MODULE-2

ELECRICAL CONDUCTIVITY IN MATERIALS

<u>DRUDE-LORENTZ THEORY OF FREE ELECTRON</u>

Paul Drude, a German Physicist gave a generally accepted theory on electrical conductivity in metals and Lorentz, a Holland Physicst improved it.

Hence this theory is named DRUDE- LORENTZ THEORY. (**Only for information**)

Every metal atom consists of valence electrons and these are responsible for electrical conduction . In a metal, the atoms are tightly packed. Each atom consists of valence electrons. These valence electrons are out of the atom and free to move within the metal. There is continuity in movement of these electrons from atom to atom.

Hence, valence electrons belong to any atom. These electrons are named as free electrons. These are responsible for conduction and hence also called as conduction electrons.

<u>ASSUMPTIONS OF CLASSICAL FREE ELECTRON THEORY</u>

1. In a metal there are freely moving valence electrons called free electrons confined to its body. The electric current in a metal due to an applied field is a consequence of the drift velocity of the free electrons in a direction opposite to the direction of the field.

2. The free electrons are treated equivalent to gas molecules and thus assumed to obey the law of kinetic theory of gases. Given by,

$=$

Where, K →Boltzmann constant

V_{th}→ Thermal velocity.

3. The electrical potential due to cores (Lattice point) is taken to be throughout the metal.

4. The attraction between the free electrons and the ions and the repulsion between the electrons themselves are considered insignificant (ignored)

MEAN FREE PATH

Mean free path is the average distance travelled by the free electrons two successive collisions. It is denoted by **" λ".**

MEAN COLLISION TIME

Mean collision time is the average time elapsed between two successive collision. It is denoted by **"τ".**

***RELATION BETWEEN λ AND* τ**

τ =

V→ Total velocity of electrons which is the sum of drift velocity(V_d) and thermal velocity(V_{th}).

RELAXATION TIME

In the absence of electric field, the average velocity of the electrons in any given direction is zero,

i.e., $\mathbf{V_{average}}$ **or** $\mathbf{V_{av}=0}$ (Absence of electric field)

But in the presence of electric field, the average velocity is not zero, i.e., = ′ (Presence of electric field)

Now, once we turn off the field, starts reducing exponentially from the value ′ as shown in the graph below

The decay process is given by

= −

"Relaxation time is the time required for the average velocity of the free electrons to reduce to 1 times its everage velocity that existed when the field is just turned

off"

LATTICE

The periodic arrangement of fixed ions in 3 dimensions is called lattice.

DRIFT VELOCITY

When an electric field is applied, the free electrons will have net displacement in one single direction and displaces with respect to time in a direction opposite to the direction of the field.

The displacement of free electrons per unit time is called drift velocity. It is called drift velocity. It is denoted by V_d. Given by $\mathbf{V_d=}$ ___

Where, e→ charge of electron=$1.6\text{x}10^{-19}$C

E→ Electric field **τ**

→mean collision time m→mass

ofelectron=$9.1\text{x}10^{-31}$Kg ***EXPRESSION FOR ELECTRICAL CONDUCTIVITY AS PER CLASSICAL FREE ELECTRON THEORY***

σ= ___

where, σ →Electrical conductivity

e →charge of electron **τ**

→Relaxation time m

→mass of electron.

FAILURES OF CLASSICAL FREE ELECTRON THEORY.

1.<u>Specific heat</u>: The theory compares free electron to the gas molecules, same specific heat should be applicable for both. The Specific heat should be applicable for both. The specific heat of a gas at constant volume is given by,

C$_V$**=** ....(1)

But experimentally it was found that, $\mathbf{C_V=10^{-4}RT}$ ....(2)

From (1) & (2), we see that ,C_V for a metal is not only far smaller than C_V for gas molecule but also its dependent on temperature.

