5. Semiconductors

The nearly free electron model applies equally in the case where the Fermi level lies within a small band gap (semiconductors), as it does when the Fermi level lies within a band (metal). By small, we mean that there is thermal excitation of electrons from one band to the next, below the melting temperature. In practice, the gap energy needs to be less than about 2eV.



Note that it is traditional to draw the diagram for semiconductors rotated 90 degrees, i.e. the version on the right above.

5.1 Semiconductor Bandstructures

There is no Fermi sphere, so we need to look at details of bandstructure near the gap. A direct gap semiconductor arises when the maximum energy of the valence band is at the same wavevector as the minimum energy of the conduction band. In this case excitation across the band gap can be brought about by photon absorption.

On the scale of the Brillouin Zone (~1 / 1 Angstrom), the photon momentum is very small. E.g. a 1eV photon has momentum ~ $5 \times 10^{-4} A^{-1}$ (where A is an Angstrom). This reflects the fact that the speed of light is much greater than the electron speeds.

An indirect semiconductor has the maximum energy of valence band not at the same wavevector as the minimum of conduction band. Excitation across the band gap requires a phonon creation (or absorption) to take up the momentum. This makes the process much less likely.

Note that in general, effective masses are not isotropic (the same in all directions). The effective mass in general is a tensor.

Indium Antimonite

This is a direct gap semiconductor.



<u>Germanium</u> An indirect gap semiconductor



The effective mass for the conduction band is a tensor.

$$m^* = \begin{pmatrix} 1.6 & 0 & 0 \\ 0 & 0.08 & 0 \\ 0 & 0 & 0.08 \end{pmatrix} m_e$$

5.1 Intrinsic Semiconductor

Observed when the semiconductor is sufficiently pure. Use an 'average' effective mass m_c in the conduction band, and m_v in the valence band. The energy ε in the conduction band with respect to the minimum energy ε_c :

$$\varepsilon - \varepsilon_c = \frac{\hbar^2 k^2}{2m_c} \, .$$

So density of states:

$$\rho(k)dk = \frac{V}{\pi^2}k^2dk$$

where we have already put in the factor of 2 due to degeneracy of spin states. We need to convert that to the density of states in energy.

$$\rho(\varepsilon)d\varepsilon = \frac{V}{\pi^2\hbar^3}\sqrt{2(\varepsilon-\varepsilon_c)}m_c^{3/2}d\varepsilon$$

for $\varepsilon > \varepsilon_c$. Below that, the density of states is 0. For the valence band,

$$\rho(\varepsilon)d\varepsilon = \frac{V}{\pi^2 \hbar^3} \sqrt{2(\varepsilon_v - \varepsilon)} m_v^{\frac{3}{2}} d\varepsilon$$

for $\varepsilon < \varepsilon_{v}$.

The number of electrons in the conduction band, n, is:

$$n = \frac{1}{V} \int_{\substack{\text{conduction}\\band}} \rho(\varepsilon) f(\varepsilon) d\varepsilon$$

Correspondingly, the number of holes in the valence band, p, is

$$p = \frac{1}{V} \int_{valence} \rho(\varepsilon) (1 - f(\varepsilon)) d\varepsilon$$

where $1 - f(\varepsilon)$ gives us the unoccupied states.

The Fermi function is very small near the top of the conduction band, so we can replace the limit by infinity. The same argument can be used for the number of holes integral.

$$n = \frac{1}{V} \int_{\varepsilon_{c}}^{\infty} \rho(\varepsilon) f(\varepsilon) d\varepsilon$$
$$p = \frac{1}{V} \int_{-\infty}^{\varepsilon_{v}} \rho(\varepsilon) (1 - f(\varepsilon)) d\varepsilon$$

We can assume that $(\varepsilon_c - \mu)\beta >> 1$, and $(\mu - \varepsilon_{\nu})\beta >> 1$. So

$$f(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)\beta}+1} \approx e^{-(\varepsilon-\mu)\beta}$$

for $\varepsilon > \varepsilon_c$, and

$$(1-f(\varepsilon)) = 1 - \frac{1}{e^{(\mu-\varepsilon)\beta} + 1} \approx e^{-(\mu-\varepsilon)\beta}$$

for $\varepsilon < \varepsilon_v$. Hence,

$$n = \frac{1}{V} e^{-(\varepsilon_{c} - \mu)\beta} \int_{\varepsilon_{c}}^{\infty} \rho(\varepsilon) e^{-(\varepsilon - \varepsilon_{c})\beta} d\varepsilon$$
$$p = \frac{1}{V} e^{-(\mu - \varepsilon_{v})\beta} \int_{-\infty}^{\varepsilon_{v}} \rho(\varepsilon) e^{-(\varepsilon_{v} - \varepsilon)\beta} d\varepsilon$$

