

Electrical Conductivity in Solids

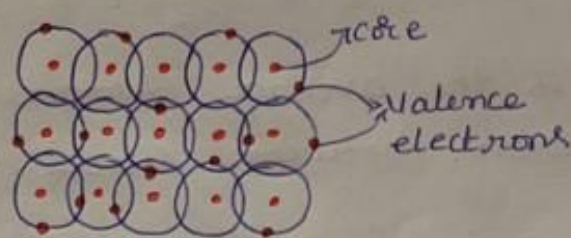
Review of classical free electron theory

Concept of Free electron / Drude - Lorentz Theory

All metal atoms consist of valence electrons. These valence electrons are responsible for electrical conduction in the bulk state of a metal.

We can consider the case of copper as an example for metals. A copper atom consists of 29 electrons out of which 28 electrons fill the first 3 shells & form the core part. The remaining lone electron of the atom will be present in the fourth shell & it is called as the valence electron of the copper atom. It is very loosely bound in the atom.

When a large number of copper atoms join to form a metal, the boundaries of the neighbouring atoms slightly overlap on each other. Due to such overlapping, though the core electrons remain unaffected, the valence electrons find continuity from atom to atom, and thus can move easily throughout the body of the metal.



Boundary overlapping

The free movement of electrons means that none of them belongs to any atom in particular, but each of them belongs to the metal to which they are confined to. Thus, each such electron is named a free electron. Since the free electrons are responsible for electrical conduction in a solid, they are also called conduction electrons.

Lattice: The displacement of a valence electron from the parent atom, results in a virtual loss of one negative charge for that atom. Consequently, the electrical neutrality of the atom is lost & it becomes an ion. The structure formulation due to the array of such fixed ions in three dimensions is called Lattice.

Thermal velocity (v_{th})

The velocity with which the free electrons keep moving due to thermal agitation is called thermal velocity.

Drift velocity (v_d)

When an electric field is applied, there will be a net displacement in the randomly moving free electron positions with time in a direction opposite to the direction of the field. This displacement per unit time is called drift velocity.

Mean free path (λ)

Mean free path is the average distance travelled by the conduction electrons between successive collisions with the lattice ions.

Mean collision time (τ)

The average time that elapses b/n two consecutive collisions of an electron with the lattice points is called mean collision time.

$$\tau = \frac{\lambda}{v}$$

$\lambda \rightarrow$ Mean free path

$v \rightarrow$ total velocity [Thermal velocity + Drift velocity]

Relaxation Time (T_r)

Relaxation time is the time required for the average velocity of free electrons to reduce to $(1/e)$ times its value that existed when the field is just turned off.

Current Density (J)

It is the current density per unit area of cross section of an imaginary plane held normal to the direction of current in a current carrying conductor.

$$J = \frac{I}{A} \quad \text{A/m}^2$$

$I \rightarrow$ current flowing in conductor

$A \rightarrow$ Area of cross section

Electric field (E)

The potential drop per unit length of a conductor is known as electric field.

$$E = \frac{V}{L}$$

$V \rightarrow$ potential difference b/n two ends

$L \rightarrow$ Length of a conductor of uniform cross section

Electrical Conductivity (σ)

It is a physical property that characterizes the conducting ability of a material. It is given by the inverse of resistivity.

$$\sigma = \frac{1}{\rho}$$

$$\sigma = \frac{L}{RA}$$

Mobility of electrons (μ)

The mobility of electrons is defined as the magnitude of the drift velocity acquired by the electrons in a unit field.

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

$v_d \rightarrow$ Drift velocity

$E \rightarrow$ Applied field

Expression for Drift velocity is given by,

$$v_d = \frac{eE}{m} \tau$$

$$\therefore \mu = \frac{1}{E} \left(\frac{eE}{m} \tau \right)$$

$$\boxed{\mu = \frac{e\tau}{m}}$$

Assumptions of free electron gas model

1) A metal contains a large number of free electrons which are free to move about in entire volume of the metal like the molecules of a gas in a container.

