

## THEORY OF FREE ELECTRONS IN GAS

→ Help to understand  
(attice, crystal)

→ solid have band form  
structure.

[solid &  
no. of atoms]

↳ degeneracy

↳ for energy eigenvalue have no. of states  
eigenvalue  $\rightarrow$  no. of wave function

→ Ex.: splitting of energy gap

⇒ Free e<sup>-</sup> gas  
→ Due to very high free e<sup>-</sup> in a metal pt resembles  
as a gas and can move anywhere in it.

⇒ Classical Approach Drude & Lorentz

Drude's theory

A1 → The mutual repulsion b/w the free e<sup>-</sup> and  
ignored because PE of e<sup>-</sup> is very high  
and kE will dominate  
over repulsion

PE of each e<sup>-</sup> very low

(negligible)

A2: The potential field inside metal is uniform  
throughout and negligible.

A3: The potential energy of e<sup>-</sup> inside metal  
is very low compared to outside of



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A.s. Since A free e-gas, can

e<sup>-</sup> can occupy any state

A.S. & energy of each free e<sup>-</sup> will be  $\frac{3}{2} kT$   
& will be same.

(using the Maxwell's Boltzmann statistics)

Avg. energy former  
in gas molecule

Reason e<sup>-</sup> is charged particle [spin =  $\pm \frac{1}{2}$ ]

spin contains  $\frac{1}{2}$  = called as fermions

and spin contains integer = called bosons  
(n = 1, 2, 3, ..., )

\* Sommerfeld's Theory for free e-gas.

→ Quantum mechanically Sommerfeld laid down the following postulates in order to understand the behaviour of free e-gas.

1. The mutual repulsive b/w the e<sup>-</sup> and consider negligible.

⇒ This implies the kinetic Energy of each constitute is very high and if  $\epsilon$  p.e. of each free is very small.

2. The potential field 'V' is taken uniform throughout the specimen of the solid



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Stabis  $\rightarrow$  perfect node and anti-node  
 condition  $\rightarrow$  boundary of vessel is equal to integral multiple of wavelength.

$\rightarrow$  such that the potential energy of each electron is very small compared to that of  $e^-$  outside the specimen.

3. Since the  $e^-$  are fermions, the distribution of these free  $e^-$  to the available energy states of free  $e^-$  gas enclosing a volume  $V$  is governed by Fermi-Dirac statistics.

According to F-D

Two identical fermions can occupy same space provided that spins are not same

4. The filling of these free  $e^-$  is followed by Pauli's exclusion principle.

5. Due to the F-D distribution of statistics)

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

$\Rightarrow$  The energy of each  $e^-$  is purely different  $E$  and thus, the different states -

\* The corresponding wavefunction of an  $e^-$  of fermic D.F

$$\therefore \Psi_{(n_x, n_y, 2)} = \sqrt{\frac{8}{L^3}} \sin \frac{n_x \pi x}{L} \sin \frac{n_y \pi y}{L} \sin \frac{n_z \pi z}{L}$$

and energy eigen values would be

$$E = \frac{\pi^2 h^2}{8m} (n_x^2 + n_y^2 + n_z^2)$$

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Real + positive (Integral)  
 the quantum state

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→ Volume of gas is governed by quantum number

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such that

$$[n_x = \frac{2\pi}{L}]$$

leads to

$$[n_x n_y n_z = \frac{8\pi^3}{L^3}]$$

thus,

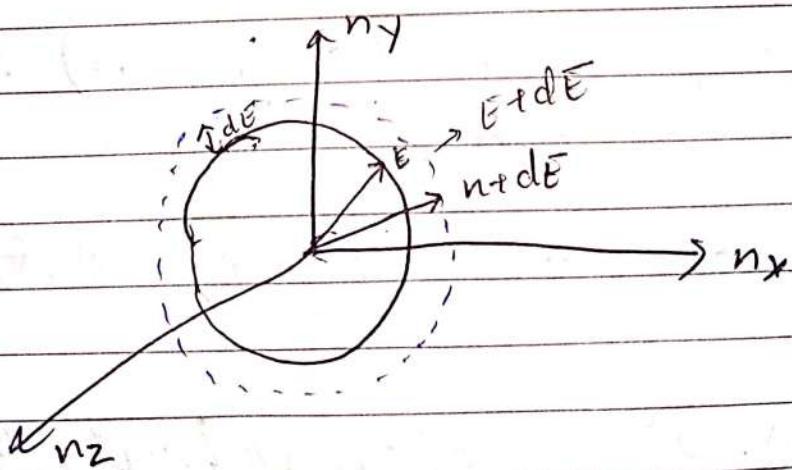
we may consider as  $n_x, n_y, n_z$  as dimensional lattice numbers in 3-D space

$$E = \frac{\pi^2 \hbar^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2)$$

further,  $\left(\frac{2mL^2}{\pi^2 \hbar^2}\right) E = n_x^2 + n_y^2 + n_z^2$

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

which represents the eq<sup>n</sup> of sphere of radius n



radius (n) is equal to Total Energy of spe<sup>sphere</sup>.



