500$  K the intrinsic contribution to  $n$  becomes non-negligible and then rapidly dominates.

A comparison of Figures 6.10 and 6.12 shows that the  $n_i$  in GaAs and Si are very low indeed at room temperature, much less than practically-achievable values of  $N_D - N_A$ ; samples of these semiconductors would have to be free of donors to better than about 1 part in  $10^{12} - 10^{15}$  (impossible!) for one to see something approaching true intrinsic behaviour.

Finally, we examine the behaviour of the chemical potential in the presence of impurities. To see where  $\mu$  goes, we repeat the derivation of Section 6.3.2, but using the number density of empty donor states ( $N_D e^{-(\mu - E_D)/k_B T}$ , where  $E_D$  is the energy of the donor groundstate) in place of the number of

<sup>6</sup>This implies that  $(E_D - \mu) \gg k_B T$  and  $(\mu - E_A) \gg k_B T$ , where  $E_D$  and  $E_A$  are the energies of the donor and acceptor groundstates respectively. Therefore  $\mu$  will not only be far from the band edges, it must also be far from the impurity levels.

holes in the valence band.<sup>7</sup> (We are thus considering an n-type semiconductor; however, an equivalent derivation for a p-type semiconductor uses the same ideas.) This gives

$$\mu = \frac{1}{2}(E_D + E_c) + \frac{1}{2}k_B T \ln\left(\frac{N_D}{N_c}\right), \quad (6.18)$$

*i.e.*  $\mu$  can either rise or fall with increasing temperature.<sup>8</sup>

### 6.3.6 Degenerate semiconductors.

Once all of the donors are ionised (the exhaustion regime),  $n = N_D$ ; equating Equation 6.9 to  $N_D$  gives

$$\mu \approx E_c + k_B T \ln\left(\frac{N_D}{N_c}\right), \quad (6.19)$$

where the  $\approx$  re-emphasises that we are approaching a dodgy situation as far as the approximations used to derive Equation 6.3 are concerned. There are two cases to note.

- $N_D < N_c$  leads to a chemical potential which is still in the bandgap. The number of electrons in the conduction band is still small compared to the number of available states, so that the quasi-classical statistics used in Equation 6.3 and the derivation that follows it are probably valid. In this case, the semiconductor is *non-degenerate*.
- $N_D > N_c$  leads to a chemical potential in the conduction band. Therefore we cannot use the quasi-classical approximation for the Fermi-Dirac distribution function. The semiconductor behaves somewhat like a metal and is said to be *degenerate*.

### 6.3.7 Impurity bands

If a large enough concentration of impurities is placed in a semiconductor, the wavefunctions of the carriers bound to the impurities will start to overlap; the criterion for this for *e.g.* donors is  $N_D \geq \sim 1/a_B^*{}^3$ . The situation becomes rather similar to the tight-binding model, and carriers will be able to move from impurity to impurity. The semiconductor will remain electrically conductive even at very low temperatures; it is another instance of a *degenerate semiconductor*. However, in contrast to the case discussed in the previous section, the chemical potential will depend rather less on the temperature; we will have a situation much more analogous to a (rather dirty) conventional metal.

### 6.3.8 Is it a semiconductor or an insulator?

Most textbooks state that insulators are just wide-gap semiconductors, the implication being that thermal effects excite a negligible number of electron-hole pairs across the band gap if it is wide (see Equation 6.12).

However, this picture is an over-simplification; as we have seen, the carriers which populate the bands at room temperature come mostly from impurities. Section 6.2.2 stated that carrier effective masses become heavier as the band gap increases; as the effective mass increases, the impurity binding energy will increase (see Equation 6.16). As the gap widens, eventually the impurity will become so deep that it will not be ionised at room temperature.

The distinction between wide-gap semiconductors and insulators is very blurred; *e.g.* studies of doped diamond for use in potential ultra-violet/blue LEDs are carried out, the aim being to find donors and acceptors which are shallow enough not to lead to carrier freeze-out at sensible operating

<sup>7</sup>So as not to complicate the discussion, the expression used for the number of empty donor states is a simplification. Those intending to embark on research should note that the number should be  $N_D(1 - 1/(1 + g^{-1}e^{(\mu - E_D)/k_B T}))$ , where  $g$  is the degeneracy of the donor groundstate. To see where  $g$  comes from, consider the 1s state of a hydrogenic donor. This is technically doubly degenerate owing to the fact that electrons can have spin up or spin down. Double occupancy of the donor is not energetically favourable; however, the statistical mechanics “knows” that there are two states available at that energy. See *e.g. Semiconductor Physics*, by K. Seeger (Springer, Berlin 1991).