Hence they are assumed to obey the laws of kinetic theory of gases.

$$\frac{3}{2} kT = \frac{1}{2} m v_{th}^2$$

2) The free electrons move in random directions & collide with either positive ions fixed in the lattice or other free electrons. All the collisions are elastic & there is no loss of energy.

3) The free electrons are moving in a completely uniform potential field due to the ions fixed in the lattice.

4) The velocity & the energy distribution of free e^- obey the classical Maxwell Boltzmann statistics.

Expression for the electrical conductivity

When an electric field ' E ' is applied to an electron of charge ' e ' of a metallic rod, the electron moves in opposite direction to the applied field with a velocity v_d .

Lorentz force acting on the electron,

$$F = eE \rightarrow (1)$$

This force is known as the driving force of the electron.

Due to this force, the electron gains acceleration ' a '.

From Newton's second law of motion,

$$F = ma \rightarrow (2)$$

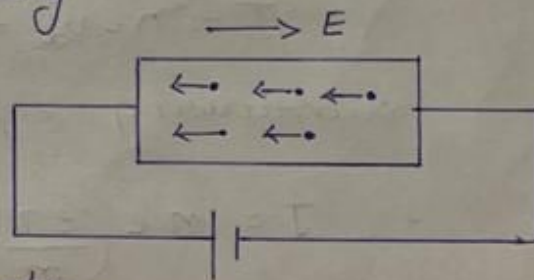
Equating eqⁿs (1) & (2), we get

$$ma = eE$$

$$a = \frac{eE}{m} \rightarrow (3)$$

$$\text{Acceleration} = \frac{\text{Drift velocity}}{\text{Relaxation Time}}$$

$$a = \frac{v_d}{\tau}$$



$$v_d = a \tau \rightarrow (4)$$

Substituting eqⁿ (3) in (4), we get

$$v_d = \left(\frac{e \tau}{m} \right) E \rightarrow (5)$$

According to Ohm's law, current density can be expressed as,

$$J = \sigma E$$

$$\sigma = \frac{J}{E} \rightarrow (6)$$

$\sigma \rightarrow$ Electrical conductivity of the electron.

But, the current density in terms of drift velocity is given as,

$$J = n e v_d \rightarrow (7)$$

Substituting eqⁿ (5) in (7), we get

$$J = n e \left(\frac{e \tau}{m} \right) E$$

$$\frac{J}{E} = \frac{n e^2 \tau}{m} \rightarrow (8)$$

Comparing eq^{ns} (6) and (8), we get

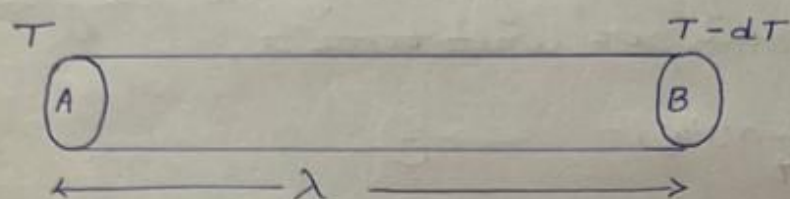
$$\sigma = \frac{n e^2 \tau}{m}$$

Hence, the required expression.

Thermal Conductivity (K)

Thermal Conductivity is defined as the amount of heat flowing per unit time through the material having unit area of cross-section per unit temp gradient.

Expression for Thermal Conductivity of a Metal



Consider two cross sections A and B in a uniform metallic rod AB separated by a distance λ . Let 'A' at a high temperature 'T' and 'B' at low temperature ($T - dT$). Now heat conduction takes place from A and B by the electrons.

Let the conduction electron per unit volume is 'n' and average velocity of these electrons is 'v'. During the movement of electrons in the rod, collision takes place. Hence, the electrons near 'A' lose their kinetic energy while electrons near 'B' gain kinetic energy.

