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MODULE 4

MATERIAL SCIENCE

Classical free electron theory

Assumptions of classical free electron theory:

- > The metal consists of free electrons; the current flowing through a metal is due drift velocity of electrons.
- ➤ The free electrons are treated as equivalent to gas molecules and they are assumed to obey the laws of kinetic theory of gases. In the absence of the field, the energy associated with each electron at a temperature T is given by 3/2 kT, where k is a Boltzmann constant. It is related to the kinetic energy.

$$3/2 kT = \frac{1}{2} mv_{th^2}$$

Where v_{th} is the thermal velocity same as root mean square velocity.

- ➤ The electric potential due to the ionic cores is assumed to be constant throughout the metal
- ➤ The attraction between the lattice ions and electrons, the repulsion between the electrons are neglected.

<u>Expression for electrical conductivity of conductor according to classical free electron theory</u>

According to classical free electron theory the expression for electrical conductivity is given by

$$\sigma_{CFET} = \frac{ne^2 \tau}{m}$$

Where σ - Electrical conductivity n- Electron density τ - mean collision time

m- mass of electron

Failures of classical free electron theory:

Electrical and thermal conductivities can be explained from classical free electron theory. It fails to account the facts such as specific heat, temperature dependence of conductivity and dependence of electrical conductivity on electron concentration.

i) Specific heat: The molar specific heat of a gas at constant volume is

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$$C_v = \frac{3}{2} R$$

As per the classical free electron theory, free electrons in a metal are expected to behave just as gas molecules. Thus the above equation holds good equally well for the free electrons also.

But experimentally it was found that, the contribution to the specific heat of a metal by its conduction electrons was

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

which is for lower than the expected value. Also according to the theory the specific heat is independent of temperature whereas experimentally specific heat is proportional to temperature.

ii)Temperature dependence of electrical conductivity:

Experimentally, electrical conductivity σ is inversely proportional to the temperature T.

i.e.
$$\sigma_{\rm exp} \ \alpha \xrightarrow[T]{1} (1)$$

According to the assumptions of classical free electron theory

Since Vth $\alpha \sqrt{T}$

But $\tau \alpha \frac{1}{V t h}$, $\tau \alpha \frac{1}{\sqrt{T}}$,

substituting in conductivity equation we get

$$\sigma_{CFET} = \frac{ne^2 \, \tau}{m} = \frac{ne^2}{m \, \sqrt{T}}$$

or $\sigma_{CFET} = \frac{1}{\sqrt{T}}$ \rightarrow (2)

From equations (1) & (2) it is clear that the experimental value is not agreeing with the theory. iii)Dependence of electrical conductivity on electron concentration:

According to classical free electron the theory

Consider copper and aluminum. Their electrical conductivities are $5.88 \times 10^7 / \Omega m$ and $3.65 \times 10^7 / \Omega m$. The electron concentrations for copper and

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aluminum are $8.45 \times 10^{28} / \text{m}^3$ and $18.06 \times 10^{28} / \text{m}^3$. Hence the classical free electron theory fails to explain the dependence of σ on electron concentration.

Experimental results:

Metals	Electron	conductivity (σ)
	concentration(n)	
Copper	8.45×10 ²⁸ /m ³	$5.88 \mathrm{x} 10^7/\Omega\mathrm{m}$
Aluminium	18.06x10 ²⁸ /m ³	$3.65 {\rm x} 10^7 / \Omega {\rm m}$

Quantum free electron theory:

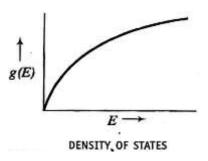
Assumptions of quantum free electron theory:

- ➤ The energy values of the conduction electrons are quantized. The allowed energy values are realized in terms of a set of energy values.
- ➤ The distribution of electrons in the various allowed energy levels occur as per Pauli's exclusion principle.
- > The electrons travel with a constant potential inside the metal but confined within its boundaries.
- ➤ The attraction between the electrons and the lattice ions and the repulsion between the electrons themselves are ignored.

