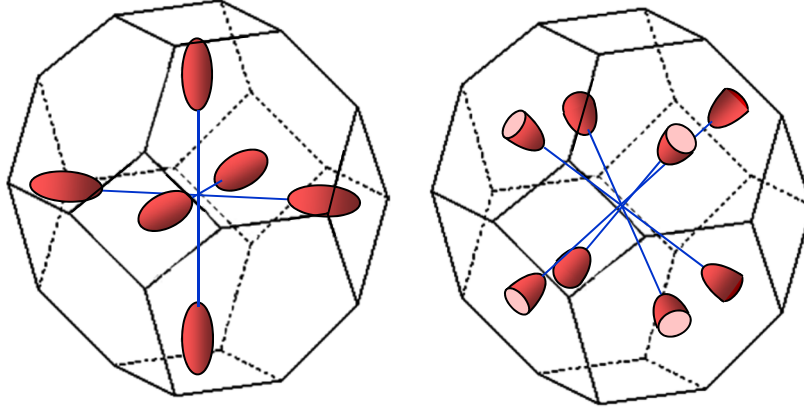


Handout 14

Statistics of Electrons in Energy Bands

In this lecture you will learn:



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Example: Electron Statistics in GaAs - Conduction Band

Consider the conduction band of GaAs near the band bottom at the Γ -point:

$$M^{-1} = \begin{bmatrix} 1/m_e & 0 & 0 \\ 0 & 1/m_e & 0 \\ 0 & 0 & 1/m_e \end{bmatrix}$$

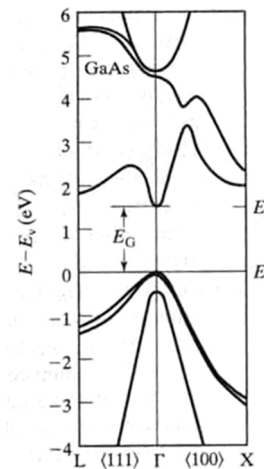
This implies the energy dispersion relation near the band bottom is:

$$E_c(\vec{k}) = E_c + \frac{\hbar^2(k_x^2 + k_y^2 + k_z^2)}{2m_e} = E_c + \frac{\hbar^2 k^2}{2m_e}$$

Suppose we want to find the total number of electrons in the conduction band:

We can write the following summation:

$$N = 2 \times \sum_{\vec{k} \text{ in FBZ}} f_c(\vec{k})$$



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Example: Electron Statistics in GaAs - Conduction Band

$$N = 2 \times \sum_{\vec{k} \text{ in FBZ}} f_c(\vec{k})$$

Where the Fermi-Dirac distribution function is:

$$f_c(\vec{k}) = \frac{1}{1 + \exp\left(\frac{E_c(\vec{k}) - E_f}{KT}\right)} \quad \left\{ \begin{array}{l} = f(E_c(\vec{k}) - E_f) \\ \text{Another way of writing it} \end{array} \right.$$

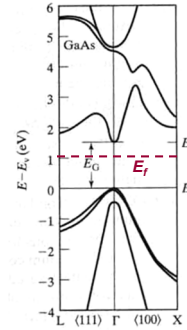
We convert the summation into an integral:

$$N = 2 \times \sum_{\vec{k} \text{ in FBZ}} f_c(\vec{k}) = 2 \times V \int_{\text{FBZ}} \frac{d^3 \vec{k}}{(2\pi)^3} \frac{1}{1 + \exp\left(\frac{E_c(\vec{k}) - E_f}{KT}\right)}$$

Then we convert the k-space integral into an integral over energy:

$$N = 2 \times V \int_{\text{FBZ}} \frac{d^3 \vec{k}}{(2\pi)^3} \frac{1}{1 + \exp\left(\frac{E_c(\vec{k}) - E_f}{KT}\right)} = \int_{?}^{?} dE g_c(E) f(E - E_f)$$

We need to find the density of states function $g_c(E)$ for the conduction band and need to find the limits of integration

