Election distribution in Solids
Fermi Dirac Statistics

The most important assumption of classical mechanics is that any number of particles may have identical energies. The classical mechanics fails to properly explains electron contribution to specific heat and magnetic susceptibility.

The electron in solid behaves as a system of fermi particle and hence obeys fermi-Dirac statistics. F.D. stati is applied to indistinguishable particles (called fermions) which are governed by Paulis exclusion principle. In solid we consider the distribution of a large no of $\bar{e}$ of the order of $10^{28}/m^3$ in thermal equilibrium ~~and~~ among various states in a three dimensional box.

According to the Paulis ex. principle not more than two $\bar{e}$s may occupy any orbital state, so that, at absolute zero of temperature two electrons will go into the ground state, two into each of next higher energy, and so on, untill all $\bar{e}$s are allocated to states of lowest possible energy. Since the no of electrons is very large, it is thus understood that even at absolute zero of T, some electrons have kinetic energies of several electron volt. For a piece of metal of macroscopic dimension say cm^3, the energy of ground state ($n_x = n_y = n_z = 1$) is of the order of 10^{-15} eV and hence may be taken to be zero for all practical purposes. Also the maximum spacing between consecutive level is less than 10^{-6} eV so that the distribution of energy may be regarded as almost continuous or some time quasi-continuous.

Since we are talking about an almost continuous distribution range of energies, we can represent the probability of occupying a given state by a continuous distribution function. The probability $F(E)$ of an electron occupying a given energy level is given by

$$F(E) = \frac{1}{1 + e^{\left(\frac{E - E_F}{kT}\right)}}$$ and is called fermi function. E is the energy of the level whose occupancy is being considered, E_F is the fermi level and is a constant for the particular system. At absolute zero $F(E) = 0$ for $E > E_F$ and $F(E) = 1$ for $E < E_F$. Thus at $T = 0$

 The Fermi level divides the occupied states from the unoccupied states: ie it is the highest energy state for the ē's to occupy at T=0

Density of Energy States and Fermi Energy —

The fermi function does not, by itself, gives the no of ē's which have a certain energy; it gives us only the probability of occupation of an energy state by a single electron. Since even at the highest energy, the difference between neighbouring energy levels is as small as 10^{-6} eV, we can say that in a macroscopically small energy interval dE there are still many discrete energy levels. To know the actual number of electrons with a given energy one should know the number of ~~st~~ states in the system which have the energy under consideration. Then by multiplying the number of states ~~by~~ the probability occupation we get the actual no of ē's. If N(E) is the no of electrons in a system that have energy E and Z(E) no of states at that energy, then

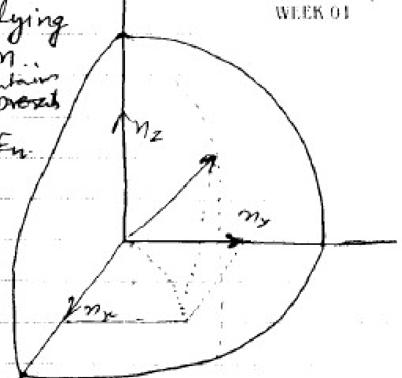
$$N(E)\,dE = Z(E)\,dE\,f(E) \quad \text{———} (1)$$

for each set of quantum numbers n_x, n_y, n_z there is energy state E_n with an energy

$$E_n = \frac{\pi^2\hbar^2}{2ma^2}\left(n_x^2+n_y^2+n_z^2\right) = \frac{\pi^2\hbar^2}{2ma^2}\,n^2 \quad \text{———} (2)$$

To each such ~~state~~ set of q·no· there exist a specific energy level E_n frequently called energy state. An energy state can therefore be represented by a point in q no space. In this space, n is the ~~~~ radius from origin of the coordinate system to a point (n_x, n_y, n_z) where

$n^2 = n_x^2 + n_y^2 + n_z^2$



Equal values of the energy E_n are lying on the surface of a sphere with radius n.. All points within the sphere therefore contains represent quantum states with energies smaller than E_n. The no of quantum states, η with an energy equal to or smaller than E_n is proportional to the volume of the sphere. Since the q-nos are +ve integers, the n-values can be only be defined in the positive octant of the n-space. One eighth of the volume of the sphere with radius n therefore gives the no of energy states, η, the energy of which is equal to or smaller than E_n. Thus using eqn (2)

$$\eta = \frac{1}{8}\,\frac{4}{3}\pi n^3 = \frac{\pi}{6}\left(\frac{2ma^2}{\pi^2\hbar^2}\right)^{3/2} E^{3/2} \qquad (3)$$