<u>2.Temperature dependence of electrical conductivity(σ)</u>

Experimentally observed value of σ for metals is inversely proportional to temperature T.

i.e., $\boldsymbol{\sigma_{exp}\ \alpha}$ .... (1)

$$\frac{3}{2}KT = \frac{1}{2}$$

2h

Now from classical assumption we have,

$V_{th} = \frac{\sqrt{3KT}}{}$

$V_{th} = \sqrt{T}$............... (2)

We know that , T α $\frac{1}{V_{th}}$

(or) T α $\frac{1}{\sqrt{T}}$ .... (3) [from eqn 2]

Also we have,

T ²σ=

σ α T

(or)σ α

From (1) & (4) it is clear that the prediction of classical free electron theory is not agreeing with the experimental observation.

3. Dependence of electrical conductivity on electron concentration ' n'

Conductivity 'σ' is given by,

σ= ____² where 'n' is electron concentration .

Metal	Valency	σ (Ωm)	n
Cu	1	$5.88*10^{7}$	$8.45*10^{28}$
Zn	2	$1.09*10^{7}$	$13.10*10^{28}$

According to classical free electron theory, n α σ, which means higher the number of free electrons higher is its conductivity.

From the above table we observe that Zn has more free electrons than Cu, but conductivity of Cu is higher than that of Zn. Hence the prediction , n α σ does not always hold good.

<u>ASSUMPTIONS MADE IN QUANTUM FREE ELECTRON THEORY.</u>

One of the important realization was, the role played by Pauli's exclusion principle. The assumptions of Quantum free electron theory are,

1. The free electrons possess energy and these energy values are quantised. The allowed energy levels are realized in terms of a set of energy levels.

2. The distribution of electrons in various energy levels occurs as per Pauli's exclusion principle...i.e., single energy level can be occupied by only 2 electrons with opposite spin.
3. The electric potential throughout the lattice is taken to be constant.
4. The attraction and the repulsion between the lattice points and electrons (or) lattice points themselves (or) electrons themselves are ignored.

DENSITY OF STATES

Energy levels of electrons in a solid will look like bands. On a closer look we see that the energy levels in the band are not uniformly distributed. The number of energy levels/unit energy range is explained by density of states.

"Density of states is the number of allowed energy levels in infinitesimally small energy increment dE in the valence band of the material.

Given by, **g(E)dE=** $\frac{\surd}{\quad}$ **dE**

g(E)α

FERMI ENERGY

Consider a metal of N atoms and hence there will be N allowed energy levels in each band. The electrons will occupy energy levels according to Pauli's exclusion principle. When no external energy is supplied for the electrons, such as thermal energy i.e., at t=0K, we see that levels above valence band will be vacant.

"Fermi energy is the energy corresponding to the highest occupied level at zero degree absolute temperature and the energy level is referred to as the **FERMI LEVEL (E_F)**"

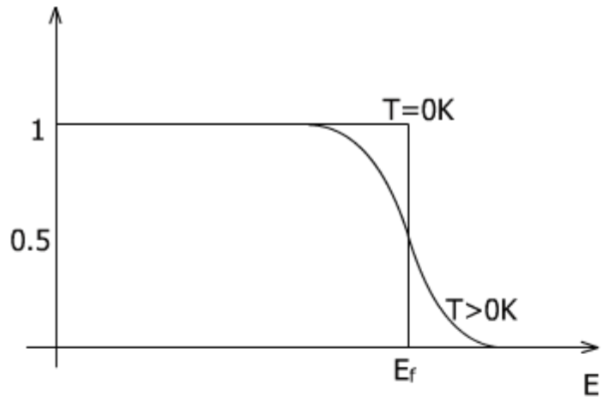
At T=0K, energy levels lying above the Fermi level are empty and those lying below are completely filled.