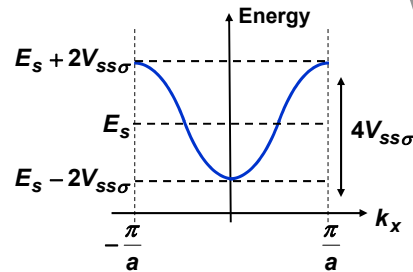


Density of States in Energy Bands

Consider the 1D energy band that results from tight binding:

$$E(k_x) = E_s - 2V_{ss\sigma} \cos(k_x a)$$

$$\Rightarrow \frac{dE}{dk_x} = 2aV_{ss\sigma} \sin(k_x a)$$

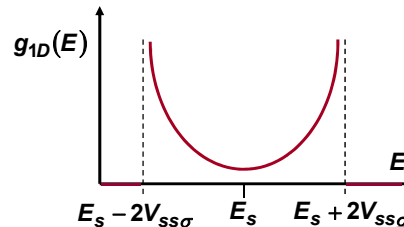


We need to find the density of states function $g_{1D}(E)$:

$$2 \times \sum_{k_x \text{ in FBZ}} \rightarrow 2 \times L \int_{-\pi/a}^{\pi/a} \frac{dk_x}{2\pi} \rightarrow 4 \times L \int_0^{\pi/a} \frac{dk_x}{2\pi} \rightarrow \frac{2}{\pi} \times L \int_{E_s - 2V_{ss\sigma}}^{E_s + 2V_{ss\sigma}} \left| \frac{dk_x}{dE} \right| dE$$


$$\rightarrow L \int_{E_s - 2V_{ss\sigma}}^{E_s + 2V_{ss\sigma}} g_{1D}(E) dE$$

$$\Rightarrow g_{1D}(E) = \frac{2}{\pi a} \frac{1}{\sqrt{(2V_{ss\sigma})^2 - (E - E_s)^2}}$$



Example: Electron Statistics in GaAs - Conduction Band

$$N = 2 \times V \int_{\text{FBZ}} \frac{d^3 \vec{k}}{(2\pi)^3} \frac{1}{1 + \exp\left(\frac{E_c(\vec{k}) - E_f}{KT}\right)} = \int_?^? dE g_c(E) f(E - E_f)$$

 Electrons will only be present near the band bottom

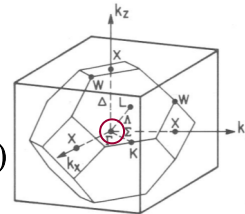
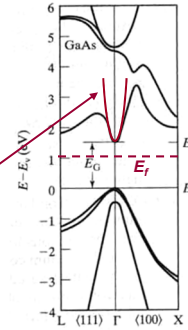
Energy dispersion near the band bottom is:

$$E_c(\vec{k}) = E_c + \frac{\hbar^2(k_x^2 + k_y^2 + k_z^2)}{2m_e} = E_c + \frac{\hbar^2 k^2}{2m_e}$$

(parabolic and isotropic)

Since the electrons are likely present near the band bottom, we can limit the integral over the entire FBZ to an integral in a spherical region right close to the Γ -point:

$$N = 2 \times V \int_{\text{FBZ}} \frac{d^3 \vec{k}}{(2\pi)^3} f_c(\vec{k}) = 2 \times V \int_{\Gamma\text{-point}} \frac{4\pi k^2}{8\pi^3} dk f(E_c(k) - E_f)$$



Example: Electron Statistics in GaAs - Conduction Band

$$N = 2 \times V \int_{\Gamma\text{-point}} \frac{4\pi k^2}{8\pi^3} dk f(E_c(k) - E_f)$$

Since the Fermi-Dirac distribution will be non-zero only for small values of k , one can safely extend the upper limit of the integration to infinity:

$$N = 2 \times V \int_0^{\infty} \frac{4\pi k^2}{8\pi^3} dk f(E_c(k) - E_f)$$

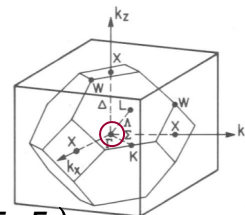
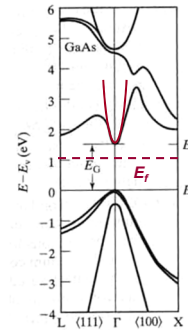
We know that:

$$E_c(\vec{k}) = E_c + \frac{\hbar^2(k_x^2 + k_y^2 + k_z^2)}{2m_e} = E_c + \frac{\hbar^2 k^2}{2m_e}$$

$$\Rightarrow k = \sqrt{\frac{2m_e}{\hbar^2} (E - E_c)} \quad \text{and} \quad \frac{dE}{dk} = \frac{\hbar^2 k}{m_e}$$

We have finally:

$$N = 2 \times V \int_0^{\infty} \frac{4\pi k^2}{8\pi^3} dk f(E_c(k) - E_f) = V \int_{E_c}^{\infty} dE g_c(E) f(E - E_f)$$