Density of states g(E):

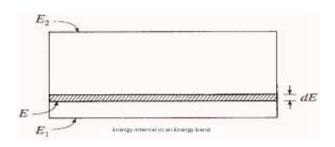
Density of states is defined as the number of allowed energy states per unit energy range per unit volume in the valance band of a material. It is denoted as g(E).

A graph of g(E) verses E is shown below.



Consider an energy band spread in an energy interval between E_1 and E_2 . Below E_1 and above E_2 there are energy gaps. g(E) represents the density of states at E. As dE is small, it is assumed that g(E) is constant between E and E+dE. The density of states in range E and (E+dE) is denoted by g(E)dE.

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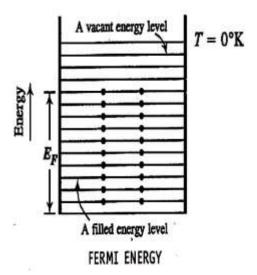


i.e.
$$g(E)dE = \begin{bmatrix} \frac{1}{8}\sqrt{2 \prod_{i} m^{\frac{3}{2}}} \\ \frac{1}{n} h^{\frac{1}{2}} \end{bmatrix} \begin{bmatrix} \frac{1}{2} \\ \frac{1}{2} \end{bmatrix} dE$$

It is clear g(E) is proportional to \sqrt{E} in the interval dE

Fermi energy and Fermi level:

The energy of electrons corresponding to the highest occupied energy level at absolute $0^{\circ}K$ is called Fermi energy and the energy level is called Fermi level.



Fermi-Dirac statistics:

- > At thermal equilibrium the free electrons acquire energy obeying a statistical rule called Fermi-Dirac statistics.
- Fermi-Dirac statistics is applicable to the assembly of particles which obeys Pauli's exclusion principle; they must also be identical particles of spin ½ and are indistinguishable.
- Fermi-Dirac statistics permits to evaluation of probability of finding the electrons occupying energy levels in a certain energy range and is given by a function called Fermi factor f(E).

Fermi factor:

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Fermi factor is the probability of occupation of a given energy state by the electrons in a material at thermal equilibrium.

The probability f(E) that a given energy state with energy E is occupied by the electrons at a steady temperature T is given by

$$f(E)$$
 $f(E)$ is called the Fermi e^{kT} $f(E)$

factor.

Dependence of Fermi factor with temperature and energy:

The dependence of Fermi factor on temperature and energy is as shown in the figure.

i) Probability of occupation for $E < E_F$ at T = 0K:

When T=0K and E<E_F

$$f(E) = \frac{1}{e^{-\infty} + 1} = \frac{1}{0 + 1} = 1$$

The probability of occupation of energy state is 100%

$$f(E)=1$$
 for $E < E_F$.

f(E)=1 means the energy level is certainly occupied and $E<E_F$ applies to all energy levels below E_F . Therefore at T=0K all the energy levels below the Fermi level are occupied. **ii) Probability of occupation for E>E_F at T=0K:**

When T=0K and $E>E_F$

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

The probability of occupation of energy state is 0%

$$f(E)=0$$
 for $E>E_F$

... At T=0K, all the energy levels above Fermi levels are unoccupied. Hence at T=0K the variation of f(E) for different energy values, becomes a step function as shown in the above figure.

ii) The probability of occupation at ordinary temperature(for $E \approx E_F$ at T>0K)

At ordinary temperatures though the value of probability remains 1, for $E < E_F$ it starts reducing from 1 for values of E close to but lesser than E_F as in the figure.

The values of f(E)becomes $\frac{1}{2}$ at E=E_F

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This is because for $E=E_F$

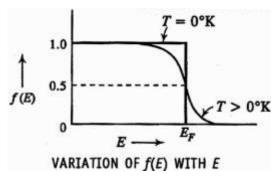
$$e(E-E_f)/kT = e_0 = 1$$

$$f(E) = \frac{1}{e^{(E-E_f)/kT} + 1} = \frac{1}{1+1} = \frac{1}{2}$$

The probability of occupation of energy state is 50%

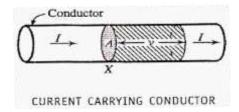
Further for E>E_F the probability value falls off to zero rapidly.