Differentiation of η with E provide the number of energy states per unit energy in the energy interval dE ie the density of energy states, briefly called $Z(E)$

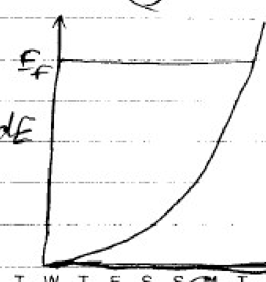
$$\frac{d\eta}{dE} = Z(E) = \frac{\pi}{6}\left(\frac{2ma^2}{\pi^2\hbar^2}\right)^{3/2}\frac{3}{2}\,E^{1/2}$$

$$= \frac{\pi}{4}\left(\frac{2ma^2}{\pi^2\hbar^2}\right)^{3/2} E^{1/2} = \frac{a^3}{\pi^3}\,\frac{\pi}{4}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$$

where a^3 is vol of space e^- can occupy.

$$Z(E) = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2} \qquad (4)$$

Plot of $Z(E)$ with E gives a parabola



It show that at lower end of the band considerably less energy levels (per unit E) are available than at higher E. So the total no of states $d\eta$ in the energy interval dE are

$$d\eta = Z(E)\,dE$$

Population Density

The no of e^- per unit-energy $N(E)$ within an energy interval dE are therefore

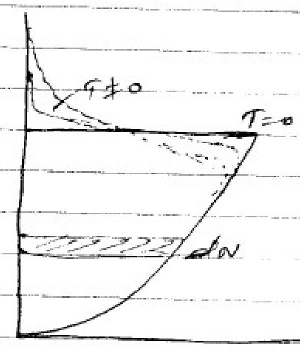
$$N(E) = 2 \cdot dn = 2\, Z(E)\, dE$$

as each state can have two e's one with spin up and other with spin down. Thus the population density of e

$$N(E) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2} \frac{1}{\left(e^{\frac{E-E_f}{kT}}+1\right)} \quad \text{—— (5)}$$

for an energy interval between E and $E+dE$ one obtain

$dN = N(E)\,dE$



for $T \to 0$ $E < E_f$ all states filled $f(E)=1$. Thus integration from lower end of band to E_f provides

$$N = \int_0^{E_f} N(E)\,dE$$

$$= \int_0^{E_f} \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2} \cdot 1\, dE = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{2}{3}(E_f)^{3/2}$$

$$N = \frac{V}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E_f^{3/2} \quad \text{—— (6)}$$

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So no of electrons per unit volume ie $\frac{N}{V}$ is electron concentration and is

$$n = \frac{N}{V} = \frac{1}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E_f^{3/2}$$

or $$n^{2/3} = \left(\frac{1}{3\pi^2}\right)^{2/3} \frac{2m E_f}{\hbar^2} \Rightarrow \boxed{E_f = \frac{\hbar^2}{2m}\left(3\pi^2 n\right)^{2/3}} \quad (7)$$

It is true for $T \to 0$ and $E < E_f$. But it does not limit the applicability of (7) since the no of $\bar{e}$'s does not change when the temperature is increased. In other words, integration from $0 - \infty$ and using $T \to 0$ would yield essentially the same results as above.

The fermi energy can be expressed as

$$E_f = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3} = \frac{h^2}{4\pi^2 2m}(3n)^{2/3}(\pi^{4/3}) = \frac{h^2}{2m}\left\{\frac{\pi^{4/3}}{4\pi^2}\right\}(3n)^{2/3}$$

$$= \frac{h^2}{2m}\left\{\frac{\pi^{-2/3}}{2^2}\right\}(3n)^{2/3} = \frac{h^2}{2m}\left\{\frac{\pi^{-2/3}}{(2^3)^{2/3}}\right\}(3n)^{2/3}$$