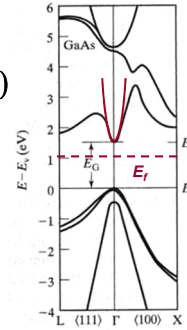
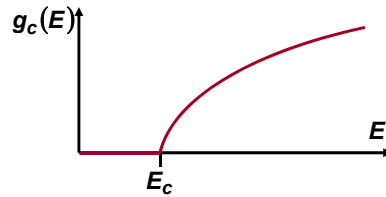
Example: Electron Statistics in GaAs - Conduction Band

We have finally:

$$N = 2 \times V \int_0^\infty \frac{4\pi k^2}{8\pi^3} dk f(E_c(k) - E_f) = V \int_{E_c}^\infty dE g_c(E) f(E - E_f)$$

Where the conduction band density of states function is:

$$g_c(E) = \frac{1}{2\pi^2} \left(\frac{2m_e}{\hbar^2} \right)^{3/2} \sqrt{E - E_c}$$

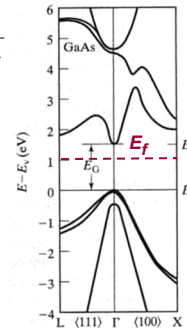
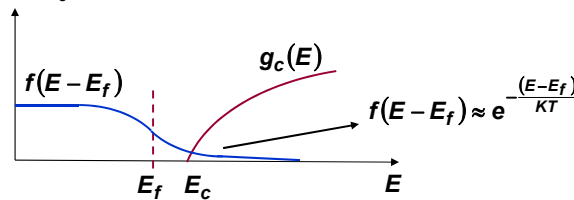


The density of states function looks like that of a 3D free electron gas except that the mass is the effective mass m_e and the density of states go to zero at the band edge energy E_c

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Example: Electron Statistics in GaAs - Conduction Band

$$n = \int_{E_c}^\infty dE g_c(E) f(E - E_f) \quad g_c(E) = \frac{1}{2\pi^2} \left(\frac{2m_e}{\hbar^2} \right)^{3/2} \sqrt{E - E_c}$$



If $E_c - E_f \gg KT$ then one may approximate the Fermi-Dirac function as an exponential:

$$f(E - E_f) = \frac{1}{1 + \exp\left(\frac{E - E_f}{KT}\right)} \approx \exp\left(-\frac{E - E_f}{KT}\right) \quad \text{Maxwell-Boltzman approximation}$$

$$n = \int_{E_c}^\infty dE g_c(E) f(E - E_f) = N_c \exp\left(-\frac{E_c - E_f}{KT}\right)$$

Where: $N_c = 2 \left[\frac{m_e KT}{2\pi \hbar^2} \right]^{3/2}$ Effective density of states (units: #/cm³)

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Example: Electron Statistics in GaAs - Valence Band and Holes

- At zero temperature, the valence band is completely filled and the conduction band is completely empty
- At any finite temperature, some electrons near the top of the valence band will get thermally excited from the valence band and occupy the conduction band and their density will be given by:

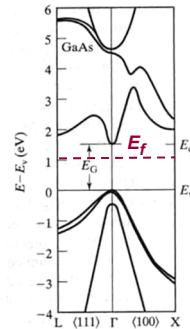
$$n = N_c \exp\left(-\frac{(E_c - E_f)}{KT}\right)$$

- The question we ask here is how many empty states are left in the valence band as a result of the electrons being thermally excited. The answer is (assuming the heavy-hole valence band):

$$2 \times \sum_{\vec{k} \text{ in FBZ}} [1 - f(E_{hh}(\vec{k}) - E_f)]$$

- We call this the number of “holes” left behind in the valence band and the number of these holes is P :

$$P = 2 \times \sum_{\vec{k} \text{ in FBZ}} [1 - f(E_{hh}(\vec{k}) - E_f)] = 2 \times V \int_{\text{FBZ}} \frac{d^3 \vec{k}}{(2\pi)^3} [1 - f(E_{hh}(\vec{k}) - E_f)]$$



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Example: Electron Statistics in GaAs - Valence Band and Holes

$$P = 2 \times V \int_{\text{FBZ}} \frac{d^3 \vec{k}}{(2\pi)^3} [1 - f(E_{hh}(\vec{k}) - E_f)]$$



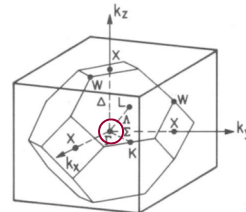
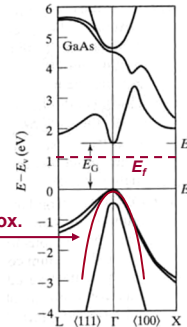
Holes will only be present near the top of the valence band