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\* Density of energy states (available only)  $D(E)$

⇒ The total no. of energy states available per unit volume per unit energy range:

→ Since  $n_x, n_y, n_z$  are real & +ve quantum numbers. Therefore, total possible no. of energy states will be only in  $Y_8^{th}$  segment of volume of sphere.

→ Total no. of energy states will be

$$N(E) = Y_8 \left( \frac{4}{3} \pi n^3 \right)$$

$$W(E) = \frac{1}{8} \left( \frac{4}{3} \pi \frac{(2mL^2)}{\pi^2 h^2} \right)^{3/2} E^{3/2}$$

for a small / infinite small energy  $dE$

$$\frac{dN(E)}{dE} = \frac{1}{8} \left( \frac{4}{3} \pi \frac{(2m)}{\pi^2 h^2} \right)^{3/2} L^3 \left( \frac{3}{2} \right) E^{1/2} \cdot dE$$

No. of energy states for  $(dE)$  expanded.  
Change sphere in figure.

⇒ Since,  $2e^-$  can occupy each states

Now,

$$dN(E) = 2 \left\{ \frac{1}{8} \left( \frac{4}{3} \pi \frac{(2m)}{\pi^2 h^2} \right)^{3/2} \right\} \frac{3}{2} L^3 E^{1/2} dE$$

Thus,

density of available energy states  $D(E)$  is



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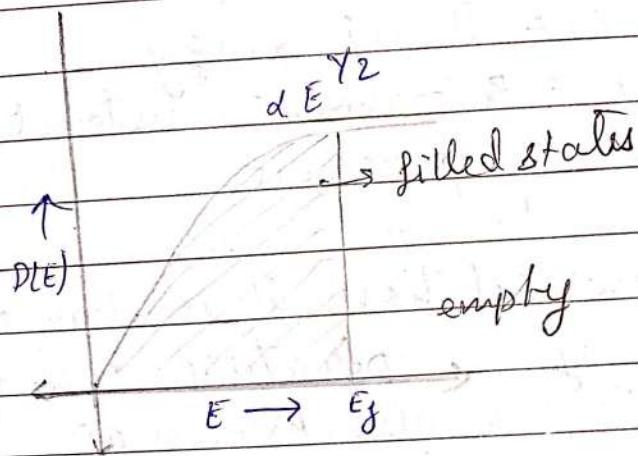
\* No. of electrons to be filled  $n_c = \text{conduction } e^- (\text{free } e^-)$   
 $\Rightarrow n_c = D(E) f(E) dE$

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$$D(E) = \frac{dN(E)}{e^3 dE} = \text{constant } E^{1/2}$$

$$D(E) \propto (E)^{1/2}$$

$D(E)$  is parabolic function of  $E$



→ Fermi energy level

→ The level which divides the field into empty states

→ Last energy level upto which last  $e^-$  fills



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\* Effect of temperature on Fermi-Diase statistics  
⇒ It is defined as

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

probability distribution function

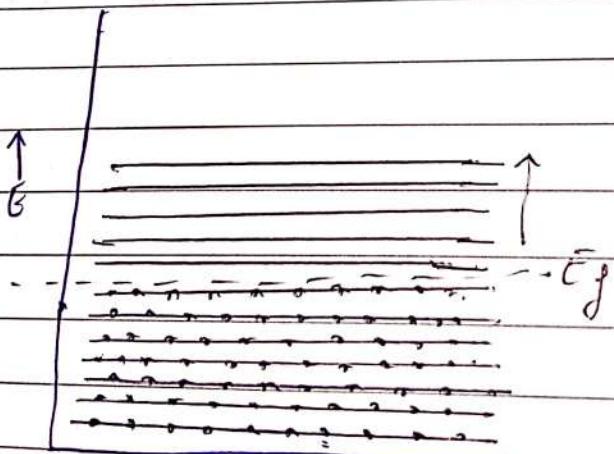
$E$  = total no. of available states.

$E_f$  = Fermi energy

$k$  = Boltzmann's constant

$T$  = temperature.

⇒ From the above relation it is clear that  $f(E)$  is a function of temperature and fermi energy - This is also known as fermi function  
⇒ where the  $E_f$  is known as fermi energy upto which all the energy states are filled up or occupied by the electrons, beyond which remaining energy states remains empty.



$T = 0 \text{ K}$  (Absolute temp)  
ground state



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$\Rightarrow$  available states

(A) At  $T = 0K$

$$\frac{E - E_f}{kT} \rightarrow -\infty \quad (E < E_f)$$

$kT$

$$f(E) = 1$$

$\Rightarrow$  probability of finding the  $e^-$  in  $E < E_f$  will be definite (100%)

$$\Rightarrow \frac{E - E_f}{k} \rightarrow +\infty \quad (E > E_f)$$

$$f(E) = 0$$

$\Rightarrow$  probability of finding the  $e^-$  in energy levels which are higher than  $E_f$  is 0.