Therefore,

$$n = \frac{\sqrt{2}m_c^{\frac{3}{2}}}{\pi^2\hbar^3}e^{-(\varepsilon_c-\mu)\beta}\int_{\varepsilon_c}^{\infty}\sqrt{\varepsilon-\varepsilon_c}e^{-(\varepsilon-\varepsilon_c)\beta}d\varepsilon$$
$$p = \frac{\sqrt{2}m_v^{\frac{3}{2}}}{\pi^2\hbar^3}e^{-(\mu-\varepsilon_v)\beta}\int_{-\infty}^{\varepsilon_v}\sqrt{\varepsilon_v-\varepsilon}e^{-(\varepsilon_v-\varepsilon)\beta}d\varepsilon$$

Substitute

$$x^{2} = \varepsilon - \varepsilon_{c}$$
$$2xdx = d\varepsilon$$

$$I = \int_{\varepsilon_v}^{\infty} \sqrt{\varepsilon - \varepsilon_c} e^{-(\varepsilon - \varepsilon_c)\beta} d\varepsilon$$
$$= 2 \int_0^{\infty} x^2 e^{-\beta x^2} dx$$
$$= \frac{1}{2} \sqrt{\frac{\pi}{\beta^3}}$$
$$n = \frac{1}{4} \left(\frac{2m_c}{\pi \hbar^2 \beta}\right)^{\frac{3}{2}} e^{-(\varepsilon_c - \mu)\beta}$$
$$p = \frac{1}{4} \left(\frac{2m_v}{\pi \hbar^2 \beta}\right)^{\frac{3}{2}} e^{-(\mu - \varepsilon_v)\beta}$$

So,

$$np = \frac{1}{16} \left(\frac{2}{\pi \hbar^2 \beta}\right)^3 \left(m_c m_v\right)^{3/2} e^{-\epsilon_g \beta}$$

where $\varepsilon_g = \varepsilon_c - \varepsilon_v$. This is independent of the chemical potential μ .

In a pure semiconductor, $n_i = p_i$ (intrinsic *n* and *p*), Hence this is equal to

$$n_{i} = n_{p} = \sqrt{np} = \frac{1}{4} \left(\frac{2}{\pi\hbar^{2}\beta}\right)^{3/2} \left(m_{c}m_{v}\right)^{3/4} e^{-\frac{\varepsilon_{g}\beta}{2}}$$

Putting this back into the expression for n means that we can find that the chemical potential for intrinsic semiconductors is

$$\mu = \varepsilon_v + \frac{1}{2}\varepsilon_g + \frac{3}{4}k_B T \ln\left(\frac{m_v}{m_c}\right)$$

So μ is the midpoint of the gap at T = 0, and lies within a fraction of $k_b T$ of the midpoint at finite temperature in intrinsic semiconductors.

5.3 Extrinsic Semiconductor

Introduce 1 atom of As (Group 5) into Ge (Group 4). Each Ge has 4 electrons in the valence band, while As has 5.

If we consider the As to be like Ge, then we have an extra proton and electron – the constituents of a hydrogen atom. Assume that the extra electron is loosly bound, moving in the conduction band with effective mass m^* .

$$F = -\frac{1}{4\pi\varepsilon\varepsilon_0}\frac{e^2}{r^2}$$

where we have introduced the dielectric constant, which reduces the forces between the atoms. For Ge, $\varepsilon \sim 15.8$. The binding energy for the electron is

$$E_0 = \frac{m_e e^4}{\left(4\pi\varepsilon\varepsilon_0\hbar\right)^2} \frac{m^*}{m_e}$$

The binding energy of the hydrogen atom is 13.6eV. m^*/m_e is 0.23. $\varepsilon^2 = 0.004$. Hence $E_0 = 12meV$ (milli-electron-volts). The Bohr radius of the atom is,

$$r_0 = \frac{4\pi\varepsilon\varepsilon_0\hbar^2}{m_e e^2} \frac{m_e}{m^*}$$

The Bohr radius for the hydrogen atom is 0.53A. $m_e/m^* = 4.3$. This means that the radius is 36 Angstrom.

We conclude that the extra electron is loosely bound, and the use of the bulk dielectric constant is reasonable.

There is a similar argument for adding an atom with one less electron to the semiconductor, which gives the acceptor impurity states.



Donor impurity states energy ε_d , acceptor impurity states energy ε_a

Usually there are impurities of both types (acceptors and donors) present. Suppose that there are more donors n_d than acceptors n_a .