Energy dispersion near the top of the valence band is:

$$E_{hh}(\vec{k}) = E_v - \frac{\hbar^2(k_x^2 + k_y^2 + k_z^2)}{2m_{hh}} = E_v - \frac{\hbar^2 k^2}{2m_{hh}} \quad \text{parabolic approx.}$$

Since the holes are likely present near the band maximum, we can limit the integral over the entire FBZ to an integral in a spherical region just close to the Γ -point:

$$P = 2 \times V \int_{\Gamma\text{-point}} \frac{4\pi k^2}{8\pi^3} dk [1 - f(E_{hh}(k) - E_f)]$$



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Example: Electron Statistics in GaAs - Valence Band and Holes

$$P = 2 \times V \int_{\Gamma\text{-point}} \frac{4\pi k^2}{8\pi^3} dk [1 - f(E_{hh}(k) - E_f)]$$

Since the Fermi-Dirac distribution will be non-zero only for small values of k , one can safely extend the upper limit of the integration to infinity:

$$P = 2 \times V \int_0^\infty \frac{4\pi k^2}{8\pi^3} dk [1 - f(E_{hh}(k) - E_f)]$$

We know that:

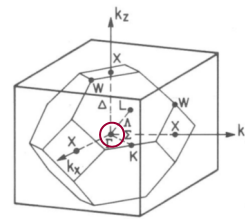
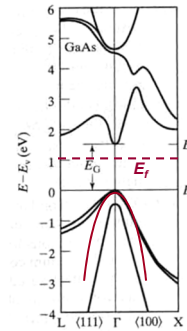
$$E_{hh}(\vec{k}) = E_v - \frac{\hbar^2(k_x^2 + k_y^2 + k_z^2)}{2m_{hh}} = E_v - \frac{\hbar^2 k^2}{2m_{hh}}$$

$$\Rightarrow k = \sqrt{\frac{2m_{hh}}{\hbar^2}(E_v - E)} \quad \text{and} \quad \frac{dE}{dk} = \frac{\hbar^2 k}{m_{hh}}$$

We have finally:

$$P = 2 \times V \int_0^\infty \frac{4\pi k^2}{8\pi^3} dk [1 - f(E_{hh}(k) - E_f)]$$

$$= V \int_{-\infty}^{E_v} dE g_{hh}(E) [1 - f(E - E_f)]$$



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Example: Electron Statistics in GaAs - Valence Band and Holes

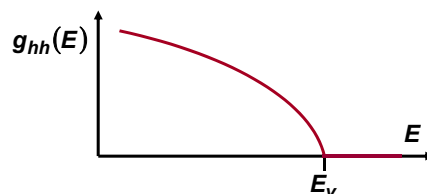
We have finally:

$$P = 2 \times V \int_0^\infty \frac{4\pi k^2}{8\pi^3} dk [1 - f(E_{hh}(k) - E_f)]$$

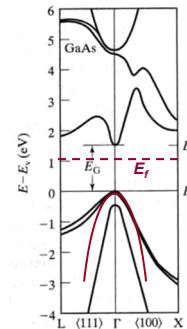
$$= V \int_{-\infty}^{E_v} dE g_{hh}(E) [1 - f(E - E_f)]$$

Where the heavy hole band density of states function is:

$$g_{hh}(E) = \frac{1}{2\pi^2} \left(\frac{2m_{hh}}{\hbar^2} \right)^{3/2} \sqrt{E_v - E}$$



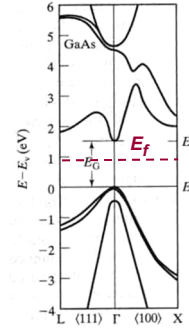
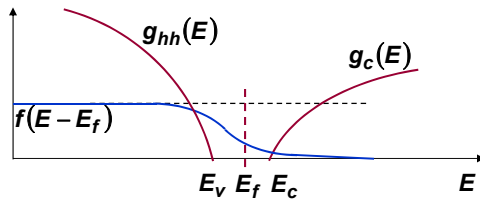
Note that the mass that comes in the density of states is the heavy hole effective mass m_{hh} and the density of states go to zero at the band edge energy E_v , and the density of states increase for smaller energies



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Example: Electron Statistics in GaAs - Valence Band and Holes

$$p = \int_{-\infty}^{E_V} dE g_{hh}(E) [1 - f(E - E_f)] \quad g_{hh}(E) = \frac{1}{2\pi^2} \left(\frac{2m_{hh}}{\hbar^2} \right)^{3/2} \sqrt{E_V - E}$$