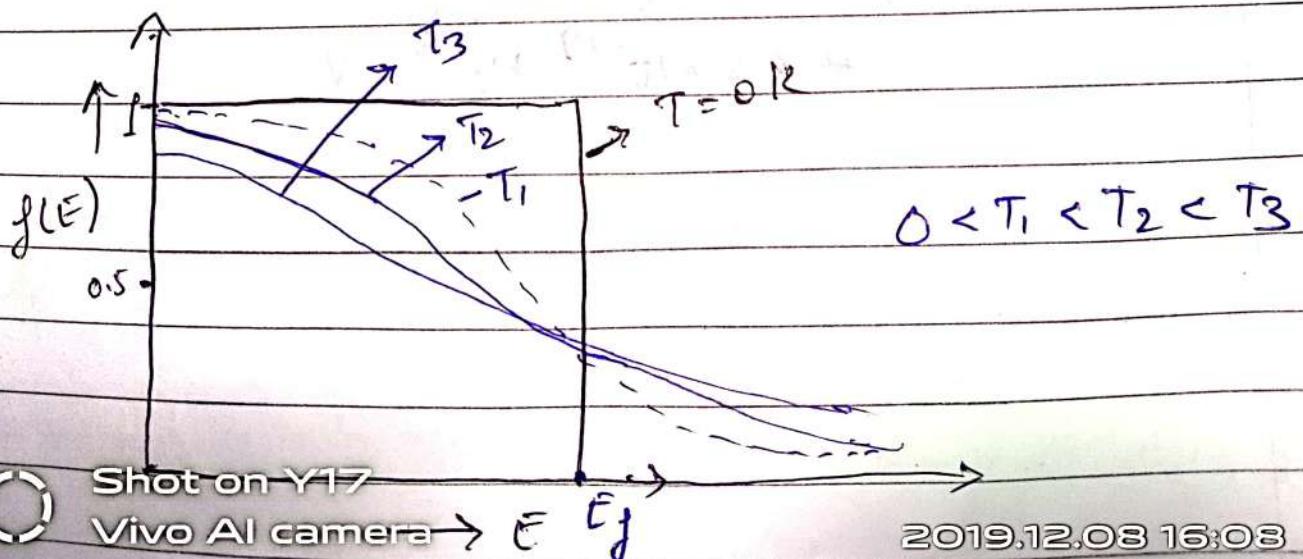
(B) At  $T > 0K$

when  $E = E_f$

$$f(E) = \frac{1}{2}$$

$\Rightarrow$  probability is about 50%, of finding the  $e^-$  upto the energy level  $E_f$  (half of the original)

$\Rightarrow f(E)$  behaves like an step-function



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⇒ In all sense,  $F(E)$  defines the probability of finding the electrons occupied by the state and  $1 - F(E)$ , represents probability of the  $e^-$  not occupied by the state.

### \* Calculation of Fermi Energy

⇒ Considering that  $e^-$  are filled upto the energy state starting from ground state to  $E_f$ .

thus, no. of electrons to be filled

$$n_e = D(E) f(E) dE$$

$$= \int_0^{E_f} \frac{\pi}{2} \left( \frac{8m_e}{\hbar^2} \right)^{3/2} E^{1/2} f(E) dE$$

$$\downarrow \\ \text{At } T=0 \times (f(E)=1, E=E_f)$$

$$n_e = \frac{\pi}{2} \left( \frac{8m_e}{\hbar^2} \right)^{3/2} \cdot \frac{2}{3} \cdot E_{f0}^{3/2}$$

$E_{f0}$  = Fermi Energy at 0 Kelvin

$$E_{f0} = 0.58 \times 10^{-37} n_e^{2/3} \text{ Joule}$$

or

$$3.65 \times 10^{-19} n_e^{2/3} \text{ eV}$$

Assignment

1) Write the differences b/w the classical and quantum approach for free  $e^-$  gas

2) Elaborate the postulates laid down by Sommerfeld

3) Obtain the expression to calculate the density of energy

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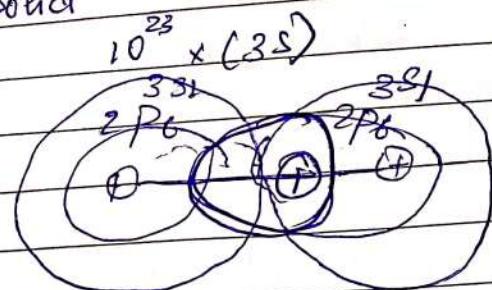
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## \* Band Theory of Solids

contains no. of atoms  
say  $N \sim (10^{23} \text{ atoms}) \text{ mole}$

lattices { Brought together at particular distances  
↓  
solid      - Inter atomic distances.



No. of continuum

No. of energy levels corresponds to particular energy level

depends on inter atomic distance as well as depends energy levels.

