§8 – Semiconductors

8.1 Semiconductors

In looking at the origin of electron bands, we have considered two main scenarios:

1. Free electrons with zone boundary scattering that can open up band gaps;

2. Bound electrons in atoms with overlap.

Although these two methods seem very different, they both show that there are discrete (quantised) bands with the number of available states **exactly equal** to the number of atoms in the crystal.

A metal has a significant density of states at the Fermi energy, while a semimetal has just a few states available at the Fermi level for excitation. Sometimes, phonons can help to stimulate excitation.

Both semiconductors and insulators have a gap between occupied and unoccupied states. A semiconductor has a small band gap energy E_g such that $k_B T$ is a reasonable fraction of the gap,so that electrons can be thermally excited across the gap, while an insulator has a larger gap.

In order to fill the band exactly, there must be an **even** number of electrons in the primitive unit cell.

The only elemental semiconductors are in group IVB (new IUPAC group 14 – the carbon group) of the period table. Of these elements, only *Si* and *Ge* are semiconductors. *C* has too high an energy gap, and is therefore classed as an insulator . Conversely, *Sn* and elements lower in the group have too small a band gap, and are therefore classed as poor metals.

Table 8.1: Energy gaps of common semiconductor elements.

Element	E_g (eV)
C	5.5
Si	1.1
Ge	0.66
Sn	~0.0

There are several semiconductor compounds. These are generally group IIIB-V compounds (new IUPAC groups 13 and 15 – boron and nitrogen groups) or group IIB-VI compounds (new IUPAC groups 12 and 16).

Table 8.2: Energy gaps of common semiconductor compounds.

Compound	***E_g (eV)***
CdS	2.42
CdSe	1.74
GaAs	1.43
InSb	0.1

8.2 Direct and Indirect Band Gaps

In 3-dimensional reciprocal space, there are several locations at which a band gap can form.

These are not necessarily in the same place for the highest energy filled states, or ***valance band maximum,*** and the lowest energy empty states, or ***conduction band minimum***.

The ***band gap*** is defined as the difference between the lowest point on the conduction band and the highest point on the valence band.

A vertical (fixed Bloch vector) transition corresponds to a ***direct gap*** (e.g. GaAs) and when there is a change of Bloch vector we have an indirect gap (e.g. Si & Ge).

An indirect absorption corresponds to an ***indirect gap***

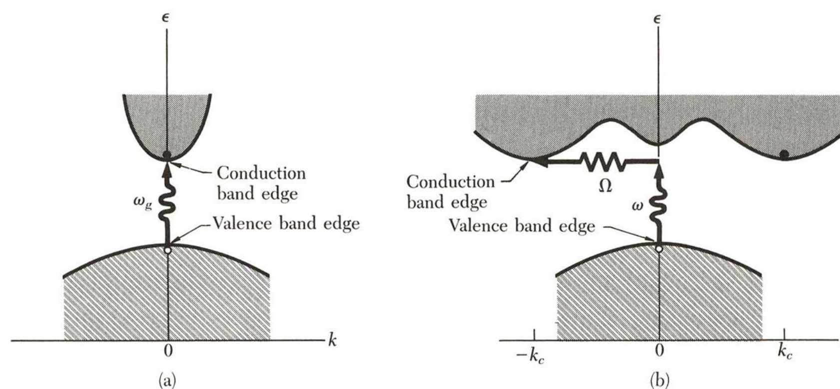

Figure 8.1: a) Direct optical transition. b) Indirect transition involving emission of a phonon with frequency Ω.

Phonons are more often created by an optical transition with an indirect gap, but can also be destroyed.

We can see this from the optical absorption spectrum.

8.3 Equations of Motion in Semiconductors

The spectrum shows the density of states but its application to electron transport depends on the electrical conduction of the semiconductor.

Neither a filled nor empty energy band can carry **any** current. The filled states precess in an electric field.

The current is carried by **two** types of "particle":

1. Electrons promoted to the conduction band;

2. ***Holes*** left behind in the valence band.

Although holes are not really particles, just the absence of an electron in the valence band, we can consider them to be charged particles. These holes will have an effective mass (which we will consider later).