Hence, the Fermi energy is the most probable or the average energy of the electrons across which the energy transitions occur at temperature above zero degree absolute.



Expression for electrical conductivity for conductor according to quantum free electron theory

Consider the motion of an electron in a metal in an influence of an electric field E. let e is the charge; m is the mass of an electron and A is the area of cross section. Let v_d (drift velocity) is the distance travelled in unit time



According to de Broglie hypothesis, $\lambda = \frac{\hbar}{4}$

$$\rightarrow p = \frac{\hbar}{\lambda} = \frac{\hbar k}{2\pi} \qquad (1)$$

 $\left(k = \frac{2\pi}{\lambda}\right)$

Since

$$p = mv = mv_d$$

By substituting for p in equation (1)

$$m^{V_d} = \frac{hk}{2\pi}$$

$$v_d = \frac{hk}{2\pi m_*}$$
-----(2)

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Where

m=m*, called effective mass of electrons.

Integrate eqn (1) w.r.t "t"

$$\frac{dp}{dt} = \frac{h}{2\pi} \frac{dk}{dt} \tag{3}$$

By applying electric field E, the force experience by the electrons is eE and is equal to rate of change of momentum of the electrons.

i.e.,
$$F = eE = \frac{dp}{dt}$$

Substitute $\frac{dp}{dt}$ in equation (3)

$$eE = \frac{h \, dk}{2\pi \, dt}$$

$$dk = \frac{2\pi}{h} eE dt$$

Integrating on both sides

$$\int dk = \frac{2\pi}{h} eE \int dt$$

$$k = \frac{2\pi}{h} eE\tau$$
 ----- (4) (since $t = {}^{\tau}$ mean collision time)

Substituting eqn (4) in eqn (2) we have

$$v_d = \frac{h}{2\pi m^*} \frac{2\pi}{h} \text{ eE}\tau$$

$$v_d = \frac{\text{eE}\tau}{m^*} \qquad (5)$$

Current density is J = neVd

Substituting eqn (5) in the above equation

$$J = ne^{\frac{eE\tau}{m*}}$$

As we know, $J = \sigma E$,

$$\sigma = \frac{J}{E}$$

$$\sigma = \frac{ne^2\tau}{m_*}$$

According to quantum free electron theory mean collision time $\tau = \frac{\Lambda}{Vf}$

Where Vf is the Fermi velocity

The expression for conductivity becomes $\sigma = \frac{ne^2\lambda}{m^2Vf}$

Where m* is the effective mass of electrons

Merits of Quantum free electron theory:

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Quantum free electron theory has successfully explained following observed experimental facts whereas the classical free electron theory failed.

i) Specific heat:

According to quantum free electron theory, it is only those electron that are occupying energy levels close to E_F , which are capable of absorbing the heat energy to get excited to higher energy levels.

Hence only a small percentage of the conduction electrons are capable of receiving the thermal energy input, thus the specific heat value becomes very small for the metal.

According to quantum free electron theory, it can be shown

$$\Box 2k \Box$$
 $C_v \Box \Box^{\Box} \Box \underline{\qquad} E_F \Box^{\Box} \Box RT$

Considering
$$E_F = 5 \text{ eV} \left(\frac{2k}{E_F}\right) \approx 10^{-4}$$

 $\Box C_V \Box 10^{\Box 4} RT$ which is close to experimental value.

ii) Temperature depends on electrical

conductivity:

Experimentally electrical conductivity $\Box^{\text{expt}} \, \Omega \frac{1}{\tau}$

According to quantum free electron theory electrical conductivity is given by

Where m* is called effective mass of an electron.

According to quantum free electron theory E_F and V_F are independent of temperature. The dependence of λ & T is as follows

Conduction electrons are scattered by the vibrating ions of the lattice. As the temperature increases the vibrational cross sectional areas (πr^2) increases and hence mean free path decreases.