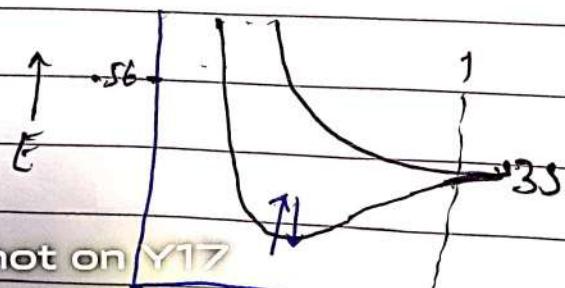
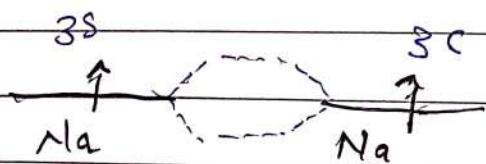
↓  
splitting of energy levels

$2S \rightarrow N$  levels  
 $2N$  electrons

$3P \rightarrow N$  levels  
 $6N$  electrons

$$\therefore Na^+ = 1S^2 2S^2 2P^6 3S^1$$

for  $2 Na$  atoms

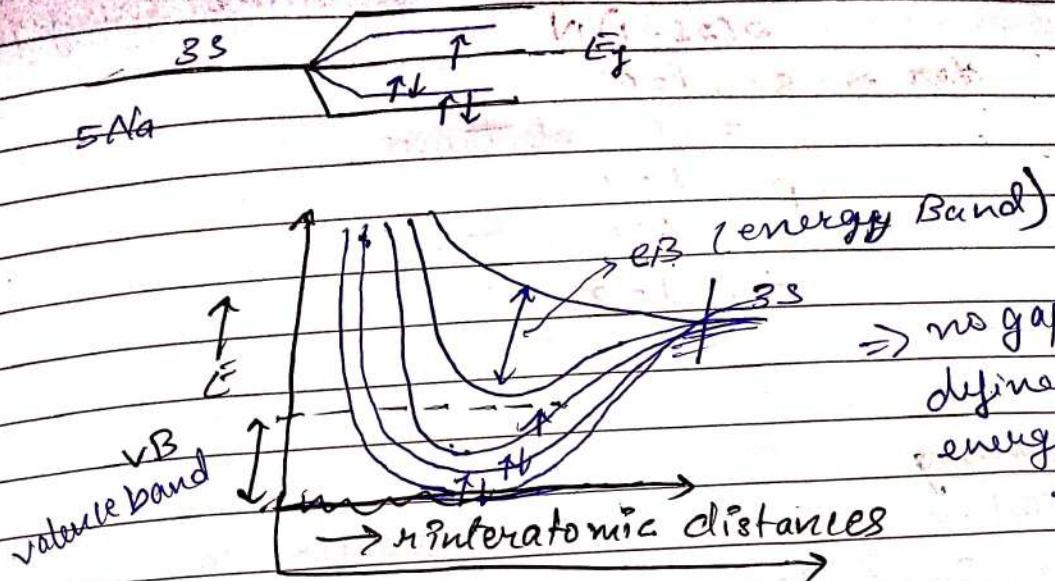


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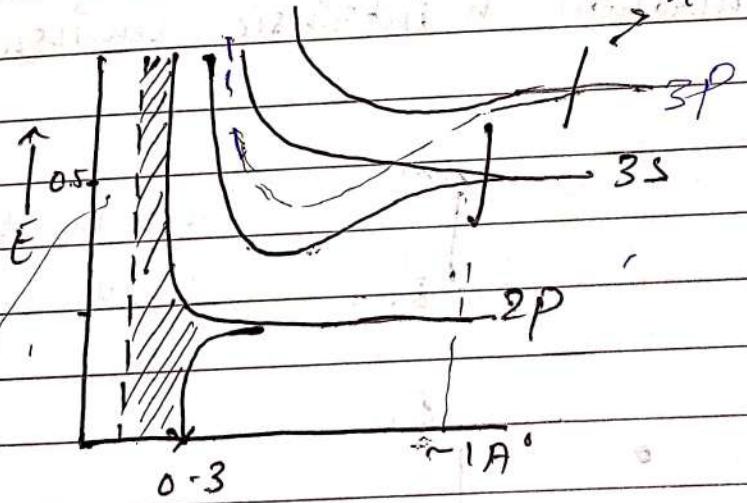
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r inter atomic dist....



→ For N - Sodium Atoms .



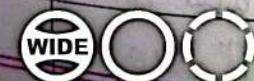
actually  
real graph

Band gap

⇒ For metal conductor  
band gap = 0 (almost negligible)

Insulator → more band gap

Semiconductor → less band gap → can conduct



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$$\Rightarrow \text{For finding } e^- \text{ in particular energy level}$$