Average kinetic energy of an electron at A, is

$$KE_{(A)} = \frac{3}{2} K_B T \rightarrow (1)$$

Average kinetic energy of an electron at B, is

$$KE_{(B)} = \frac{3}{2} K_B (T - dT) \rightarrow (2)$$

The excess of kinetic energy carried by the electron from A to B is,

$$\frac{3}{2} K_B dT \rightarrow (3)$$

Number of electrons crossing per unit area per time from A and B is,

$$\frac{1}{6} n v$$

The excess of energy carried from (A to B) per unit area in time is $= \frac{1}{4} n v K_B dT \rightarrow (4)$

Similarly, the deficient of energy carried from B to A per unit area per unit time is,

$$= -\frac{1}{4} n v K_B dT \rightarrow (5)$$

Hence, the net amount of energy transferred from A to B per unit area per unit time is,

$$Q = \frac{1}{2} n v K_B dT \rightarrow (6)$$

But from the basic definition of thermal Conductivity, the amount of heat conducted per unit area per unit time is,

$$Q = K \frac{dT}{\lambda}$$

$$\text{ie } \frac{1}{2} n v K_B dT = K \frac{dT}{\lambda}$$

$$\therefore \boxed{K = \frac{1}{2} n v K_B \lambda} \rightarrow (7)$$

We know that for the metals, $\tau = \tau_r$

$$\tau = \frac{\lambda}{v} \Rightarrow \lambda = \tau v \rightarrow (8)$$

Substituting eqⁿ (8) in (7), we get

$$K = \frac{1}{2} n v K_B (\tau v)$$

$$\boxed{K = \frac{1}{2} n v^2 K_B \tau}$$

Hence, the required expression

Density of States

The Density of states can be explained using Quantum free electron theory.

According to Quantum free electron theory, the electron is treated as wave and its Energy and velocity is given by Fermi-Dirac distribution function. The electrons must obey the Pauli's Exclusion principle.

According to this theory, the energy of the particle (electron) is given by,

$$E_n = \frac{n^2 h^2}{8ma^2} \rightarrow \text{①}$$

The lowest energy of the particle is obtained by putting $n=1$. i.e.

$$E_1 = \frac{h^2}{8ma^2}$$

Now, the density of state is defined as the number of electronic states per unit energy range.

WKT

$$E_n = \frac{h^2}{2m} \left(\frac{n}{2a} \right)^2 \quad [\text{From eqn 1}]$$

Differentiating above eqn,

$$dE_n = \frac{h^2}{2m} \left(\frac{n}{2a} \right) \frac{dn}{2a}$$

Where $\frac{dn}{dE_n}$ represents number of Energy level per unit energy.

$\therefore g(E) = 2 \frac{dn}{dE_n} \rightarrow$ Density of states of a free electron gas.

Density of States $g(E)dE$

It is defined as the number of available electron states per unit volume in an energy interval E and $E+dE$. It is denoted by $Z(E)dE$.

Carrier Concentration

The number of electrons per unit volume in a given energy interval is calculated by assuming the product of the density of states $Z(E)$ & the occupation probability $F(E)$.

Such number of electrons per unit volume is known as carrier concentration.

$$n_e = \int Z(E) F(E) dE$$

$$Z(E) = \frac{4\pi}{h^3} (2m)^{3/2} E^{1/2} dE$$

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

$$\therefore n_e = \int \frac{4\pi}{h^3} (2m)^{3/2} E^{1/2} \frac{1}{1 + e^{\left(\frac{E-E_F}{kT}\right)}} dE$$

Wiedemann - Franz Law

The law states that the ratio of thermal conductivity to electrical conductivity of the metal is directly proportional to the absolute temperature of the metal.