As every hole in the valence band is matched by an electron in the conduction band (in the absence of dopants) these two mechanisms occur together, often giving similar contributions to current.

Current is carried by the wave packet, whilst the velocity of the wave packet is given by the group velocity.

Consider the motion of a wave packet in an applied electrical field.

Suppose that the wave packet is made up of wavefunctions near a particular wavenumber *k*.

The group velocity is as with the phonons, but we can use the relation $\epsilon=\hbar\omega$ to give:

$$v_g=\frac{1}{\hbar}\frac{d\epsilon}{dk} \tag{8.1}$$

The band structure determines v_g everywhere.

The work done $\delta\epsilon$ on an electron by an electric field of strength E in a small interval δt is given by:

$$\delta\epsilon=-eEv_g\delta t \tag{8.2}$$

And since $\delta\epsilon = \left(\frac{d\epsilon}{dk}\right)\delta k$, we can write this as:

$$\delta\epsilon = \hbar v_g \delta k \tag{8.3}$$

Substituting equation (8.2) into (8.3) and rearranging gives:

$$\delta k = -\left(\frac{eE}{\hbar}\right)\delta t \tag{8.4}$$

Thus, we have $\frac{dk}{dt} = -\frac{eE}{\hbar}$, the same relation as for free electrons.

From the Lorenz force, we know that for an electron in an applied electric field, with no magnetic field is given by $\vec{F} = -e\vec{E}$.

So, in 3-dimensions, we can write equation (8.4) in terms of an external force:

$$\vec{F} = \hbar \frac{d\vec{k}}{dt} \tag{8.5}$$

In free space this force is just equal to the classical force $\frac{d}{dt}(m\vec{v})$, so clearly, $\hbar\vec{k}$ is identified as the crystal momentum.

Equation (8.5) is the Lorentz force, so we can also consider the case of an electron in a magnetic field, with no electric field:

$$\frac{d\vec{k}}{dt} = -\frac{e}{\hbar}\vec{v}\times\vec{B} = -\frac{e}{\hbar^2}(\vec{\nabla}_k \epsilon)\times\vec{B} \tag{8.6}$$

Where ∇_k is the gradient operator in reciprocal space.

From equation (8.6), we can see that in a magnetic field, an electron moves in reciprocal space in a direction normal to the direction of the gradient of the energy.

This means that **the electron moves on a surface of constant energy**, with the ***orbit*** defined by the intersection of a plane normal to $\vec{B}$ with this surface.

8.4 Hole Dynamics

A hole is a missing electron in an otherwise filled valence band. Symmetry tells us that:

1. $\vec{k}_h = -\vec{k}_e$. Since the total wavevector for a filled band is zero, it is clear that the hole has wavevector $-\vec{k}_e$;

2. $\epsilon(\vec{k}_h) = -\epsilon(\vec{k}_e)$. If we assume that the top of the valence band is the zero of energy (since they are bound states), then the deeper states have lower energy for electrons, but higher energy for holes, since they require promotion of an electron to the band edge;

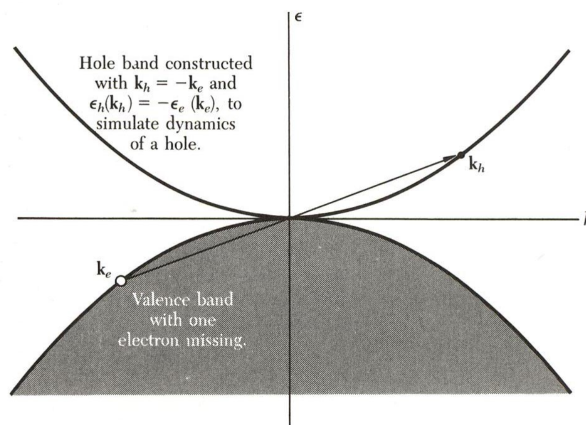

Figure 8.2: The upper half of the figure shows the hole band that simulates the dynamics of a hole. The wavevector and energy of the hole are equal, but opposite sign to the wavevector and energy of the empty electron orbital in the valance band.