$$2(2l+1)N$$

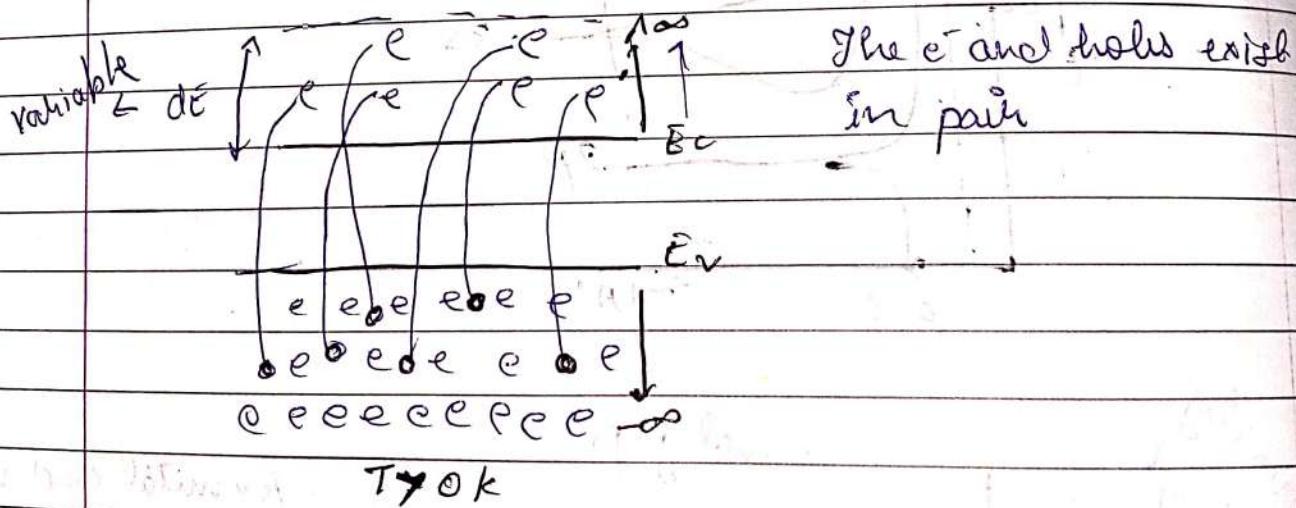
For  $S$ ,  $l=0$   
 $= 2N$  electrons

P,  $l=1$   
 $= 6N$  electrons

d,  $l=2$   
 $= 10N$  electrons

→ self learning  
 → Distinction between semi-insulator, conductor and semiconductor  
 (Based on Energy gap)

\* Carrier concentration in intrinsic semiconductor.



→ Making use of expression for density of  $e^-$  (free) in CB (conduction Band) for the energy range ( $\Delta E$ )

$\Delta E$

$$dn_c = D(E) \cdot f(E - \Delta E) \rightarrow \text{energy states}$$

$D(E)$  = Density of available states in CB

$f(P)$  = probability distribution for  $e^-$  to be filled in available energy states



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$$d_{nc} = \frac{4\pi}{h^3} (2me)^{3/2} \cdot (E - E_c)^{1/2}$$

$$d_{nc} = \frac{4\pi}{h^3} (2me)^{3/2} \cdot \frac{(E - E_c)^{1/2}}{e^{(E - E_c)/KT} + 1} \cdot dE$$

$$\because E > E_c \Rightarrow (E - E_f) \geq KT$$

$$\Rightarrow \frac{1}{e^{(E - E_c)/KT} + 1} \approx \frac{1}{e^{(E - E_f)/KT}}$$

$$\Rightarrow d_{nc} = \frac{4\pi}{h^3} (2me)^{3/2} \cdot \frac{(E - E_c)^{1/2}}{e^{(E - E_f)/KT}} \cdot dE$$

$$\hookrightarrow E - E_c + E_c - E_f$$

$$\Rightarrow d_{nc} = \frac{4\pi}{h^3} (2me)^{3/2} \cdot \frac{(E - E_c)^{1/2} \cdot dE}{e^{(E - E_c)/KT} \cdot e^{(E_c - E_f)/KT}}$$

then total no. of possible electrons in C-B

$$n_c = \frac{4\pi}{h^3} (2me)^{3/2} \cdot e^{\frac{(E_f - E_c)/KT}{(E - E_c)}} \int_{E_c}^{\infty} (E - E_c)^{1/2} \cdot e^{\frac{-(E - E_c)/KT}{(E - E_c)}} dE$$

$$\text{taking } \frac{(E - E_c)}{KT} = n, \Rightarrow (E - E_c) = nKT$$

$$\Rightarrow dE = KT dn$$

$$n_c = \frac{4\pi}{h^3} (2me)^{3/2} \cdot e^{\frac{(E_f - E_c)/KT}{(KT)^{3/2}}} \int_0^{\infty} n^{1/2} e^{-n} dn$$



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 $\sqrt{n}$

$$n_c = \frac{4\pi}{h^3} (2m_e)^{3/2} (kT)^{3/2} \cdot \frac{\sqrt{\pi}}{2} \cdot e^{(E_g - E)/kT}$$

$$n_c = (\text{const.}) \cdot m_e^{3/2} \cdot e^{(E_g - E)/kT}$$

↓ concentration of  $e^-$  in C.B

$1 - f(E)$  → probability distribution of holes in the valence band.

→ Now, calculating the concentration of holes in Valence Band.

→ Since, in intrinsic semiconductor the holes are created by the removal or ejection of electron from valence band to conduction band.

i.e. the holes and  $e^-$  are created in pairs where

$f(E)$  represent the probability distribution for  $e^-$  in conduction band.

then,

$1 - f(E)$  represent the probability distribution of holes in valence band.