FERMI FACTOR AND DEPENDANCE OF FERMI FACTOR ON TEMPERATURE AND ENERGY (PROBABILITY OF OCCUPATION OF VARIOUS ENERGY STATES BY ELCTRONS AT T=0K AND T>0K, ON THE BASIS OF FERMI FACTOR)

Fermi-Dirac Statistics permits the evaluation of probability of finding electrons occupying energy levels in a certain energy range. This is done through a function called Fermi Factor f(E).It is given by, f(E)= –

"Fermi factor is the probabilit~~y of~~ occupation of a given energy state for a material in thermal equilibrium"

Probability of occupation is considered for following cases,



i) **Probability of accupation for $E<E_F$ at T=0K**

We have, F(E)= – 1

+1

If $E<E_F$, $E-E_F$ ~~will be n~~egative and T=0,

f(E)= $\frac{}{e^{-\infty}+1}$

f(E) = $\frac{1}{0+1}$

f(E)=1

- f(E)=1 means, the energy level is certainly occupied.i.e,there is 100% probability that the electrons occupy the energy level below Fermi energy
- All the energy levels below Fermi level are occupied
- $E<E_F$ applies to all the energy levels below E_F

ii) **Probability of accupation for $E>E_F$ at T=0K**

If $E>E_F$, $E-E_F$ will be positive and for T=0,

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

∞

f(E)=0

All the energy levels above Fermi level are unoccupied.i.e, 0% probability for the electrons to occupy the energy level above the Fermi level

iii) **Probability of occupation at ordinary temperature.**

At ordinary temperature, though value of probability remains 1 for $E<<E_F$,it starts decreasing from 1 as the value of E become closer to E_F For $E=E_F$,

f(E)= ——— —— $0^1+=\,1=1$

11+12

f(E)=

There is 50% probability for the electrons to occupy the Fermi energy level

EXPRESSION FOR ELECTRICAL CONDUCTIVITY AS PER QUANTUM FREE ELECTRON THEORY

$$\sigma = \frac{}{*}$$

where,

m* → effective mass of the electron

V_F → Fermi velocity

λ →Mean free path

e →charge of the electron

n →electron concentration

MERITS OF QUANTUM FREE ELECTRON THEORY (SUCCESS OFQUANTUM FREE ELECTRON THEORY IN OVERCOMING THE FAILURES OF CLASSICAL FREE ELECTRON THEORY)

1.Specific heat(C_V)- The small value of specific heat (C_V) for the conduction electrons can be explained as follows.

According to quantum theory, only those electrons that occupy energy levels close to E_F can absorb the energy and move to the higher energy states. Number of such electrons absorbing the energy is small and hence C_V is small, It is given by,

$$C_V = \left(\frac{2K}{\quad}\right)RT$$

Ex., For E_F=5eV

$C_V=10^{-4}RT$.

This confirms with the experimentally observed values.

2.**Temperature dependence of electrical conductivity.**

The experimental fact that the electrical conductivity σ has a dependence on 1 and not $\frac{1}{\sqrt{T}}$ on is explained here,

2

We have, σ= ____ ....(1)

The dependence of σ on T is analysed as follows,

The free electrons are subjected to scattering due to vibration of ion in the lattice.If ‘r’ is the amplitude of vibration ,it is same in all the directions then the ions can be considered to be present effectively in a circular cross-section of area Πr^2.The value of mean free path λ decreases when Πr^2 increases.i.e,

λα 1 2.........(2)

Now consider the facts,

- Energy of ion α square of the amplitude
  i.e, E α r^2........(3)
- Energy of ion α Temperature
  i.e, E α T..........(4) from eqn (3) & (4)
  →r^2 α T............(5)
  (2) → λ α 2..........(6) 1 from eqn
  1 from eqn
  (5) & (6)→ λ α ....(7)
  1
  from (1) & (7)→ σ α

3.Electrical conductivity and electron concentration.

It was not possible to understand why metals such as Aluminium and gallium which have 3 free electrons/atom have lower electrical conductivity than metals such as copper and silver which possess only 1 free electron/atom. Quantum free electron theory could explain why,

2

We know that , σ= ____ ....(1)

From(1),it is clear that ‘σ’ depends on both ‘n’ and also on ⌊ ⌋ ratio

The value of ‘n’ for ~~alum~~inium is 2.13 times higher than that of copper. But the values of ⌊ ⌋for copper is about 3.73 times higher than that of aluminium.