3. $v_e = v_h = \frac{1}{\hbar}\frac{d\epsilon}{dk}$. This follows from the two above properties;

4. $m_e = -m_h$

5. The Lorenz force for a hole is given by $\hbar\frac{d\vec{k}_h}{dt} = +e(\vec{E} + \vec{k}_h \times \vec{B})$. The charge has opposite sign to the electron.

Creation of electron-hole pairs (e.g. in absorption processes) requires **two** contributions to the energy:

$$\Delta\epsilon = E_g + \epsilon_h + \epsilon_e \tag{8.7}$$

Where for a vertical transition, $k_e + k_h = 0$.

8.5 Effective Mass

When we look at the energy-wavevector relation for free electrons $\epsilon=\left(\frac{\hbar^2}{2m}\right)k^2$, we see that the coefficient of k^2 determines the curvature of ϵ versus k .

Since $\frac{\hbar^2}{2}$ is a constant, then it is the reciprocal mass $\frac{1}{m}$ that determines the curvature.

For electrons in a band, we may have regions of unusually high curvature near the band gap at the zone boundary. If the energy gap is small compared to the free electron energy λ at the boundary, then the curvature, and therefore the reciprocal mass, is enhanced by a factor $\frac{\lambda}{E_g}$.

The crystal does not weigh any less if the effective mass of the carrier is less than the free electron mass, nor is Newton's second law violated if we consider the crystal **as a whole**, i.e. both the ions and carriers.

The important point to note here is that an electron in a periodic potential is accelerated relative to the lattice in an applied electric/magnetic field as if the electron mass were equal to an effective mass.

Let us consider the value of the effective mass.

First, differentiate the group velocity as defined in equation (8.1) with respect to time:

$$\frac{d v_g}{d t}=\frac{1}{\hbar}\frac{d^2\epsilon}{d k\, d t}=\frac{1}{\hbar}\left(\frac{d^2\epsilon}{d k^2}\frac{d k}{d t}\right) \tag{8.8}$$

We know from equation (8.5) that $\hbar\frac{d k}{d t}=F$, so we have:

$$F=\frac{\hbar^2}{d^2\epsilon/d k^2}\frac{d v_g}{d t} \tag{8.9}$$

We know from Newton's second law that $F = m\,a$ and since $\frac{d\,v_g}{d\,t}$ is an acceleration, Newton's second law is upheld if $\frac{\hbar^2}{d^2\epsilon/d\,k^2}$ is a mass. Thus we can define the ***effective mass*** by:

$$\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{d^2\epsilon}{d\,k^2} \tag{8.10}$$

We can check that this gives the correct value for a free electron:

$\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{d^2}{d\,k^2}\left(\frac{\hbar^2 k^2}{2m}\right) = \frac{1}{m}$ as expected.

We can easily generalise this result to account for an anisotropic energy surface, as for electrons in Si or Ge. The ***reciprocal effective mass tensor*** is given by:

$$\left(\frac{1}{m^*}\right)_{\mu\nu} = \frac{1}{\hbar^2}\frac{d^2\epsilon_k}{d\,k_\mu\,d\,k_\nu} \tag{8.11}$$

Using, the reciprocal effective mass tensor, equation (8.9) becomes:

$$\frac{d\,v_\mu}{d\,t} = \left(\frac{1}{m^*}\right)_{\mu\nu} F^\nu \tag{8.12}$$

Where μ,ν are the Cartesian coordinates.

8.6 Physical Interpretation of Effective Mass

Inertial mass is defined as the resistance to acceleration.

Forces acting on electrons in a crystal will change the crystal momentum: $F = \hbar\frac{d\,k}{d\,t}$.

The rate at which the energy rises is given by the shape of the band structure.

In order to explain why a mass *m* placed in a crystal responds to an applied field as if the mass were m^* , it is useful to consider Bragg reflection of electron waves in a lattice.

Near the bottom of the lower band, we can adequately represent the orbital by a plane wave e^{ikx} , with momentum $\hbar k$. The wave component $\exp[i(k-G)x]$, with momentum $\hbar(k-G)$ is small, and increases slowly as *k* increases. Thus, in this region $m^* \simeq m$. An increase in the reflected component $\exp[i(k-G)x]$ with *k* represents the momentum transfer to the electron from the lattice.