If $E_f - E_V \gg KT$ then one may approximate the Fermi-Dirac function as an exponential:

$$1 - f(E - E_f) = \frac{1}{1 + \exp\left(\frac{E_f - E}{KT}\right)} \approx \exp\left(-\frac{(E_f - E)}{KT}\right)$$

$$p = \int_{-\infty}^{E_V} dE g_{hh}(E) [1 - f(E - E_f)] = N_{hh} \exp\left(-\frac{(E_f - E_V)}{KT}\right)$$

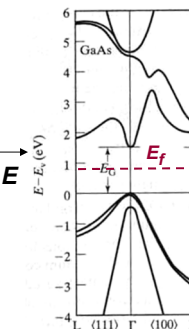
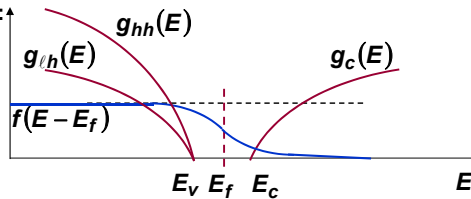
Maxwell-Boltzman approximation for holes

Where: $N_{hh} = 2 \left[\frac{m_{hh} KT}{2\pi \hbar^2} \right]^{3/2}$ → Effective density of states (units: #/cm³)

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Example: Electron Statistics in GaAs - Valence Band and Holes

In most semiconductors, the light-hole band is degenerate with the heavy hole band at the Γ -point. So one always needs to include the holes in the light-hole valence band as well:



$$p = \int_{-\infty}^{E_V} dE g_{hh}(E) [1 - f(E - E_f)] + \int_{-\infty}^{E_V} dE g_{lh}(E) [1 - f(E - E_f)]$$

$$= \int_{-\infty}^{E_V} dE [g_{hh}(E) + g_{lh}(E)] [1 - f(E - E_f)]$$

$$= \int_{-\infty}^{E_V} dE g_v(E) [1 - f(E - E_f)]$$

$$\begin{cases} g_v(E) = g_{lh}(E) + g_{hh}(E) \\ = \frac{1}{2\pi^2} \left(\frac{2m_h}{\hbar^2} \right)^{3/2} \sqrt{E_V - E} \end{cases}$$

$$p = N_v \exp\left(-\frac{(E_f - E_V)}{KT}\right)$$

Where: $N_v = 2 \left[\frac{m_h KT}{2\pi \hbar^2} \right]^{3/2}$ and

$$m_h = \left(m_{hh}^{3/2} + m_{lh}^{3/2} \right)^{2/3}$$
 → Density of states effective mass

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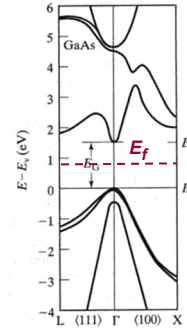
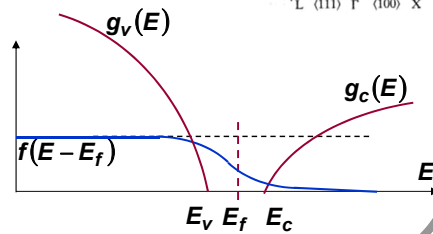
Example: Electron Statistics in GaAs – Electrons and Holes

At any temperature, the total number of electrons and holes (including both heavy and light holes) must be equal:

$$\begin{aligned} \Rightarrow p &= n \\ \Rightarrow N_v \exp\left(-\frac{(E_f - E_v)}{KT}\right) &= N_c \exp\left(-\frac{(E_c - E_f)}{KT}\right) \\ \Rightarrow \frac{N_v}{N_c} &= \exp\left(\frac{2E_f - E_c - E_v}{KT}\right) \\ \Rightarrow E_f &= \frac{E_c + E_v}{2} + \frac{KT}{2} \log\left(\frac{N_v}{N_c}\right) \end{aligned}$$

Because the effective density of states for electrons and holes are not the same (i.e. $N_v \neq N_c$), the Fermi level at any finite temperature is not right in the middle of the bandgap.

But at zero temperature, the Fermi-level is exactly in the middle of the bandgap



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Example: Electron Statistics in GaAs – Electrons and Holes