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The mean free path of the electrons is given by

1
$$\Box\Box$$
 ______2 Where 'r' is the amplitude of vibrations of lattice ions $\Box r$

Considering the facts the energy of vibrating body is proportional to the square of amplitude and the energy of ions is due to the thermal energy.

The thermal energy is proportional to the temperature T'.

We can write $r^2 \alpha T$

 \square λ α 1/T substituting for λ in eqn (1)

Hence
$$\sigma_{QFT} \stackrel{\Omega}{=} \frac{1}{r}$$

Thus σ_{OFT} a $\frac{1}{r}$ is correctly explained by quantum free electron theory.

iii) Electrical conductivity and electron concentration:

Aluminium and gallium which have three free electrons per atom have lower electrical conductivity than that of copper and silver, which have only one free electron per atom.

As per quantum free electron the electrical conductivity is

$$ne^2\square$$
 $\square m^* V_F \square$
i.e $\sigma \alpha$ (n) and $\sigma \alpha$ (λ/V_F)

The value of (n) for aluminium is 2.13 times higher than that of copper. But the value of (λ/v_f) for copper is about 3.73 times higher than that of aluminium. Thus the conductivity of copper exceeds that of aluminium.

Physics of Semiconductors:

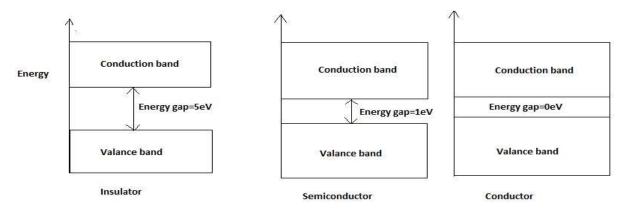
Semiconductors are materials whose electrical conductivity lies between conductors and insulators. The conductivity of semiconductors is in the order of 10^4 to 10^{-4} mho/m.

Valance band: Energy level occupied by valance electrons is called valance band. Valance band may be fully filled or partially filled at O k

Conduction band: Energy level occupied by conduction electrons (free electrons) is called conduction band. The conduction band is an empty band at $O\ k$

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Forbidden energy gap: The separation between valance band and conduction band is known as forbidden energy gap. The energy gap is measured in electron volt (eV).



Fermi level in intrinsic semiconductor

Fermi level represent the average energy of conduction electrons.

For a semiconductor at T=0K all the energy levels in the valance band are completely filled and all energy levels in conduction band are empty. At room temperature due to thermal excitation some of the electron will jump to bottom of conduction and return soon to the energy levels in top of valance band. Therefore conduction electrons are distributed between top of valance band and bottom of conduction band. Hence the average energy of electrons will be equal to (1/2) Eg. Thus Fermi level lies at the middle of the forbidden energy gap for an intrinsic semiconductor.

Concentration of electrons and holes in intrinsic semiconductors:

The number of electrons in conduction band per unit volume of a material is called electron concentration and is given by

$$N_e = \frac{4\sqrt{2}}{h^3} (\pi m_e * KT)^{3/2} e^{\frac{Ef - Eg}{KT}}$$

Where, m* is the effective mass of

electrons k is the Boltzmann

constant

E_f is the Fermi

level E_g is the

energy gap h is

Planck's constant

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Similarly, the number of holes in valance band per unit volume of a material is called holes concentration and is given by

$$N_{\rm h} = \frac{4\sqrt{2}}{h^2} (\pi \ m_{\rm h} * KT)^{3/2} \, e^{\frac{-Ef}{KT}}$$

mh* is the effective mass of holes

Relation between fermi energy and energy gap in an intrinsic semiconductor

For intrinsic semiconductor the number of electrons in conduction band is equal to the number of holes in valance band

$$i.e Ne = Nh$$

$$N_{e} = \frac{4\sqrt{2}}{h^{3}} (\pi \ m_{e} * KT)^{3/2} e^{\frac{Ef - Eg}{KT}} = N_{h} = \frac{4\sqrt{2}}{h^{3}} (\pi \ m_{h} * KT)^{3/2} e^{\frac{-Ef}{KT}}$$