Near the zone boundary, the reflected component is quite large. At the zone boundary, it is equal in amplitude to the incident component, where the eigenfunctions are standing waves. Here, the momentum component $\hbar(-1/2G)$ cancels the momentum component $\hbar(1/2G)$, and the mass is small unless the gap is large.

If we consider the tight binding approach, small overlap integrals (γ) correspond to shallow bands with large effective mass m^* (it is difficult to move electrons from one atom to the next).

For example, group III-V (13-15) semiconductors have direct gaps. In three-dimensions, there are 3 bands. So, each *k* has three eigenstates.

Each eigenstate has a different curvature and two are degenerate at the zone centre.

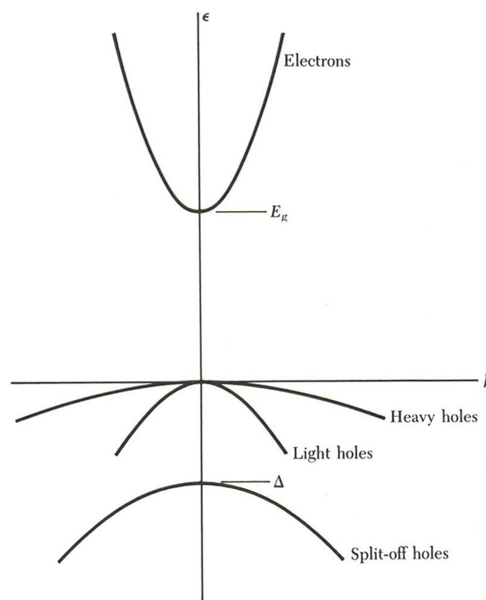

Figure 8.3: Simplified view of the band edge structure of a direct gap semiconductor.

Consider GaAs. The effective masses are as follows (see next section for explanation of heavy/light holes and spin-orbit splitting) :

Table 8.3: Effective masses of electrons and holes for Gallium Arsenide.

Carrier	***Effective Mass (m_e)***
Electrons	0.066
Heavy Holes	0.5
Light Holes	0.082
Split-off Holes	0.17

The spin-orbit splitting for GaAs, Δ, is 0.34 eV.

8.7 Measurement of m^*

Cyclotron resonance detects the characteristic frequencies of motion of free carriers in an applied magnetic field:

$$\vec{F}=e\,\vec{v}\times\vec{B}=-m\frac{v^2}{R^2}\vec{R} \tag{8.13}$$

Where: v^2/R is the centripetal acceleration.

We can use this to define the ***cyclotron (resonance) frequency***:

$$\omega_c=\frac{e\,B}{m^*} \tag{8.14}$$

A typical setup may be $\frac{\omega_c}{2\pi}\sim 20\,\text{GHz}$ (mm wavelength), which corresponds to $B\sim 1000\,G$ in CGS units or $0.1\,T$ in SI units.

All electrons (and holes) near the band edge contribute, as long as they are free carriers.

For example, consider the edge of the valence band in *Ge*:

The $p_{3/2}$ level has fourfold degeneracy and the $p_{1/2}$ level has double degeneracy. From Hund's rules, we know that 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 interactions.

Holes near the band edge are characterised 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 from the $p_{3/2}$ level by the spin-orbit interaction.

The edge of the conduction band is not at the zone centre, but shifted along [1 1 1] to the zone boundary.

Silicon is similar, but the conduction band edge is shifted along [1 0 0].