→ Again making use of expression for density of holes in V.B. of intrinsic semiconductor.

$$dn_h = D(E) \cdot \{1 - f(E)\} \cdot dE$$

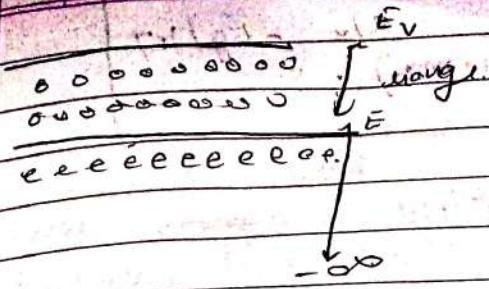
$$\downarrow \quad \rightarrow e^{(E - E_g)/kT}$$

$$dn_h = \frac{4\pi}{h^3} (2m_h)^{3/2} \cdot e^{(E - E_g)/kT} \cdot dE$$

$$\text{Shot on Y17} \quad \frac{4\pi}{h^3} \cdot (2m_h)^{3/2} \cdot (E_g - E)^{1/2} \cdot e^{(E_g - E)/kT}$$



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Total possible no. of holes in V.B  $\sim E + E_V - E_C - E_f$

$$n_h = \frac{4\pi}{h^3} \cdot (2m_h)^{3/2} \int_{-\infty}^{E_V} (E_V - E) \cdot e^{(E - E_f)/kT} dE$$

$$= \frac{4\pi}{h^3} \cdot (2m_h)^{3/2} \frac{(E_V - E_f)/kT}{e} \int_{-\infty}^{\infty} (E_V - E) \cdot e^{(E - E_f)/kT} dE$$

Taking

$$\frac{E_V - E}{kT} = x \quad \frac{E_V - E}{kT} = x \quad \Delta E = kT dx$$

$$n_h = \frac{4\pi}{h^3} \cdot (2m_h)^{3/2} \cdot e^{(E_V - E_f)/kT} \cdot (kT)^{3/2} \cdot \int_{-\infty}^{\infty} x^{3/2} \cdot e^{-x^2/kT} dx$$

$$n_h = \frac{2\sqrt{2\pi kT}}{h^2} \cdot m_h^{3/2} \cdot e^{(E_V - E_f)/kT}$$

Concentration of

Holes in V.B.

$$n_e = \frac{2\sqrt{2\pi kT}}{h^2} \cdot m_e^{3/2} \cdot e^{(E_f - E_C)/kT}$$

C-B.

Total no. of charge carriers is given by .

$$n_e n_h = \frac{4\sqrt{2\pi kT}}{h^2} m_e^{3/2} m_h^{3/2} e^{(E_V - E_C)/kT}$$

~~E\_C - E\_V = E\_g~~ (band gap).

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$E_C - E_V = E_g$

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$$n_c n_h = \frac{4(2\pi k)^3}{h^2} T^3 \text{ (memes)} \cdot e^{3/2 - E_g/kT}$$

Total no. of charge carriers in a pure semiconductor depends on the temperature and energy band gap, but does not depend on fermi energy ( $E_f$ )

since, in pure (intrinsic) semiconductor, no. of electrons and holes are equal

$$\Rightarrow n_c = n_h = n_i$$

$$n_i^2 = A T^3 e^{-E_g/kT}$$

## \* Position of Fermi-level in Intrinsic Semiconductor.

Since, we known that

$$n_c = n_h$$

$$\cancel{\frac{4(2\pi kT)^{3/2}}{h^2}} m_e^{3/2} e^{(E_g - E_c)/kT} = \cancel{\frac{4(2\pi kT)^{3/2}}{h^2}} m_h^{3/2} e^{(E_v - E_f)/kT}$$

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

$\therefore$  effective masses of  $e^-$  & holes are same

$$1 = e^{(2E_f - E_c - E_v)/kT}$$

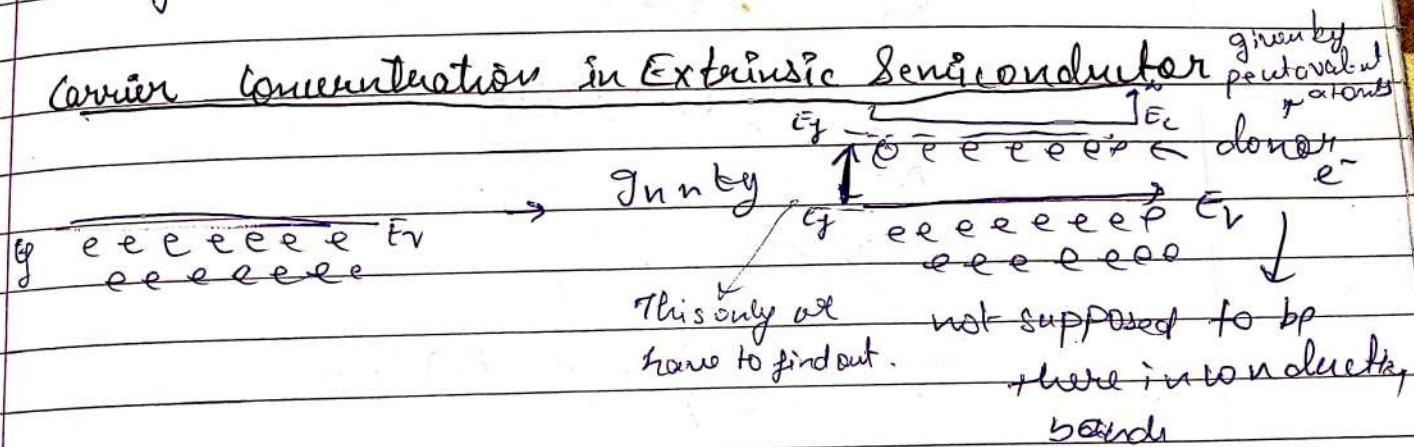
Taking natural log

$$kT \ln(2) = \alpha E_g - E_c - E_v$$

$$E_g = \frac{E_c + E_v}{2}$$

$\Rightarrow$  In pure semiconductor (intrinsic), the fermi level lies just in the middle of band gap.