$$= \left(\frac{h^2}{2m}\right)\left(\frac{1}{8\pi}\right)^{2/3}(3n)^{2/3} = \frac{h^2}{2m}\left(\frac{3n}{8\pi}\right)^{2/3}.$$

$$E_n = \frac{h}{2m}\left(\frac{3n}{8\pi}\right)^{2/3} = \frac{h}{2m}\left(\frac{3}{8\pi}\right)^{2/3} n^{2/3}$$

$$= \frac{(6.6\times10^{-34})^2}{2\times9.1\times10^{-31}}\left(\frac{3}{8\pi}\right)^{2/3} n^{2/3} = \frac{(6.6\times10^{-34})^2}{18.2\times10^{-31}}(.2424)\, n^{2/3}$$

$$\boxed{E_n = 3.648\times10^{-19}\, n^{2/3}\ eV} \quad \text{---} (8)$$

This expression for fermi energy is a very useful quantity because it gives the top most energy level at absolute zero from the knowledge of free electron concentration n.

E_f is the maximum energy of the filled state. The corresponding velocity of $\bar{e}$ having KE equal to E_f is called fermi velocity and is given by $\frac{1}{2}mv_f^2 = E_f \Rightarrow \boxed{v_f = \sqrt{\frac{2E_f}{m}}}$ ——— (9)

And corresponding temperature is called fermi temp and is

$$KT_f = E_f \Rightarrow \boxed{T_f = \frac{E_f}{K}} \quad \text{———} (10)$$

For sodium with E_f 3.2eV $v_f = 1.1\times10^6$ m/s and $T_f = 37100$ K.

Mean Energy of Electron Gas at Absolute 0K

The fermi energy at absolute zero is given as

$$E_f = \left(\frac{h^2}{2m}\right)\left(\frac{3n}{8\pi}\right)^{2/3} \quad \text{——— (1a)}$$

The average energy of electrons can be obtained by dividing total energies of e's by total no of electrons in the solid. As given by eqn (5) of previous section the total no of e's is

$$N = \int_0^{E_f} N(E)\,dE \quad \text{——— (1)}$$

Total energies of e^- is no of electrons x energy of e^- ie

$$E = \int_0^{E_f} N(E)\,E\,dE \quad \text{——— (2)}$$

$$\therefore \bar{E} = \frac{E}{N} = \frac{\int_0^{E_f} \cancel{\frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}} E^{3/2}\,dE}{\int_0^{E_f} \cancel{\frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}} E^{1/2}\,dE}$$

$$= \frac{\frac{2}{5}\left(E_F^{5/2}\right)}{\frac{2}{3}\left(E_F\right)^{3/2}} = \frac{3}{5}E_f$$

Thus the average energy of e's is

$$\boxed{\bar{E} = \frac{3}{5}\left(\frac{h^2}{2m}\right)\left(\frac{3n}{8\pi}\right)^{2/3}} \quad \text{——— (3)}$$

Carrier concentration in Conduction Band.

Density of states per unit volume in the energy range E and dE is

$$Z(E)dE = \frac{1}{4\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{3/2} E^{1/2}\, dE \quad \text{---} (1)$$

The number of é s in the conduction band is therefore

$$N(E)\,dE = 2\,\frac{1}{4\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{3/2}(E-E_c)^{1/2} f_n(E)\, dE \quad \text{---} (2)$$

m_e^* is the effective mass of the electron

where the

$$f_n(E) = \frac{1}{1+\exp\left(\frac{E-E_f}{kT}\right)} \quad \text{---} (3)$$

Since the fermi level for an intrinsic semi conductor must lie well within the forbidden energy region and since $k_B T \ll E_g$ at all temp, the $\frac{E_c - E_f}{E_f} \gg kT$ is satisfied always. Therefore $e^{\frac{E_c-E_f}{kT}} \gg 1$

Thus neglecting factor unity w.r.t. exponential term we can write

$$f_n(E) = \frac{1}{\exp\left(\frac{E-E_f}{kT}\right)} = e^{-\left(\frac{E-E_f}{kT}\right)}$$

Therefore the density of é s becomes

$$N(E)\,dE = \frac{1}{2\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{3/2} e^{-\left(\frac{E-E_f}{kT}\right)} (E-E_c)^{1/2}\, dE$$