WKT

$$\sigma = \frac{ne^2\tau}{m} \rightarrow \textcircled{1}$$

$$K = \frac{1}{2} n v^2 K_B T \rightarrow (2)$$

$$\frac{\text{Thermal Conductivity}}{\text{Electrical Conductivity}} = \frac{K}{\sigma} = \frac{\frac{1}{2} n v^2 K_B T}{n e^2 \tau / m}$$

$$\frac{K}{\sigma} = \frac{1}{2} \frac{m v^2 K_B}{e^2} \rightarrow (3)$$

WKT, Kinetic energy of an electron is given by

$$\frac{1}{2} m v^2 = \frac{3}{2} K_B T \rightarrow (4)$$

Substituting eqⁿ (4) in (3), we get

$$\frac{K}{\sigma} = \left(\frac{3}{2} K_B T \right) \frac{K_B}{e^2}$$

$$= \frac{3 K_B^2 T}{2 e^2}$$

$$= \frac{3}{2} \left(\frac{K_B}{e} \right)^2 T$$

$$\frac{K}{\sigma} = L T$$

where $L = \frac{3}{2} \left(\frac{K_B}{e} \right)^2$ is a constant & it is known as Lorentz number.

$$\therefore \boxed{\frac{K}{\sigma} \propto T}$$

Hence, it is proved that the ratio of thermal conductivity of a metal is directly proportional to the absolute temperature of the metal.

Limitations of Classical Free Electron Theory

- 1) The free electron theory completely fails to explain the heat capacity of conduction electrons & also electronic specific heat.
- 2) It fails to explain the superconducting properties of metals.
- 3) It fails to explain photo-electric, Compton effect & black body radiation.
- 4) Classical free electron model predicts the incorrect temperature dependence of σ .
- 5) It also fails to give correct mathematical expression for thermal conductivity.

Introduction to Semiconductors

Semiconductor

A semiconducting material has electrical conductivity considerably greater than that of an insulator but significantly lower than that of a conductor. The value of resistivity varies from 10^{-4} to 0.5 ohm metre .

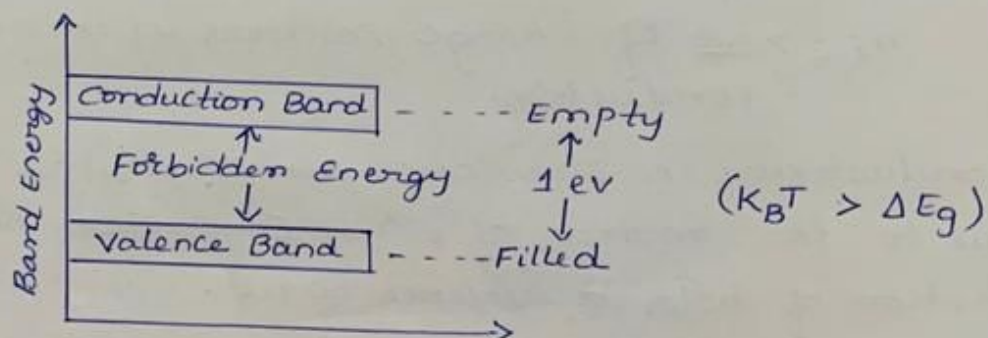
properties of Semiconductor

- 1) The resistivity lies between 10^{-4} to 0.5 ohm metre .
- 2) At 0K , they behave as insulators.
- 3) The conductivity of a semiconductor increases both due to the temperature & impurities.
- 4) They have negative temperature coefficient of resistance.
- 5) In semiconductors both the electron & holes are charge carriers & will take part in conduction.

Types of Semiconductors

(i) Intrinsic Semiconductor

Semiconductor in a pure form is called intrinsic semiconductor.



At higher temperatures such that the thermal energy $k_B T$ is more than the Energy gap ΔE_g . Some of the valence electrons are also able to jump over the gap into the conduction band.

This creates free electrons in the conduction band and free holes in valence band. Thus the electron-hole pairs are thermally generated & can carry a small current through the solid.