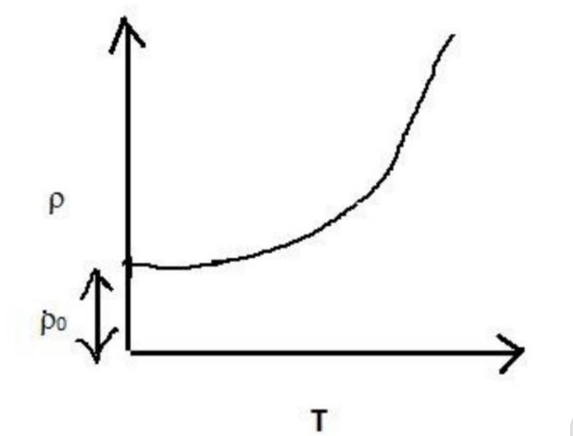
Therefore, conductivity of copper exceeds that of aluminium.

SUPERCONDUCTORS

TEMPERATURE DEPENDENCE OF RESISTIVITY OF A METAL.

Metals have loosely bound electrons in their outermost shell or valence shell which is responsible for conduction. These electrons are called free electrons/conduction electrons.

The dependence of resistivity ( ) on temperature is as shown below.



The total resistivity of a metal is the sum of the resisitivity due to impurities($_{o}$) at T=0K and the resistivity due to phonon scattering which is temperature dependent (T). We can see that the resistance decreases with temperature and reaches minimum at T=0K

The Variation is expressed by the **Matthiessen's rule**

= $_{o}$ + (T)

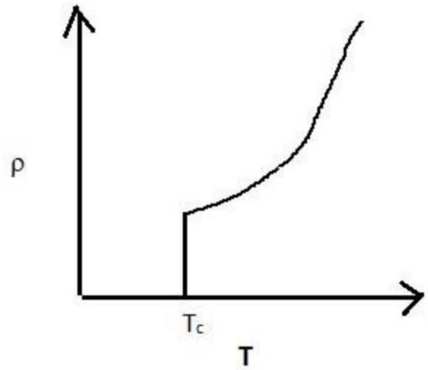
Where, →is the resistivity of the given metal

$_{o}$ → is the residual resistivity

(T)→ is the temperature dependent of resistivity

(Note: Lattice vibrations are called phonons)

TEMPERATUREDEPENDENCE OF RESISTIVITY OF A SUPERCONDUCTOR:



Resisitivity ( ) is the non superconducting state decreases with decrease in temperature upto a particular temperature $T_{C.}$ At Tc, abruptly drops to zero. Tc is called the critical temperature and signifies the transition from normal state to the superconducting state of the material under study.

"The resistance offered by certain materials to the flow of electric current abruptly drops to zero below a certain temperature. This phenomenon is called Superconductivity"

- Materials exhibiting this property are called superconductors.
- The temperature at which the resistance becomes zero is called the critical temperature.
- Critical temperature is different for different materials . The critical temperature is different for different superconductors.

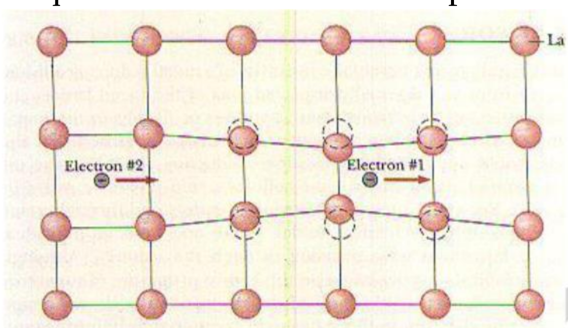
Superconductors elements	**symbol**	**T_c(K)**
Mercury	Hg	4.2
Gallium	Ga	1.15
Aluminium	Al	1.20
Indium	In	3.40
Ti n	Sn	3.72
Tantaum	Ta	4.48
Vanadium	V	5.38
Lead	Pb	7.19
Lanthanum	La	6.00