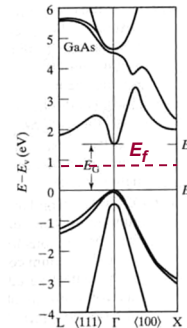
At any temperature, the total number of electrons and holes (including both heavy and light holes) must be equal:

$$\Rightarrow p = n = n_i$$

where n_i is called the **intrinsic electron (or hole) density**

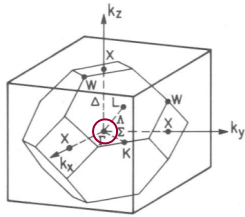
$$\begin{aligned} \Rightarrow p &= n = n_i \\ \Rightarrow p n &= n_i^2 \\ \Rightarrow N_v \exp\left(-\frac{(E_f - E_v)}{KT}\right) N_c \exp\left(-\frac{(E_c - E_f)}{KT}\right) &= n_i^2 \\ \Rightarrow N_v N_c \exp\left(-\frac{(E_c - E_v)}{KT}\right) &= n_i^2 \\ \Rightarrow n_i &= \sqrt{N_v N_c} \exp\left(-\frac{E_g}{2KT}\right) \end{aligned}$$

Note that the smaller the bandgap the larger than intrinsic electron (or hole) density



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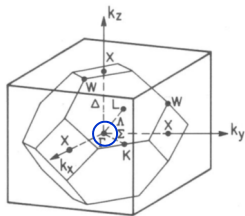
Electron and Hole Pockets in GaAs



Electron pocket

- At any non-zero temperature, electrons occupy states in k-space that are located in a spherically symmetric distribution around the Γ -point

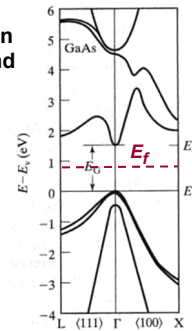
- This distribution is referred to as the “electron pocket” at the Γ -point



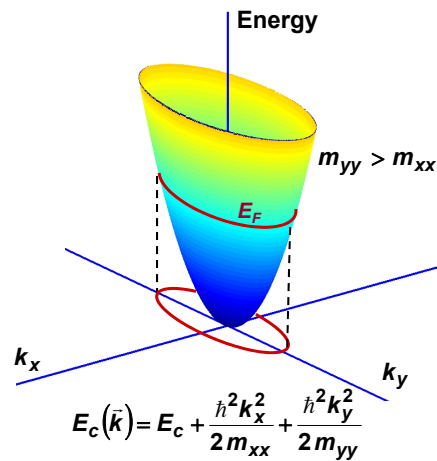
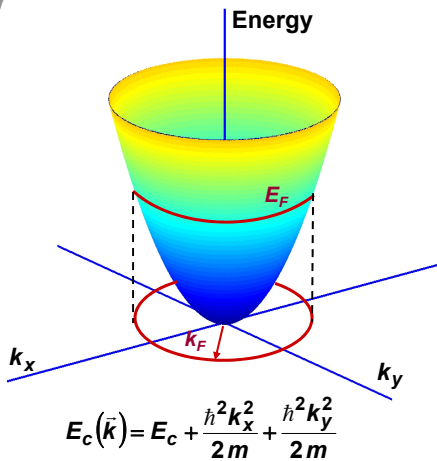
Hole pocket

- At any non-zero temperature, the holes (heavy and light) also occupy states in k-space that are located in a spherically symmetric distribution around the Γ -point

- This distribution is referred to as the “hole pocket” at the Γ -point



Shape of Fermi Surface/Contour and Mass Tensor: 2D Example



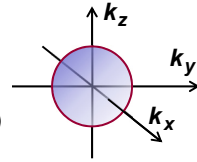
When the energy dispersion relation is anisotropic, the distribution of carriers in k-space, and the Fermi surface/contour, are not spherical/circular but become ellipsoidal/elliptical

Constant Energy Surfaces

Constant energy surfaces are in the reciprocal space and are such that the energy of every point on the surface is the same.

For example, the conduction band energy dispersion:

$$E_c(\vec{k}) = E_c + \frac{\hbar^2 k^2}{2m_e}$$



All points in k-space that are equidistant from the origin (Γ -point) have the same energy.

\Rightarrow Constant energy surfaces in 3D are spherical shells, and in 2D are circles, with the origin as their center.

Equation of a Constant Energy Surface with Energy E_o :

$$E_c + \frac{\hbar^2 k^2}{2m_e} = E_o \quad \Rightarrow \quad \underbrace{k_x^2 + k_y^2 + k_z^2}_{\text{Equation of a sphere in k-space of radius}} = \frac{2m}{\hbar^2} (E_o - E_c)$$

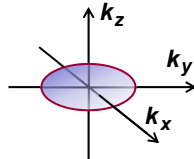
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Constant Energy Surfaces

Now consider the energy band dispersion: $E_c(\vec{k}) = E_c + \frac{\hbar^2 k_x^2}{2m_{xx}} + \frac{\hbar^2 k_y^2}{2m_{yy}} + \frac{\hbar^2 k_z^2}{2m_{zz}}$

Now the equation of a constant energy surface with energy E_o is:

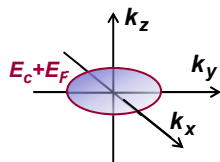
$$E_c + \frac{\hbar^2 k_x^2}{2m_{xx}} + \frac{\hbar^2 k_y^2}{2m_{yy}} + \frac{\hbar^2 k_z^2}{2m_{zz}} = E_o \quad \Rightarrow \quad \underbrace{\frac{k_x^2}{m_{xx}} + \frac{k_y^2}{m_{yy}} + \frac{k_z^2}{m_{zz}}}_{\text{Equation of an ellipsoid in k-space with semi-major axes given by:}} = \frac{2}{\hbar^2} (E_o - E_c)$$



Equation of an ellipsoid in k-space with semi-major axes given by:

$$\sqrt{\frac{2m_{xx}}{\hbar^2} (E_o - E_c)} \quad \sqrt{\frac{2m_{yy}}{\hbar^2} (E_o - E_c)} \quad \sqrt{\frac{2m_{zz}}{\hbar^2} (E_o - E_c)}$$

Fermi-Surfaces are Examples of Constant Energy Surfaces:



$$E_c + \frac{\hbar^2 k_x^2}{2m_{xx}} + \frac{\hbar^2 k_y^2}{2m_{yy}} + \frac{\hbar^2 k_z^2}{2m_{zz}} = E_c + E_F$$

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Silicon: Electrons in the Conduction Band

In Silicon there are six conduction band minima that occur along the six Γ -X directions. These are also referred to as the six valleys. For the one that occurs along the Γ -X($2\pi/a, 0, 0$) direction:

$$\vec{k}_0 = 0.85 \left(\frac{2\pi}{a}, 0, 0 \right) \quad E_c(\vec{k}_0) = E_c$$

$$M^{-1} = \begin{bmatrix} 1/m_\ell & 0 & 0 \\ 0 & 1/m_t & 0 \\ 0 & 0 & 1/m_t \end{bmatrix} \quad \text{Not isotropic!}$$

$$m_\ell = 0.92 m$$

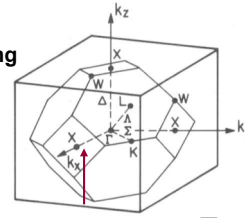
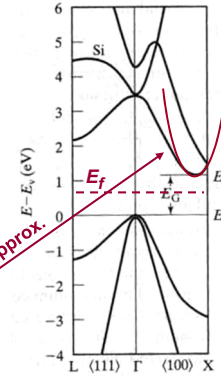
$$m_t = 0.19 m$$

This implies:

$$E_c(\vec{k}) = E_c + \frac{\hbar^2(k_x - k_{0x})^2}{2m_\ell} + \frac{\hbar^2(k_y - k_{0y})^2}{2m_t} + \frac{\hbar^2(k_z - k_{0z})^2}{2m_t}$$

Expression for the electron density in the valley located at along the Γ -X($2\pi/a, 0, 0$) direction can be written as:

$$2 \int_{\vec{k} \text{ near } \vec{k}_0} \frac{d^3\vec{k}}{(2\pi)^3} f(E_c(\vec{k}) - E_f)$$



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Silicon: Electrons in the Conduction Band

Define:

$$q_x = \sqrt{\frac{m}{m_\ell}}(k_x - k_{0x}) \quad q_y = \sqrt{\frac{m}{m_t}}(k_y - k_{0y})$$

$$q_z = \sqrt{\frac{m}{m_t}}(k_z - k_{0z})$$

This implies:

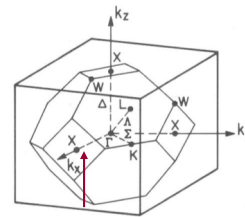
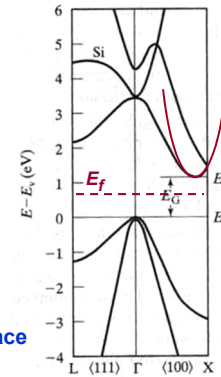
$$E_c(\vec{k}) = E_c + \frac{\hbar^2(k_x - k_{0x})^2}{2m_\ell} + \frac{\hbar^2(k_y - k_{0y})^2}{2m_t} + \frac{\hbar^2(k_z - k_{0z})^2}{2m_t}$$

$$E_c(\vec{q}) = E_c + \frac{\hbar^2 q^2}{2m} \quad \longrightarrow \quad \text{Dispersion is isotropic in q-space}$$