The total number of electrons per unit volume in the conduction band is

$$n = \int_{E_c}^{\infty} N(E)\, dE = \int_{E_c}^{\infty} \frac{1}{2\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{3/2} e^{-\left(\frac{E-E_f}{kT}\right)} (E-E_c)^{1/2}\, dE$$

$$= \frac{1}{2\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{3/2} \int_{E_c}^{\infty} e^{-\left(\frac{E-E_f}{kT}\right)} (E-E_c)^{1/2}\, dE$$

$$n = \frac{1}{2\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{3/2}\int_{E_c}^{\infty} e^{-\frac{(E_c - E_f + x)}{kT}}\, x^{1/2}\,dx$$

$$= \frac{1}{2\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{3/2} e^{-\frac{(E_c-E_f)}{kT}}\int_0^{\infty} e^{-\frac{x}{kT}}\, x^{1/2}\,dx$$

$$= \frac{1}{2\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{3/2} e^{-\frac{(E_c-E_f)}{kT}}\,\frac{\sqrt{\pi}}{2}\,(kT)^{3/2}$$

$$= \frac{1}{2\pi^2}\frac{\sqrt{\pi}}{2}\left(\frac{2m_e^*}{\hbar^2}\right)^{3/2}(kT)^{3/2}\, e^{-\frac{(E_c-E_f)}{kT}}$$

$$= \frac{1}{2\cancel{2}\,\pi^{3/2}}\left(\frac{2m_e^*\,4\pi^2}{h^2}\right)^{3/2}(kT)^{3/2}\, e^{-\frac{(E_c-E_f)}{kT}}$$

$$= \frac{1}{2^2}\left[\frac{\cancel{2}\,m_e^*\,8\pi^{\cancel{2}}\,kT}{\cancel{2}\,\cancel{\pi}\,h^2}\right]^{3/2} e^{-\frac{(E_c-E_f)}{kT}}$$

$$n = 2\left[\frac{2\pi m_e^* kT}{h^2}\right]^{3/2} e^{-\frac{(E_c-E_f)}{kT}} \quad \text{——— (4)}$$

Let $E - E_c = x$

$dE = dx$

$E = E_c \Rightarrow x = 0$

$E = \infty \Rightarrow x = \infty$

$E - E_f = E_c + x - E_f$

$= E_c - E_f + x$

Using Gamma function

$$\int_0^{\infty} e^{-\alpha t}\, t^{1/2}\,dt = \frac{\sqrt{\pi}}{2}\frac{1}{\alpha^{3/2}}$$

The term $2\left(\frac{2\pi m_e^* kT}{h^2}\right)^{3/2}$ is almost constant compared with the exponential term, and so it is called pseudo constant and is given by the symbol N_c. thus

$$n = N_c \exp -\left(\frac{E_c - E_f}{kT}\right) \quad \text{——— (5)}$$

Density of holes in the valence Band

The number of holes p per unit ~~range~~ volume in the ~~range~~ valance band of a semiconductor can be found in a similar manner, As the presence of hole can be regarded as the absence of an electron the fermi function of holes in the valence band is $(1 - f_n(E))$. In this case we can write $p(E)\,dE$ as the number of holes in the valence band in the energy range dE about E, then density of holes in the valence band is

$$p = \int p(E)\,dE = \int_{-\infty}^{E_v} Z_v(E)\, f_p(E)\,dE \qquad \text{—— (1)}$$

$$= \int_{-\infty}^{E_v} 2\,\frac{1}{4\pi^2}\left(\frac{2m_h^*}{\hbar^2}\right)^{3/2} (E_v - E)^{1/2} f_p(E)\,dE \qquad \text{—— (2)}$$

$$\text{Now } f_p(E) = 1 - F_n(E) = 1 - \frac{1}{1 + e^{\frac{E-E_f}{kT}}} = \frac{e^{\frac{E-E_f}{kT}}}{1 + e^{\frac{E-E_f}{kT}}}$$

$$= \frac{1}{1 + e^{-\left(\frac{E-E_f}{kT}\right)}}$$

Again as E_f is much above E so $(E_f - E) \gg kT$ so unity term in the denominator can be neglected a compared to exponential term, therefore

$$f_p(E) = \frac{1}{e^{-\left(\frac{E - E_f}{kT}\right)}} = e^{\frac{E-E_f}{kT}}$$