<sup>8</sup>Beware! The derivation of this Equation assumes that  $E_c - \mu$  and  $\mu - E_D$  are both much greater than  $k_B T$ . We have already seen that  $E_c - E_D > \sim k_B T$  at room temperature; therefore this formula is only valid at much lower temperatures. It is, nevertheless, a useful guide to the low-temperature movement of  $\mu$ .

temperatures of  $\sim 300$  K. Conversely, much work has been done to dope semiconductors like GaAs with so-called *deep traps*, impurity states which are deliberately made so deep that the electrons and holes will remain frozen on them even at room temperature. Excess impurities will “soak up” any other carriers that are around, giving very high resistivities indeed. Such *semi-insulating* material is often used as a substrate to support devices made from more highly-conductive GaAs and (Ga,Al)As.

### 6.3.9 A note on photoconductivity.

It has been mentioned that semiconductors are often employed to detect photons. The detection involves *photoconductivity*, which can occur via three mechanisms;

1. the creation of electron-hole pairs through interband (intrinsic) absorption of radiation; typically this occurs at photon energies  $\sim E_g \sim 1$  eV or wavelengths  $\lambda \sim 1$   $\mu\text{m}$ ; later we shall see that by alloying semiconductors such as CdTe with semimetals such as HgTe, materials with band gaps as small as 0.1 eV (corresponding to  $\lambda \sim 10$   $\mu\text{m}$ ) can be made;
2. the excitation of electrons (or holes) from donor (acceptor) impurities into the conduction (valence) band; typically this occurs at energies  $\sim 5$  meV to 50 meV, corresponding to  $\lambda \sim 200 - 20$   $\mu\text{m}$ ;
3. free-carrier absorption.

In cases 1 and 2, the carrier numbers are increased; in case 3, the number of carriers remains constant but the conductivity changes because of a change in mobility. The latter mechanism is usually important in cases where the carrier effective mass is low and the band is strongly nonparabolic<sup>9</sup> as the low density of band states (from the small effective mass) results in long relaxation times for the excited carriers. Free-carrier absorption is proportional to the real part of the conductivity  $\sigma = \sigma_0/(1 + i\omega\tau)$ , and so increases rapidly at low energies/long wavelengths.

## 6.4 Reading.

Useful alternative treatments are given in *Electricity and Magnetism*, by B.I. Bleaney and B. Bleaney, revised third/fourth editions (Oxford University Press, Oxford) Chapters 17-19, *Solid State Physics*, by G. Burns (Academic Press, Boston, 1995) Sections 10.10-10.20 and Chapter 18, and *Low-Dimensional Semiconductor Structures*, by M.J. Kelly, (Clarendon Press, Oxford 1995) Chapter 1 and Sections 2.1-2.3, 2.7, 4.4, 5.1-5.3, 9.1-9.2. Optical properties of semiconductors are tackled in depth in *Optical Properties of Solids*, by A.M. Fox (OUP 2000).

*Essentials of semiconductor physics* by Tom Wenckebach (Wiley, New York, 1999) provides a slightly offbeat, but algebraically rigorous treatment of many of the properties of semiconductors which would be useful for those embarking on research or calculations. A similarly detailed but more traditional approach is given in *Semiconductor Physics*, by K. Seeger (Springer, Berlin 1991) and *Fundamentals of semiconductors*, by P. Yu and M. Cardona (Springer, Berlin, 1996). The methods used to calculate the bandstructure of semiconductors have been reviewed by F. Bassani (Chapter 2 of *Semiconductors and Semimetals*, Volume 1, edited by R.K. Willardson and A.C. Beer (Academic Press, New York, 1966)) and E.O. Kane (Chapter 4 of *Handbook on Semiconductors*, volume 1, edited by T.S. Moss (North Holland, Amsterdam, 1982)); the latter reference includes the famous **k.p** method for evaluating the bandstructure close to band extrema (see also *Fundamentals of semiconductors*, by P. Yu and M. Cardona (Springer, Berlin, 1996) Chapter 2.).

A very wide range of properties of semiconductors (band gaps, effective masses *etc.*) can be looked up in the comprehensive Landolt-Börnstein series, *Numerical data and functional relationships in science and technology*, New Series, Group III, Volume 17, edited by O. Madelung (Springer, Berlin, 1982).

Impurities in semiconductors are dealt with comprehensively in the mammoth tome *Doping in III-V semiconductors*, by E.F. Schubert (Cambridge University Press, 1993).

<sup>9</sup>This is the case in the conduction bands of narrow-gap semiconductors such as  $\text{Cd}_{0.2}\text{Hg}_{0.8}\text{Te}$  and  $\text{InSb}$ .