Niobium	Nb	9.50

BCS THEORY

BCS theory-(Bardeen,Cooper and Schrieffer theory)

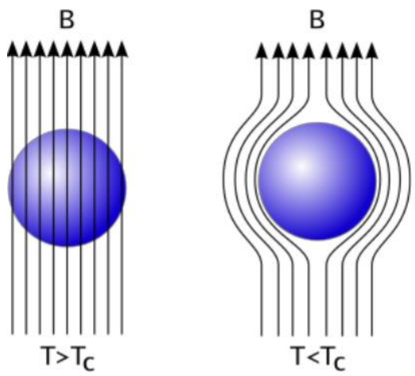
- This theory explains the phenomenon of Superconductivity. This theory is based upon the formation of cooper pairs, which is a quantum mechanical concept.



- When the free electron leaves the atom, the atom becomes positively charged. When electron comes near a positive ion core of the lattice,it experiences an attractive force because of the opposite polarity between electron and ion.
- Due to this attraction ,the ion is displaced from its position, leading to lattice distortion.At the same time,if other electron which comes near that place will also interact with the distorted lattice. This process is looked upon as equivalent to interaction between the two electrons through the lattice .The process is called "electronlattice-electron interaction through the phonon field"
- The attractive force between two electrons will be maximum if they have equal and opposite spin and momenta.This force will even exceed the coulomb repulsive force between electrons. "Hence ,cooper pair is a bound pair of electrons formed by the interaction between the electron with opposite spin and momenta in a phonon field"
- Each cooper pair is associated with a wavefuction. The wavefuction with similar cooper pairs start overlapping which may extend over 10^6 other pairs. This leads to a union of vast number of cooper pairs.
- When the electron flow in the form of cooper pairs,they do not encounter any scattering and the resistance factor vanishes or in other words conductivity becomes infinite hence a material becomes superconductor.

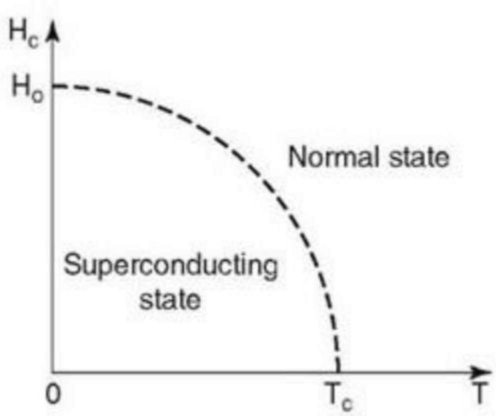
MEISSNER EFFECT.

When a superconducting material is cooled in a magnetic field below the critical temperature, the flux lines are expelled from the body of the material .i.e. the material behaves like a perfect Diamagnetic. This effect is known as Meissner effect.



CRITICAL FIELD

The strength of minimum magnetic field required to just switch a material from Superconducting state to normal state is called Critical field.



- If "T" is the temperature of the superconducting material($T<T_C$)

  "Hc" is the critical field and

  "H_0" is the field required to turn the superconductor to normal conductor at 0 K.

Then the relation for critical field (H_C) is given by

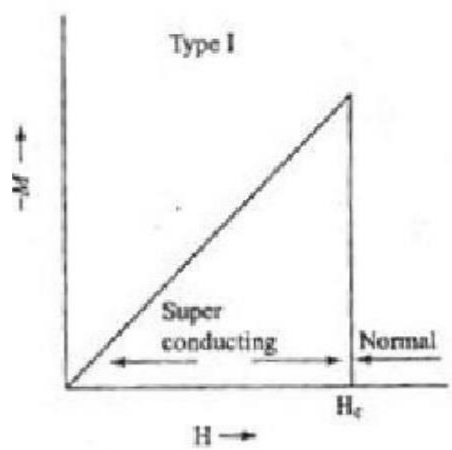
$$\boxed{H_C = H_0 \left[1 - T^2/T^2_c\right]}$$

TYPES OF SUPERCONDUCTORS:

Superconductors are classified into two types they are,

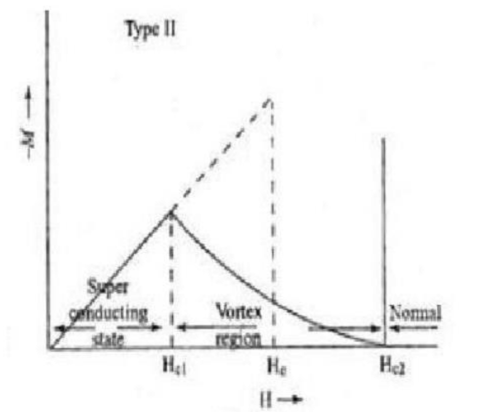
1. Type -I Superconductors(soft)
2. Type-II superconductors(hard)

Type -I Superconductors (soft)



- When magnetic field $H<H_C$,they exhibit complete Meissner effect. In the presence of external magnetic field the material is in the superconducting state and behaves as a perfect diamagnet.
- When H> c the magnetic flux enters the material and it loses its diamagnetic property and the material comes to normal state.
- It is found that for type I superconductors the critical field values are low.

Type –II Superconductors (hard)



Where-H is the External magnetic field and M is the -ve magnetic moment.
H_{c1} and H_{c2} are the lower & higher critical fields.

- They are characterized by two critical fields H_{c1} and H_{c2} when $H<H_{c1}$ the Material is in the superconducting state and it behaves as a perfect Diamagnet.
- When $H>H_{c1}$ the flux penetrates the body and fills partially with further increase in H, the flux filling also increases thereby decreasing the diamagnetic part of the material and covers the entire body when H becomes equal or greater than a second critical value H_{c2} .the material then turns into a normal conductor.$H_{c1}$and H_{c2} are called lower critical field and upper critical field respectively.
- When H lies between $H_{c1}$and H_{c2} the material loses some of its diamagnetic properties and enters into a mixed state called vortex state.
- When $H>H_{c2}$ the material enters into the normal state .it is found that for type –II superconductor's critical field values are high.

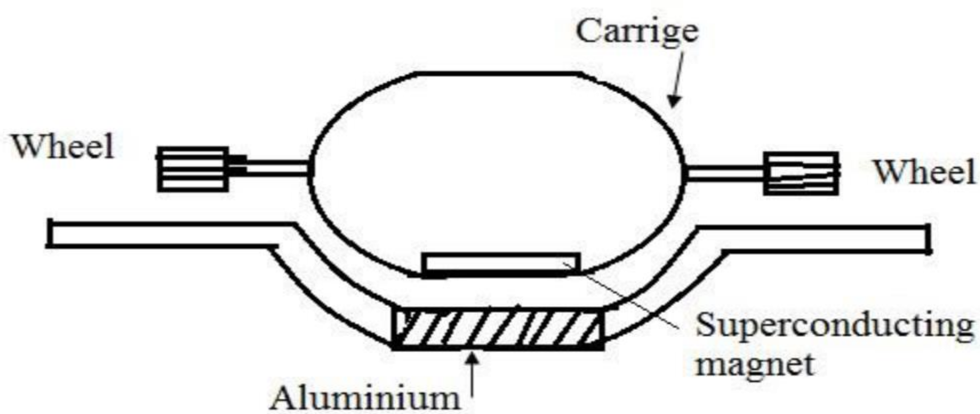
Note: The number of magnetic lines flowing per unit area is called flux. **High temperature superconductivity:**

"Superconductors having higher critical temperatures are called high temperature superconductors".

All high temperature superconductors are not pure metals, but they are different types of oxides of copper. And bear a particular type of crystal structure called Pervoskite crystal structure. It is found that, the critical temperature is higher for those materials having more number of copper oxygen layers. It is found that the formations of super currents in high temperature superconductors are directional dependent.

The super currents are strong in copper oxygen planes and weak in a direction perpendicular to the copper oxygen planes. **Applications superconductors:**

Maglev vehicles:



Magnetically levitated vehicles are called maglev vehicles.The vehicle is levitated above the tracks hence friction is eliminated.