8.8 Intrinsic Carrier Concentration

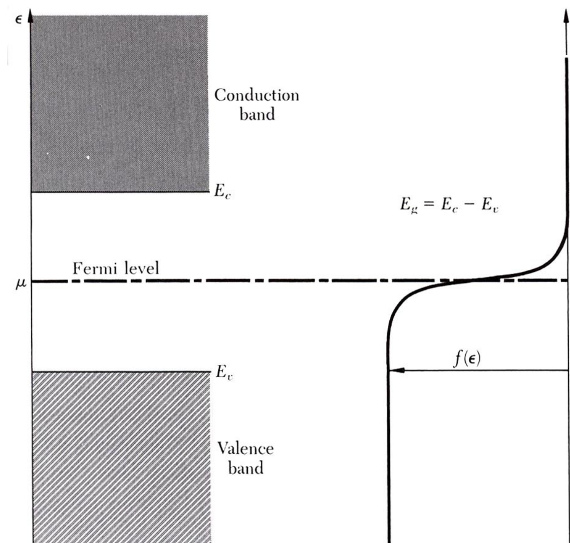

Figure 8.4: The energy scale for statistical calculations. The right side of the figure also shows the Fermi-Dirac distribution function on the same scale. For $k_B T \ll E_g$, the Fermi level is taken to lie well within the band gap.

a) Electron Concentration

At finite temperature, carriers are excited by the Fermi-Dirac distribution. The occupation number is therefore given by:

$$f_e = \frac{1}{\exp[(\epsilon - \mu)/k_B T] + 1} \approx \exp\left(\frac{(\epsilon - \mu)}{k_B T}\right) \tag{8.15}$$

For $(\epsilon-\mu)\gg kT$ in the conduction band, we have:

$$\epsilon_k=E_c+\frac{\hbar^2}{2m_e}k^2 \tag{8.16}$$

Where E_c is the energy of the conduction band edge. Here, $m_e=m^*$, the effective mass of the electron.
For $\epsilon>E_c$, the density of states is given by the usual argument:

$$2\frac{4}{3}\pi k^3=N\left(\frac{2\pi}{L}\right)^3=(2\pi)^3 n$$

$$D_e(\epsilon)=\frac{dn}{d\epsilon}=\frac{2}{(2\pi)^3}\frac{4}{3}\pi\frac{d}{d\epsilon}\left((\epsilon-E_c)\frac{2m_e}{\hbar^2}\right)^{\frac{3}{2}}=\frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{\frac{3}{2}}(\epsilon-E_c)^{\frac{1}{2}} \tag{8.17}$$

Thus, the concentration of electrons in the conduction band is given by:

$$n=\int_{E_c}^{\infty}D_e(\epsilon)\exp\left(\frac{(\mu-\epsilon)}{k_BT}\right)d\epsilon \tag{8.18}$$

Substituting equation (8.17) into (8.18):

$$n=\frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{\frac{3}{2}}\exp\left(\frac{\mu}{k_BT}\right)\int_{E_c}^{\infty}(\epsilon-E_c)^{\frac{1}{2}}\exp\left(-\frac{\epsilon}{k_BT}\right)d\epsilon \tag{8.19}$$

Integrating, using a standard integral, gives:

$$n=2\left(\frac{m_ek_BT}{2\pi\hbar^2}\right)^{\frac{3}{2}}\exp\left(\frac{(\mu-E_c)}{k_BT}\right) \tag{8.20}$$

The only unknown variable here is the chemical potential μ, which could be anywhere.

However, there is a constraint in that the electron and hole concentrations are linked, so we can use this relation to determine μ.

b) Hole Concentration

Since a hole is an absence of an electron, the occupation number is given by:

$$f_h = 1 - f_e = 1 - \frac{1}{\exp\left[(\epsilon - \mu)/k_B T\right] + 1} = \frac{1}{1 + \exp\left[(\mu - \epsilon)/k_B T\right]} \tag{8.21}$$

Now, assume that $(\mu - \epsilon) \gg k_B T$, or alternatively, the energy states we are considering are much less that ϵ. Thus, we can approximate the occupation number as:

$$f_h \approx \exp\left(\frac{(\epsilon - \mu)}{k_B T}\right) \tag{8.22}$$

The hole density of states is "upside down" compared with the electron density of states:

$$D(\epsilon) = \frac{1}{2\pi^2}\left(\frac{2 m_h}{\hbar^2}\right)^{\frac{3}{2}} (E_v - \epsilon)^{\frac{1}{2}} \tag{8.23}$$

So, the concentration of holes in the valence band is given by:

$$p = \int_{-\infty}^{E_v} D_h(\epsilon) \exp\left(\frac{(\epsilon - \mu)}{k_B T}\right) d\epsilon \tag{8.24}$$