Therefore we can write

$$p = 2\,\frac{1}{4\pi^2}\left(\frac{2m_h^*}{\hbar^2}\right)^{3/2} \int_{-\infty}^{E_v} e^{\frac{E-E_f}{kT}} (E_v - E)^{1/2}\,dE$$

$$= \frac{1}{2\pi^2}\left(\frac{2m_h^*}{\hbar^2}\right)^{3/2} \int_{\infty}^{0} e^{\frac{-x}{kT}} e^{\frac{E_v - E_f}{kT}} \left(-x^{1/2}\,dx\right)$$

$E_v - E = x$
$dE = -dx$
$E = -\infty \Rightarrow x = \infty$
$E = E_v \Rightarrow x = 0$
$E - E_f = E_v - x - E_f$
$= E_v - E_f - x$

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or
$$p = \frac{1}{2\pi^2}\left(\frac{2m_h^*}{h^2}\right)^{3/2} e^{\frac{E_v-E_f}{kT}} \int_0^\infty e^{-\frac{x}{kT}} x^{1/2}\,dx$$

$$= \frac{1}{2\pi^2}\left(\frac{2m_h^*}{h^2}\right)^{3/2} e^{-\frac{(E_f-E_v)}{kT}} \frac{\sqrt{\pi}}{2}(kT)^{3/2}$$

$$= \frac{1}{2^2\pi^{3/2}}\left(\frac{2m_h^*}{h^2}\right)^{3/2}(\pi^2)^{3/2}(kT)^{3/2} e^{-(E_f-E_v)/kT}$$

$$= \frac{1}{2^2}\left[\frac{2m_h^*\, 2\pi^2\, kT}{\pi\, h^2}\right]^{3/2} e^{-(E_f-E_v)/kT}$$

$$p = 2\left[\frac{2\pi m_h^* kT}{h^2}\right]^{3/2} e^{-(E_f-E_v)/kT} \qquad \text{—(3)}$$

$$\boxed{p = N_v\, e^{-(E_f-E_v)/kT}} \qquad \text{—(4)}$$

N_v is referred to as the effective DOS

For intrinsic semiconductor $n = p$ thus equating the two

$$(m_e^*)^{3/2} e^{-(E_c-E_f)/kT} = (m_h^*)^{3/2} e^{-(E_f-E_v)/kT}$$

or $$\exp\left[\frac{E_f+E_f-(E_c+E_v)}{kT}\right] = \left(\frac{m_h^*}{m_e^*}\right)^{3/2}$$

or $$\frac{2E_f}{kT} - \frac{(E_c+E_v)}{kT} = \ln\left(\frac{m_h^*}{m_e^*}\right)^{3/2}$$

or $$\boxed{E_f = \frac{E_c+E_v}{2} + \frac{3kT}{4}\ln\left(\frac{m_h^*}{m_e^*}\right)}$$

If $m_h^* = m_e^*$ $\Longrightarrow$ $\boxed{E_f = \frac{E_c+E_v}{2}}$ —(5)

that is the fermi level is mid-way between the valence band and conduction band, but normally $m_p^* > m_e^*$, so E_F is just above the middle and rises slightly with increasing temperature.

In terms of pseudo constants

$$\frac{N_C}{N_V} = \left(\frac{m_e^*}{m_p^*}\right)^{3/2}$$

Therefore $$E_F = \frac{E_C + E_V}{2} + \frac{kT}{2}\ln\left(\frac{N_V}{N_C}\right) \quad (6)$$

Now the product

$$np = 2^2\left(\frac{2\pi kT}{h^2}\right)^3 \left(m_e^* m_p^*\right)^{3/2} e^{-\frac{(E_C - E_V)}{kT}}$$

$E_C - E_V = E_g$ forbidden gap.

$$np = 2^2\left(\frac{2\pi kT}{h^2}\right)^3 \left(m_e^* m_p^*\right)^{3/2} e^{-\frac{E_g}{kT}}$$

or $$np = N_C N_V e^{-E_g/kT} \quad (7)$$

Since Energy gap and effective masses of semiconductor are const hence product np in a given semiconductor is function of temp only.