Therefore when the conductivity in crystalline semiconductor is only due to breaking of covalent bonds of electron in the valence band, then the substance is said to be intrinsic semiconductor.

The number of electrons in conduction band & the number of holes in valence band increase simultaneously with increase in temperature. So these semiconductors have negative temp coefficient.

No of electrons in conduction band (n) and no of holes in valence band (p) are always same.

$$\text{ie } n = p$$

$$n = p = n_i$$

$n_i \rightarrow$ No of charge carriers in intrinsic semiconductor.

conductivity in intrinsic semiconductor is caused due to the motion of e^- s in conduction band and motion of holes in valence band.

Ex: Silicon, Germanium.

Fermi Level in an Intrinsic Semiconductor

The maximum energy that electrons may possess at 0 K is known as Fermi energy. The level corresponding to the Fermi energy is known as the Fermi level.

The position of Fermi level in an intrinsic semiconductor can be calculated in the following way that the Fermi level will be somewhere in the forbidden gap. Since all the valence band states are occupied and few electrons will be present in the conduction band.

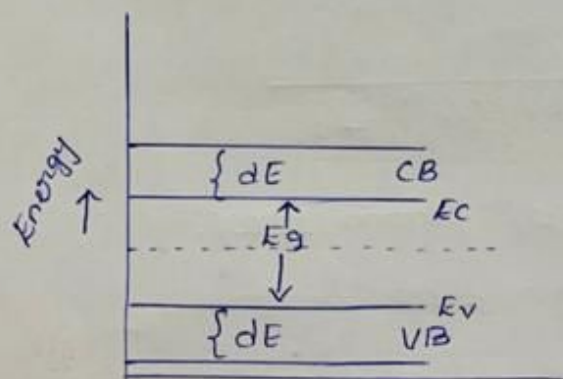
To check the position of Fermi level, a Fermi factor is introduced, which is the number that expresses the probability that a state of energy (E) is occupied by an electron under the condition of thermal equilibrium.

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

where $k \rightarrow$ Boltzmann Constant

$T \rightarrow$ Temp in Kelvin

$E_F \rightarrow$ Fermi level



The Energy level E_c is conduction band & E_v is valence band which are symmetrically placed about the centre of the energy gap E_g .

The number of electrons in conduction band is
 $n(E_c) dE = g(E_c) f(E_c) dE \rightarrow (1)$

The number of holes in valence band is

$$p(E_v) dE = g(E_v) [1 - f(E_v)] dE \rightarrow (2)$$

$g(E_c) = g(E_v) \rightarrow$ Represents the no of available state in conduction & valence region are same.

$f(E_c)$ & $f(E_v) \rightarrow$ Represents the Fermi factor

$$\frac{n(E_c)}{p(E_v)} = \frac{f(E_c)}{[1 - f(E_v)]} \rightarrow (3)$$

$$\text{WKT } f(E_c) = \frac{1}{e^{(E_c - E_F / k_B T)} + 1} \rightarrow \text{Fermi factor}$$

Since $E_c > E_F$, $\exp\left(\frac{E_c - E_F}{kT}\right) \gg 1$

$$\therefore f(E_c) = e^{-\left(\frac{E_c - E_F}{kT}\right)}$$

$$\& f(E_c) = e^{(E_F - E_c / kT)} \rightarrow (4)$$

Similarly $E_v \rightarrow$ valence level is much below than E_F .

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

where $E_F - E_v \gg kT$ at room temp.