Again, substituting equation (8.23) into (8.24), and using a standard integral gives:

$$p = 2\left(\frac{m_h k_B T}{2\pi\hbar^2}\right)^{\frac{3}{2}} \exp\left(\frac{(E_v - \mu)}{k_B T}\right) \tag{8.25}$$

c) Law of Mass Action

We can multiply equations (8.20) and (8.25) together to obtain the equilibrium relation, involving the band gap $E_g = E_c - E_v$:

$$n\,p = 4\left(\frac{k_B T}{2\pi\hbar^2}\right)^3 (m_e m_h)^{3/2} \exp\left(-\frac{E_g}{k_B T}\right) \tag{8.26}$$

This is a very useful result, because it does **not** depend on the Fermi level/chemical potential. It is an expression of the ***law of mass action***.

Nowhere in the derivation have we assumed that the material is intrinsic: the result holds for a material with impurities. The only assumption we have made is that the distance of the Fermi level from the edges of both band gaps is large in comparison with $k_B T$.

With this information, we can calculate the expected concentrations. At 300K, and expressing $n\,p$ in CGS units, examples of carrier concentrations are:

Table 8.4: Carrier concentrations of various semiconductors at room temperature in CGS units.

Semiconductor	***n p (cm^{-6})***	***E_g (eV)***
Si	2.10×10^{19}	1.1
Ge	2.89×10^{26}	0.7
GaAs	6.55×10^{12}	1.4

For an intrinsic case, where every electron in the conduction band leaves a hole in the valence band, the the electron and hole number densities are equal, so they are given by:

$$n = p = n_i = \sqrt{n\,p} = 2\left(\frac{k_B T}{2\pi\hbar^2}\right)^{\frac{3}{2}} (m_e m_p)^{3/4} \exp\left(-\frac{E_g}{2 k_B T}\right) \tag{8.27}$$

Ge has a carrier concentration of $n_i \sim 10^{13}\,cm^{-3}$, and atomic density $\rho \sim 10^{22}\,cm^{-3} \sim N_A$, so only around 1 in 10^9 of all the electrons is in the conduction band. The number of electrons in the conduction band for Si and GaAs are much smaller still. So, intrinsic semiconductors are actually pretty bad conductors!

For the intrinsic case, we can determine easily the chemical potential μ_i . Since $n=p$ we can equate equations (8.20) and (8.25) to give:

$$m_e^{3/2}\exp\left(\frac{(\mu-E_c)}{k_B T}\right)=m_h^{3/2}\exp\left(\frac{(E_v-\mu)}{k_B T}\right)$$

Where terms the same on both sides have been cancelled out.

Now, multiply both sides by $m_e^{-3/2}\exp\left(\frac{(\mu+E_c)}{k_B T}\right)$:

$$\exp\left(\frac{2\mu}{k_B T}\right)=\left(\frac{m_h}{m_e}\right)^{3/2}\exp\left(\frac{(E_v+E_c)}{k_B T}\right)$$

Take logarithms to base *e* on both sides:

$$\frac{2\mu}{k_B T}=\frac{3}{2}\ln\left(\frac{m_h}{m_e}\right)+\frac{(E_v+E_c)}{k_B T}$$

Substituting $E_v+E_c=E_g+2E_v$ and multiplying both sides by $\frac{k_B T}{2}$ gives the final expression for the chemical potential:

$$\mu=\underbrace{E_v+\frac{1}{2}E_g}_{\text{Mid-gap energy}}+\frac{3}{4}k_B T\ln\left(\frac{m_h}{m_e}\right) \qquad (8.28)$$

If $T = 0$, then the chemical potential is the Fermi energy by definition. From equation (8.28), we can see that this is equal to the mid-gap energy: the energy mid-way between the band edges.

If the electron and hole effective masses are equal, $m_e=m_h$ then the chemical potential is equal to the mid-gap energy for all temperatures.

In general, the chemical potential is approximately equal to the intrinsic Fermi energy $E_i=E_v+\frac{1}{2}E_g$ for intrinsic semiconductors because the logarithmic term, which corrects for the effective mass is small and varies weakly with temperature.