### A Carrier Concentration in Extrinsic Semiconductor given by pentavalent atoms



$\Rightarrow$  n-type semiconductor

$\Rightarrow$  In this semiconductor is created or fabricated by carrying the impurities of pentavalent group element.

$\Rightarrow$  By doing so, impurity (element) give up their unsaturated electrons and make a co-valent bond with the electron of valence band. Thus, there will be huge amount of free  $e^-$  available without removal or ejection of  $e^-$  from valence band.

$\Rightarrow$  Thus, the fermi energy level must move closer to the bottom of conduction band.

$\Rightarrow$  These free  $e^-$  (donor  $e^-$ ) resides near by conduction



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therefore, concentration of donor  $e^-$   
 $= \text{no. of donor atoms.}$

$$\Rightarrow N_c = 2 \left( \frac{2\pi k T}{h^2} \right) \cdot m_e e^{-\frac{E_f - E_c}{kT}}$$

$$= N_d e^{-\frac{(E_f - E_c)}{kT}}$$

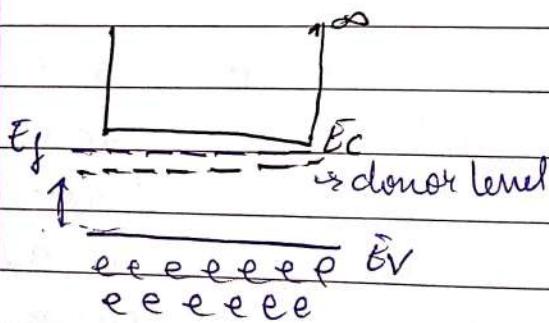
$$\Rightarrow \frac{N_c}{N_d} = e^{-\frac{(E_f - E_c)}{kT}}$$

$$\Rightarrow N_d = e^{-\frac{(E_f - E_c)}{kT}} N_c$$

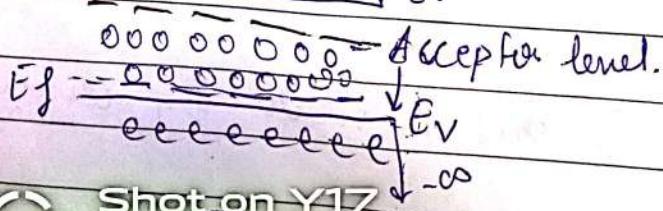
Taking natural log.

$$\log \ln \left( \frac{N_d}{N_c} \right) = (E_c - E_f) / kT$$

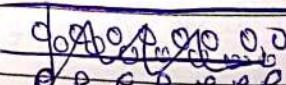
$$\Rightarrow E_f = E_c - kT \ln \left( \frac{N_d}{N_c} \right)$$



⑤ Concentration of Holes in p-type.



fermi level should move closer to the V.B



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P type



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∴ therefore, concentration of holes = no. of acceptor atoms.

$$N_V = \omega \left( \frac{2\pi kT}{h^2} \right)^{3/2} \cdot m_h^{3/2} \cdot e^{(E_V - E_f)/kT}$$

$$N_V = N_A \cdot e^{(E_V - E_f)/kT}$$

$$\frac{N_V}{N_A} = e^{(E_V - E_f)/kT}$$

Taking natural log.

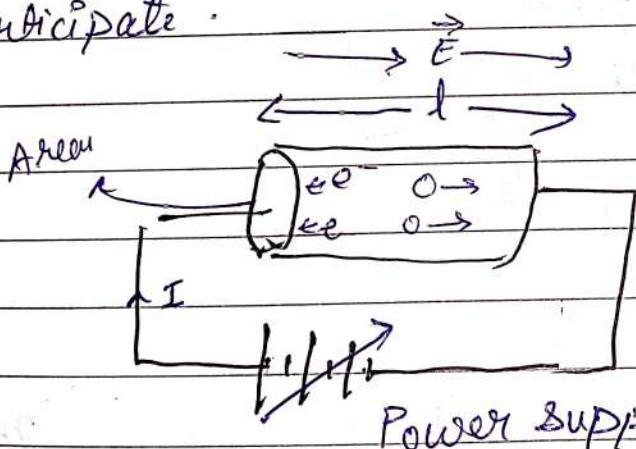
$$KT \ln \left( \frac{N_V}{N_A} \right) = (E_V - E_f)$$

$$E_f = E_V + KT \ln \left( \frac{N_A}{N_V} \right)$$

→ just closer (upper)  
of V.B.

## \* Mobility and Conductivity

Whenever there is conduction, both  $e^-$  and holes participate.



$$J = J_e + J_h$$

$$J_e = n e v_{de} \cdot A$$

drift velocity

$n$  = no. of charge carriers  
(electrons).