- Maglev vehicles do not slide over the tracks.
- The maglev vehicles work on the principle of Meissner effect.
- Superconducting magnets are built onto the base of the vehicle, and current is passed through the guide way.
- Magnetic field is produced by the superconducting magnet and current in the guideway.
- Now, enormous repulsion happens between these two magnetic fields as the result vehicle will be set a float.
- The vehicle is levitated to about 10 to 15cm above the guideway.
- When the vehicles runs on the guideway, the wheels are retraced into its body, while stopping the wheels are drawn out and the vehicle slowly settles on the guideway.

SEMICONDUCTORS

Semiconductors have conductivity in the range intermediate between those of conductors and insulators.

The resistivity of semiconductors lie in the range 10^{-6} to $10^{+8}\Omega$m.

Elements such as Silicon(Si), Germanium (Ge) , Selenium (Se) and compounds such as Gallium Arsenide (GaAs), Gallium Phosphide (GaP) are some examples of semiconductors.

Conductivity of Semiconducting Materials:

Carrier concentration in an intrinsic semiconductor:

The number of electrons in the conduction band per unit volume of the material is called electron concentration (N_e) given as,

$N_e = \frac{4\sqrt{2}}{h^3}$ (KT *)3/2 ………….. (1)

Where * is the effective mass of electron E_F is the Fermi Energy and E_g is the energy gap.

Similarly, the number of holes in the valence band per unit volume of the material is called hole concentration. (N_h)

N_h (KT $\overset{*}{h})^{3/2}$ …………… (2)

Where h* is the effective mass of holes E_F is the Fermi Energy and E_g is the energy gap.

T is the absolute temperature and h is the Planck's constant.

In general, the number of charge carriers per unit volume of the material is called carrier concentration.

The charge carriers, both electrons and holes contribute to the conductivity of the semiconductor.

The conductivity of a semiconductor is given by the expression $\sigma = e [(N_e\mu_e) + (N_h\mu_h)]$ where N_e and N_h are the carrier concentrations of electrons and holes respectively.

μ_e and μ_h are mobility of electrons and holes respectively and ‘e’ is the magnitude of charge of the electron.

Law of Mass Action for Semiconductors:

Law of mass action says that, for a given semiconductors material either intrinsic or extrinsic, the product of the charge carrier concentration remains a constant at any given temperature, even if the doping is varied. We have the equations for N_e and N_h as

$$N_e = \frac{4\sqrt{2}}{h^3}\left(KT^{3/2} \quad {}^{*}_{e}\right) \text{———}\ldots\ldots\ldots\ldots \text{(1) and}$$

$$N_h = \frac{4\sqrt{2}}{h^3}\left(KT \quad h*\right)^{3/2} \text{———}\ldots\ldots\ldots\ldots\ldots \text{(2)}$$

In the above expressions, we see that N_e and N_h depends on E_F .

Consider the product of N_e and N_h,

$N_e . N_h = 32h$——$6 . ($ KT$)3.($ $h)3/2 . –$ /

The above equation shows that N_e and N_h do not sepend on E_F, but remains a constant.

$$\boxed{N_e . N_h = \text{constant}}$$

Therefore,

This condition is applicable to both intrinsic and extrinsic semiconductors.

In the case of an intrinsic semiconductor,

$$N_e = N_h = n_i$$

Where n_i is the intrinsic charge carrier concentration. Therefore,

$N_e . N_h = n_i^2$ = constant.

QUESTION BANK

1) Describe Type I and Type II superconductors
2) Explain the terms a) relaxation time, b) mean collision time, c) mean free path, and drift velocity
3) Discuss in brief BCS theory of superconductivity
4) Write a note on maglev vehicles
5) Describe how quantum free electron theory has been successful in overcoming the failure of classical free electron theory.

6) Define Fermi energy and Fermi factor. Discuss the variation of Fermi factor with temperature and energy