Therefore, expression for the electron density in the valley located at along the Γ -X($2\pi/a, 0, 0$) direction can be written as:

$$2 \int_{\vec{k} \text{ near } \vec{k}_0} \frac{d^3\vec{k}}{(2\pi)^3} f(E_c(\vec{k}) - E_f)$$

$$= \sqrt{\frac{m_\ell m_t m_t}{m^3}} 2 \int_{\vec{q} \text{ near } 0} \frac{d^3\vec{q}}{(2\pi)^3} f(E_c(\vec{q}) - E_f)$$



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Silicon: Electrons in the Conduction Band

$$\sqrt{\frac{m_l m_t m_t}{m^3}} 2 \int_{\bar{q} \text{ near } 0} \frac{d^3 \bar{q}}{(2\pi)^3} f(E_c(\bar{q}) - E_f)$$

$$\approx \sqrt{\frac{m_l m_t m_t}{m^3}} 2 \int_0^\infty \frac{4\pi q^2}{8\pi^3} dq f(E_c(q) - E_f)$$

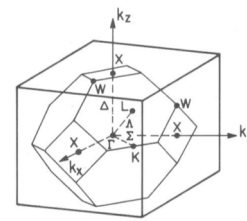
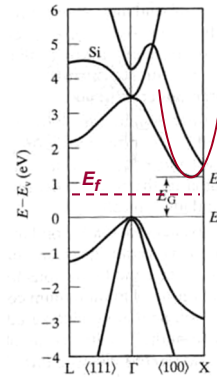
Total electron density in the conduction band consists of contributions from electron density sitting in all the six valleys:

$$n = 6 \times \sqrt{\frac{m_l m_t m_t}{m^3}} 2 \int_0^\infty \frac{4\pi q^2}{8\pi^3} dq f(E_c(q) - E_f)$$

$$\Rightarrow n = \int_{E_c}^\infty dE g_c(E) f(E - E_f)$$

Where: $g_c(E) = \frac{1}{2\pi^2} \left(\frac{2m_e}{\hbar^2} \right)^{3/2} \sqrt{E - E_c}$

and: $m_e = 6^{2/3} (m_l m_t m_t)^{1/3}$ \rightarrow Density of states effective mass



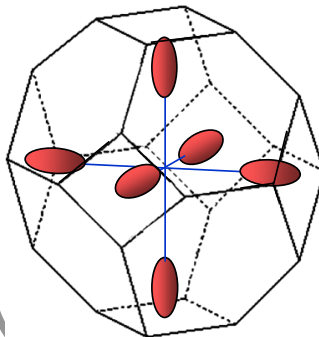
Silicon: Electrons in the Conduction Band

$$n = \int_{E_c}^\infty dE g_c(E) f(E - E_f) = N_c \exp\left(-\frac{E_c - E_f}{KT}\right)$$

Where: $N_c = 2 \left[\frac{m_e KT}{2\pi \hbar^2} \right]^{3/2}$

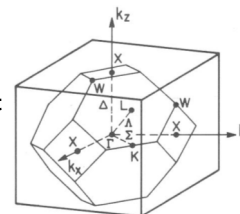
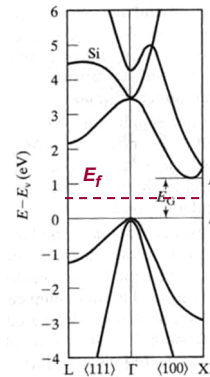
And: $m_e = 6^{2/3} (m_l m_t m_t)^{1/3}$

Six electron pockets in FBZ:



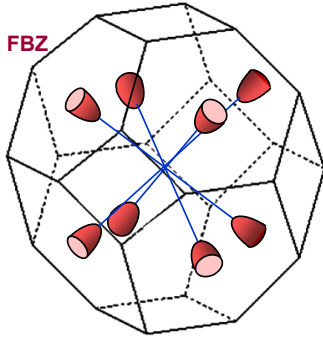
There are six electron pockets in Silicon - one at each of the valleys (conduction band minima)

The electron distribution in k-space in each pocket is not spherical but ellipsoidal since the electron masses in different directions are not the same



Germanium: Electrons in the Conduction Band

In germanium there are eight conduction band minima that occur at the L-points



The L-point is at the edge of the FBZ, so one-half of each electron pocket is not in the FBZ and therefore one-half of the electron distribution in each L-valley should not be counted in the sum for calculating the number of electrons:

$$N = 2 \times \sum_{\vec{k} \text{ in FBZ}} f(E_c(\vec{k}) - E_f)$$

The other way to look at the problem is to realize that the other-half of each pocket is also located in the FBZ on the opposite side – so in reality there are four complete pockets of electrons in the FBZ