⇒ Current density

$$J_e = I_e / A = n e v_{de}$$

for from ohm's law

$$J = \sigma E$$

where

$\sigma$  = conductivity

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$$\sigma_e = \frac{n_e v_d}{E}$$

Similarly

$$\sigma_h = \frac{p_e v_{dn}}{E}$$

→ Mobility

$$\mu = \frac{V_d}{E}$$

$$\Rightarrow \sigma_e = n_e \mu_e; \sigma_h = p_e \mu_h$$

Total conductivity in Siemens (~~per centimeter~~)

$$\sigma = (n_e \mu_e + p_e \mu_h) e$$

→ for Intrinsic Semiconductor

$$n = p = n_i^2$$

$$\sigma_i = n_i (\mu_e + \mu_h) e$$

$$\text{where } \mu_e \approx \alpha T^{-3/2}$$

$$\mu_h \approx \beta T^{-3/2}$$

where  $\alpha$  and  $\beta$  are ionization coefficient.

$$\sigma_i = n_i e \cancel{\mu} T^{-3/2} - ①$$

$$\cancel{\mu} = \alpha + \beta$$

expression in terms of temp.

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⇒ since for intrinsic semiconductor.

$$n_i = CT^{3/2} e^{-E_g/2kT}$$

$$n_i = CT^{3/2} e^{-E_g/2kT} \quad \text{--- (2)}$$

putting this (1)

$$\sigma_i = Ce^{\chi} e^{-E_g/2kT}$$

also depends on the band gap.

## \* Specific Heat of Solids

⇒ Molar Specific Heat

→ The amount of energy required to raise the temperature by 1 Kelvin or 1 K mole is known as molar specific heat.

→ Classical Approach

→ The average total internal energy is  $\approx 3kT$  {in 3-D each constituent multiplied by 3}

$$\text{for 1 mole} \approx 3N_A kT$$

where

$$N_A = \text{Avogadro's No.} = 10^3 \times 10^{23}$$

$k$  = Boltzmann constant

$$E_{av} \approx 3RT$$

$$\approx 1.99 \text{ kcal/kmole.}$$

⇒ Dulong - Petit suggested

$$\text{Shot on Y17v} \quad \frac{C_v}{V} = \left( \frac{\partial E}{\partial T} \right)_V \approx 3R$$



Vivo AI camera

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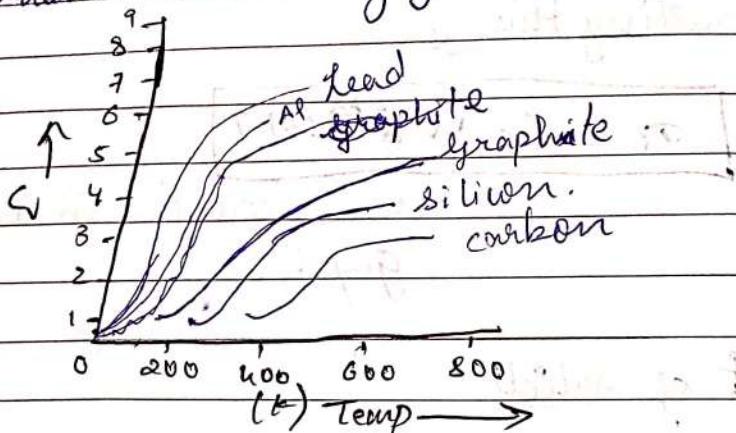
⇒ This implies,  
→ All the solid will have almost same specific heat

⇒ Spec

⇒ But experimental facts shows that

① The lighter element like (B, Be, C) does not  
behave accordingly. (At temperature, 20°C)

②



⇒ The value of  $C_v$  sharply decreases and falls off as the temperature approaches to zero.

⇒ Modifications by Einstein

⇒ After in quantum mechanical approach, Einstein suggested that average energy of each oscillator is discrete and given by probability function.

$$\bar{E}_{av} = h\nu f(\nu)$$

↳ probability function of energy distribution.

$$\Rightarrow \bar{E}_{av} = h\nu$$

$$e^{\frac{h\nu}{kT}} - 1$$

⇒ Total internal energy of a 1 kilomole is

$$E_T = 3N_0 h\nu$$

Shot of  $\frac{h\nu}{kT}$   
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## Specific Heat

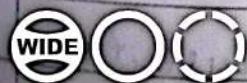
$$C_V = \left(\frac{\partial E_T}{\partial T}\right)_V = \frac{3N_0 \hbar^2 v^2}{K^2 T^2} (e^{EVT/KT} - 1)^{-2} e^{-EVT/KT}$$

$$= \frac{3N_0 K \cdot \hbar^2 v^2}{K^2 T^2} (e^{EVT/KT} - 1)^{-2} e^{-EVT/KT}$$

$$= 3R \cdot \left(\frac{\hbar v}{K T}\right)^2 \frac{e^{-EVT/KT}}{(e^{EVT/KT} - 1)^2}$$

on taking, if  $\hbar v \gg KT$

$$C_V \approx 3R$$



Shot on Y17

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