This requires the chemical potential to be at the donor level, $\mu = \varepsilon_d$ (the Fermi level is in the only state which can have partly-filled states; this is that of the donor state). It will not move far at finite temperature while there are un-ionized donors. Using the expression for *n* derived earlier,

$$n = \frac{1}{4} \left(\frac{2m_c}{\pi \hbar^2 \beta} \right)^{3/2} e^{-(\varepsilon_c - \varepsilon_d)\beta}$$

When all the donors are ionized, the number of carriers will reach a plateau at $n_d - n_a$.

At higher temperatures, when the number of intrinsic carriers becomes comparable with the number of impurities, μ ends up near the middle of the gap, just as it did in the intrinsic case, and *n* reverts to its intrinsic value.



The intrinsic slope is $\sim -\frac{\varepsilon_g}{2k_B}$. The extrinsic slope is $\sim -(\varepsilon_c - \varepsilon_d)/k_B$.

Note that the number of electrons is greater in the extrinsic region than the intrinsic value at the same temperature.

A semiconductor with more donors than acceptors is called n-type, and one with more acceptors than donors is called p-type.

Note that even when there are impurities present,

$$np = n_i^{2} = \frac{1}{16} \left(\frac{2}{\pi \hbar^2 \beta} \right)^3 \left(m_c m_v \right)^{3/2} e^{-\varepsilon_s \beta}$$

as before, and this may be used to calculate the number of minority carriers at any temperature once the number of majority carriers has been established.

5.4 Intrinsic v Extrinsic

How pure do materials need to be to see intrinsic behaviour at room temperature? For germanium, $n_i (T = 300k)$ is $1.6 \times 10^{18} m^{-3}$, compared to the number density of atoms which his $4.4 \times 10^{28} m^{-3}$. So purity needs to be better than 1 part in 10^{10} . In silicon, the requirement is even stricter because the band gap is larger.

Zone refining

Take a bar of the required semiconductor material. Melt a small zone. Very slowly move this zone down the bar. The impurities prefer to remain in the liquid phase, and tend not to crystallize out when the semiconductor solidifies. The zone needs to move up and down the bar many times to get the required accuracy. In the end, the impurities are concentrated at either end of the bar. The material in the middle gets to the level of purity required.

5.5 Semiconductor Properties

We continue to use the nearly free electron model, but we may have both conduction band electrons and valence band holes contributing. The main difference from metals is in the temperature dependence of the number of carriers.

1. Electrical Conductivity

$$\sigma = n \frac{e^2 \tau}{m_c} + p \frac{e^2 \tau}{m_v}$$

It is customary to separate out the mobility (drift velocity / e-field) which shows the temperature dependence arising from collisions, as opposed to the effects of the changing number of carriers. (don't confuse with chemical potential.)

$$\mu = \frac{|\underline{v}|}{|\underline{E}|} = |e|\frac{\tau}{m^*}$$
$$\sigma = |e|(n\mu_e + p\mu_h)$$

It varies in a similar way to metals – decreasing at higher temperatures because of phonon collisions.

$$f(\varepsilon) \approx e^{-(\varepsilon-\mu)\beta}$$

if $\varepsilon = \varepsilon_c + \Delta \varepsilon$,

$$f(\varepsilon) = e^{-(\varepsilon_c - \mu)\beta} e^{-\beta \Delta \varepsilon}$$
$$\Delta \varepsilon = \frac{1}{2} \frac{\partial^2 \varepsilon}{\partial k^2} (\Delta k)^2$$
$$v = \frac{1}{\hbar} \frac{\partial \varepsilon}{\partial k} = \hbar \frac{\Delta k}{m^*}$$
$$\Delta \varepsilon = \frac{1}{2} m^* v^2$$
$$\frac{1}{2} m^* \overline{v^2} = \frac{3}{2} k_B T$$
$$\sqrt{\overline{v^2}} = \left(\frac{3k_B T}{m^*}\right)^{\frac{1}{2}}$$

Assume that the mean free path, ℓ , goes like T^{-1} in the phonon regime, so the mean collision time τ is

$$\tau = \frac{\ell}{\sqrt{v^2}}$$
$$\mu_e \propto \tau \propto T^{-\frac{3}{2}}$$

Conductivity increases as the temperature is raised, because the number of carriers increases, e.g. Si conductivity increases by 4 orders of magnitude between 500k and 1000k.



2. Hall Effect $R_{H} = -\frac{1}{ne}$ for electrons, and $R_{H} = +\frac{1}{pe}$ for holes.

If there are appreciable numbers of both electrons and holes, the calculation is complicated by transverse currents with creation of electron-hole pairs at one side, and their annihilation at the other, together with a temperature gradient. See Hook and Hall, pp153-154.

Note: R_H together with σ , gives mobility since $\mu = \frac{e\tau}{m^*} = -\frac{\sigma}{ne} = R_H \sigma$.