$$\left((m^{*}_{e})^{3/2} \right) e^{\frac{E_{F - Eg}}{KT}} = \left((m^{*}_{h})^{3/2} \right) e^{\frac{-E_{F}}{KT}}$$

$$e^{\frac{2E_{F - Eg}}{KT}} = \left(\frac{m^{*}_{e}}{m^{*}_{h}} \right)^{3/2}$$

By taking natural log on both sides

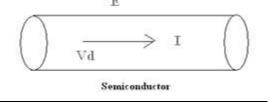
$$\frac{2E_{F} - E_{g}}{KT} = \frac{3}{2} \ln \left(\frac{m_{e}^{*}}{m_{h}^{*}} \right)$$

$$\mathbf{Or} E_{F} = \frac{3}{4} KT \ln \left(\frac{m_{e}^{*}}{m_{h}^{*}} + \frac{E_{g}}{2} \right)$$

Since $m_e^* = m_h^*$ and $\ln 1 = 0$

$$E_F = \frac{E_g}{2}$$

Expression for electrical conductivity of semiconducting materials:



Consider a semiconductor of area of cross section A, carrying a current I. Let V_d be the drift velocity of the charge carriers.

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In the presence of electric field, both electrons and the holes contribute to the conductivity of the semiconductor. Let us consider first the conductivity in a semiconductor is due to the flow of electrons only.

 $N=N_e$ = concentration of charge carriers (electrons)

The current density of electrons is given by $J_e = N_e e V_d$ (2) [J = I/A]

Vd

The quantity $\underline{}$ is a constant, specific for a particular type of charge carriers

and is called mobility of charge carriers. i.e., $\frac{Vd}{\textit{E}} = \mu$

 $V_d = \mu_e E$ in the above equation

$$J_e = N_e e \mu_e E$$
(3)

But current density is given by

$$J_e = \sigma_e E \qquad(4)$$

$$O_e = \frac{J}{E}$$

$$\sigma_e = N_e e \mu_e \dots (5)$$

eqn(5) represents the conductivity due to electrons in conduction band.

similarly the conductivity due holes in valance band is given by

$$\sigma_h = N_h e \mu_h \dots (6)$$

Total conductivity

$$\sigma = \sigma_e + \sigma_h = e (N_e \mu_e + N_h \mu_h)$$

$$\sigma = e (N_e \mu_n + N_h \mu_h)$$

For intinsic semiconductors

$$N_e = N_h = n_i$$

Hence the expression for conductivity in intrinsic semiconductor is given by

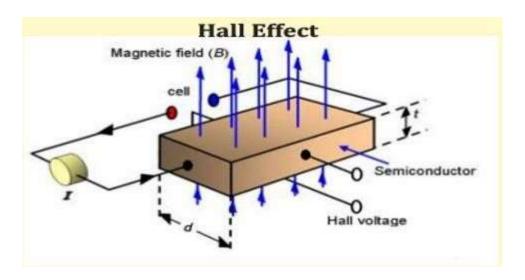
$$\sigma = \mathbf{n}_i \mathbf{e} (\mu_e + \mu_h)$$

Hall Effect:

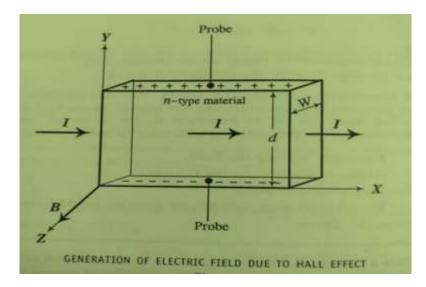
"When a current carrying conductor / semiconductor subjected to external magnetic field perpendicular to the direction of current. The electric field induced (produced) across the material in a direction perpendicular to both the magnetic field and direction of current flow". This phenomenon is called Hall Effect.

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Expression for Hall coefficient and Hall voltage:



Consider a rectangular n -type semiconductor material in which current is flowing in +ve $\, x$ -direction.

Let the magnetic field (B) applied along z-direction.