Since density of electrons equals the density of holes and they are both called the intrinsic carrier concentration n_i, then

$$n_i^2 = np = N_C N_V \exp\left(\frac{-E_g}{kT}\right)$$

or $$n_i = \sqrt{np} = \sqrt{N_C N_V}\exp\left(-\frac{E_g}{2kT}\right)$$

Substituting $N_C N_V$ and simplifying (8)

$$n_i = 2\left(\frac{2\pi kT}{h^2}\right)^{3/2}\left(m_e^* m_h^*\right)^{3/4}\exp\left(\frac{-E_g}{2kT}\right)$$

or $$\boxed{n_i = CT^{3/2}\exp\left(\frac{-E_g}{2kT}\right)}$$ where $C = 2\left(\frac{2\pi k\, m}{h^2}\right)^{3/2}$ for $m_e^* = m_h^* = m$

$= 4.83 \times 10^{21} / m^3$ for $T = 300$ K and $E_g = 1$ eV

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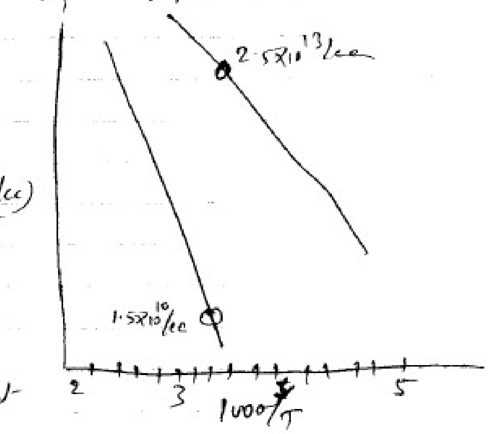
$$n_i \simeq 10^{17} / m^3.$$

Since the no of atoms / m³ is 10, only a very small fraction of valence electron are excited to the conduction band.

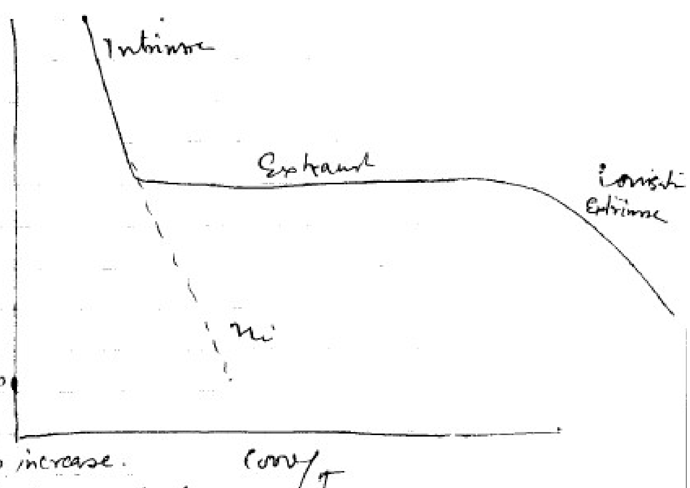
<u>Temperature dependence of Carrier Concentration</u>

The exponential temperature dependence in eqn (8) dominates $n_i(T)$ so plot of $\ln(n_i)$ vs $\frac{1000}{T}$ appears almost linear. Here we neglect the variation due to $T^{3/2}$ dependence of DOS and little variation of E_g with T. The value of n_i at any T is a definite number for a given semiconductor and its value is known for most materials. Thus one can take n_i in place of n_0 & p_0.



Intrinsic carrier concentration for Si & Ge as function of inverse temperature.

The plot of $\ln(n_i)$ vs $1/T$ is not truly linear [because of $T^{3/2}$ factor] and it is often preferred to construct a graph of $\ln(n_i/T^{3/2})$ vs $\frac{1}{T}$ which shows that the relationship is accurately linear.



(1) Eq. (7) means product of n & p is constant and independent of n_0 of exact position of E_F.

(2) if E_F moves towards CB, n increases and p decreases

(3) if E_F moves towards VB, p increases and n decreases

(4) if T rises both n and p increase.

E_F plays a crucial role in the balance between n and p and can be shifted in silicon and germanium if doped with three- or five valence atoms.