Therefore, the electrons experience the Lorentz force (F_L) along –ve y-direction given by, $F_L = -Bev \dots (1)$

Therefore, the electrons density increases in lower surface and in the upper surface become positively charged due to deficiency of electrons. Hence the potential developed between two surfaces called Hall voltage, which produces an electric field E_H called Hall field (E_H).

The electrons exerts an upward force FH due to the Hall field and is given by,

$$F_H = -eE_H \dots (2)$$

Equating equations (1) and (2)

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$$-eE_H = -BeV_d$$

$$E_H = BV_d$$
(3) $V_d \rightarrow drift$ velocity.

If "d" is the distance between upper and lower surface then

$$E_H = V_H/d$$

$$V_H = E_H d$$
 (from 3)

$$V_H = BV_dd$$
(4)

The current density $J = I / A = neVd = \rho V_d$ (5)

Therefore, $\rho = ne$

For the given semiconductor, $J = I/A = \frac{I}{\omega d}$

..... (6) ω —thickness of the material . therefore

(A =
$$\omega$$
 d) equating (5) & (6)
$$\rho V_d = \frac{l}{\omega d} V_d$$

$$= \frac{I}{\rho \omega d} \qquad (7) Substituting eqn (7) in$$

$$V_{H} = \frac{B d I}{\rho \omega d} = \frac{B I}{\rho \omega}$$
.....

(8)
$$\rho = \frac{BI}{VH\omega}$$

Expression for Hall coefficient:

Since, E_H a J B

$$E_H = R_H J B$$
 ($R_H \rightarrow Hall coefficient$)

$$R_H = E_H / J B$$
 [From eqn (3) and (5)]

$$R_{H} = BV_{d} / \rho V_{d} B = 1 / \rho = 1 / ne$$

$$R_{H} = 1 / ne$$
(9) The

above expression represents Hall coefficient.

Expression for Hall Voltage:

From (8)
$$V_{H} = \frac{BI}{\rho\omega} = \frac{RHBI}{\omega}$$
 (since, $R_{H} = \frac{1}{\rho} = \frac{1}{ne}$)
$$V_{H} = \frac{RHBI}{\omega}$$

The above expression represents **Hall voltage**.

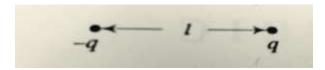
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DIELECTRIC MATERIALS

Dielectric materials are nothing but insulators which have the ability to get electrically polarized with the application of external electric field.

Examples: Glass, rubber, plastic, mica.

Electric dipole:



Two equal and opposite charges separated by a distance is called dipole.

The product of one of the charge and distance of separation between them is called dipole moment (μ).

$$\mu = q 1$$

Polarization: The displacement of charges in the atoms or molecules of a dielectric under the action of an applied electric field loads to the development of dipole moment is called polarization.

Types of dielectric materials:

Polar dielectrics: In some dielectric materials, the effective centers of the negative and positive charges in the molecules do not coincide with each other and exhibit permanent dipoles in the absence of electric field are called polar dielectrics. **Example**: H₂O.

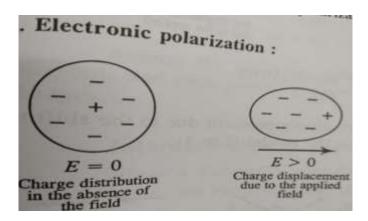
Non polar dielectrics: In some dielectric materials, the effective centers of the negative and positive charges in the molecules do not coincide with each other and do not exhibit permanent dipoles in the absence of electric field are called non polar dielectrics. **Examples:** paper, wood, glass.

TYPES OF POLARIZATION MECHANISMS:

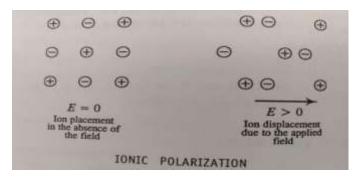
Electronic Polarization: The electronic polarization occurs due to displacement of the positive and negative charges in a dielectric material with the application of external electric field, which leads to development of dipole moment. The electronic polarizability is given by,

$$\alpha e = \epsilon_0 (\epsilon r - 1) / N$$
.

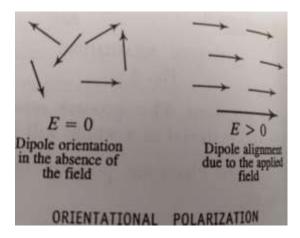
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➤ **Ionic Polarization:** This is kind of polarization occurs in some dielectric materials which have ionic bonds like Nacl. When ionic solids are subjected to an external electric field, the adjacent ions of opposite sign undergo displacement. The distance of separation between the ion pair depends on the location of atoms in the lattice results in the development of dipole moment



➤ **Oriental Polarization:** This type of polarization occurs in polar dielectric material. (Permanent dipoles).



The orientation of molecules is random in the absence of electric field; therefore net dipole moment in the material is zero. But under the influence

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of an applied electric field each dipole reorient along the field direction. Thus the material develops an electrical polarization. This type of polarization is temperature dependent. In polar dielectrics the orientation polarizability α_0 is given by α_0 = μ^2 / 3KT

➤ Space charge Polarization: It occurs in multiphase dielectric materials in which change in resistivity between different phases. When such materials subjected to external electric field at high temperatures, the charges get accumulated at the interface leads to change in conductivity across the material.

Relation between Polarization and Dielectric constant:

For isotropic materials, the applied electric field (E), flux density (D) are related by

$$D = \epsilon_0 \epsilon_r E$$

 $\epsilon_0 \rightarrow \text{ dielectric constant of vacuum}$

 $\epsilon \rightarrow$ relative dielectric constant of the material

The relation between dielectric er and polarization p is given by $P = \mathcal{E}_0(\mathcal{E}_r - 1)$ E

Internal fields in solids: When dielectric material subjected to an external electric field, each atom develops a dipole moment and acts as electric dipole. Hence the field at any given atom will be the applied electric field and the electric field due to the surrounding dipoles. "The internal field is the electric field that acts at the site of any atom of a solid subjected to an external external electric field and is the resultant of the applied field and the field due to all the surrounding dipoles".

In one dimension the internal field is given by

$$E_i = E_{applied} + E_{dipoles} E_i = E + (\frac{v}{\epsilon \cdot 0})P$$
 where

 $v \rightarrow$ internal field constant, $p \rightarrow$ polarization

For, 3D the internal field is **called Lorentz field** and is given by

$$\mathbf{E}_{\mathbf{Lorentz}} = \mathbf{E} + \frac{P}{360}$$

Clausius - Mossotti Equation:

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Consider a solid dielectric material with dielectric constant Er. If 'n' is the number of atoms/unit volume and ' μ ' is the dipole moment of the atoms in the material.

Therefore, the dipole moment / unit volume = N μ (1)

The field experienced by the atom is an internal field Ei. ae is the electronic polarizability of the atoms.

Then dipole moment / unit volume = $N\alpha_e E_i$

The dipole moment $\mu = \alpha_e \operatorname{Ei}$ (2)

Dipole moment / unit volume is nothing but polarization (P)

 $P = N \alpha_e E_i$

$$E_i = \frac{P}{N\alpha e}$$
(3) we have $P = E0$ (Er -1) E

$$E = \frac{P}{60 (6r - 1)} \qquad \dots (4)$$

The expression for internal field for 3D material is given by $E_i = E + \frac{P}{360}$ Substituting (3) and (4) in the above equation

$$\begin{split} \frac{P}{N\alpha e} &= \frac{P}{\epsilon 0 (\epsilon r - 1)} + \frac{P}{3\epsilon 0} \\ \frac{1}{N\alpha e} &= \frac{1}{\epsilon 0 (\epsilon r - 1)} + \frac{1}{3\epsilon 0} = \frac{1}{\epsilon 0} \left[\frac{1}{(\epsilon r - 1)} + \frac{1}{3} \right] \end{split}$$

$$\frac{\epsilon r - 1}{\epsilon r + 2} = \frac{N\alpha e}{3 \epsilon 0}$$

This is called Clausius Mossotti equation.