Hence the above expression becomes,

$$[1 - f(E_v)] \simeq 1 - \left[1 - e^{\left(\frac{E_v - E_F}{kT}\right)}\right]$$

$$[1 - f(E_v)] \simeq e^{\left(\frac{E_v - E_F}{kT}\right)} \rightarrow (5)$$

\therefore eqⁿ (3) becomes,

$$\frac{n(E_c)}{p(E_v)} = \frac{e^{\left(\frac{E_F - E_c}{kT}\right)}}{e^{\left(\frac{E_v - E_F}{kT}\right)}}$$

Since $(E_c - E_F) \gg kT$ & $(E_F - E_v) \gg kT$ at room temperature,

$$\frac{n(E_c)}{p(E_v)} = \frac{E_F - E_c / kT}{E_v - E_F / kT} \rightarrow (6)$$

For intrinsic semiconductor, $n_i = p_i$

$$\therefore \frac{n(E_c)}{p(E_v)} = \frac{n_i}{p_i} = 1$$

\therefore Eqⁿ (6) becomes

$$\frac{E_F - E_c}{kT} = \frac{E_v - E_F}{kT}$$

$$E_F - E_c = E_v - E_F$$

$$E_F + E_F = E_v + E_c$$

$$2E_F = E_v + E_c$$

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

This shows that Fermi level lies at the centre of energy gap for intrinsic semiconductor & it is independent of temperature.

Other form

For an intrinsic semiconductor, the number of holes per unit volume in valence band is equal to number of electrons/unit volume in conduction band.

$$N_e = N_h$$

WKT

$$N_e = \frac{4\sqrt{2}}{h^3} (\pi m_e^* kT)^{3/2} e^{\left(\frac{E_F - E_g}{kT}\right)}$$

$$N_h = \frac{4\sqrt{2}}{h^3} (\pi m_h^* kT)^{3/2} e^{-E_F/kT}$$

$$\therefore \frac{4\sqrt{2}}{h^3} (\pi m_e^* kT)^{3/2} e^{\left(\frac{E_F - E_g}{kT}\right)} = \frac{4\sqrt{2}}{h^3} (\pi m_h^* kT)^{3/2} e^{-E_F/kT}$$

$$(m_e^*)^{3/2} e^{\left(\frac{E_F - E_g}{kT}\right)} = (m_h^*)^{3/2} e^{-E_F/kT}$$

$$\frac{e^{\left(\frac{E_F - E_g}{kT}\right)}}{e^{-E_F/kT}} = \left(\frac{m_h^*}{m_e^*}\right)^{3/2}$$

$$e^{\left(\frac{2E_F - E_g}{kT}\right)} = \left(\frac{m_h^*}{m_e^*}\right)^{3/2}$$

Taking natural logarithm on both sides, we get

$$\frac{2E_F - E_g}{kT} = \frac{3}{2} \ln\left(\frac{m_h^*}{m_e^*}\right)$$

$$2E_F - E_g = \frac{3}{2} kT \ln\left(\frac{m_h^*}{m_e^*}\right)$$

$$2E_F = \frac{3}{2} kT \ln\left(\frac{m_h^*}{m_e^*}\right) + E_g$$

$$\therefore E_F = \frac{3}{4} kT \ln\left(\frac{m_h^*}{m_e^*}\right) + \frac{E_g}{2}$$

Under practical considerations, $m_e^* = m_h^*$, because of which the first term in the RHS of above equation goes to zero. Since $\ln 1 = 0$.

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

Thus, the Fermi level is in the middle of the band gap for an intrinsic semiconductor.

Extrinsic Semiconductors

The electrical conductivity of intrinsic semiconductors are very less. To increase the conductivity of intrinsic semiconductors, a small percentage of trivalent or pentavalent atoms are added to the pure semiconductor in the process of crystallification. Adding of impurities to the pure semiconductor is called as doping and it results in extrinsic semiconductor.

The conductivity of extrinsic semiconductor is much higher than pure semiconductor.

The impurity atom has a size which is almost of the same order of the host lattice. Basic structure of the crystal will not get altered after doping.

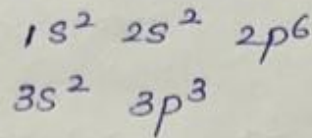
Types of Extrinsic Semiconductors

- 1) N-type
- 2) P-type

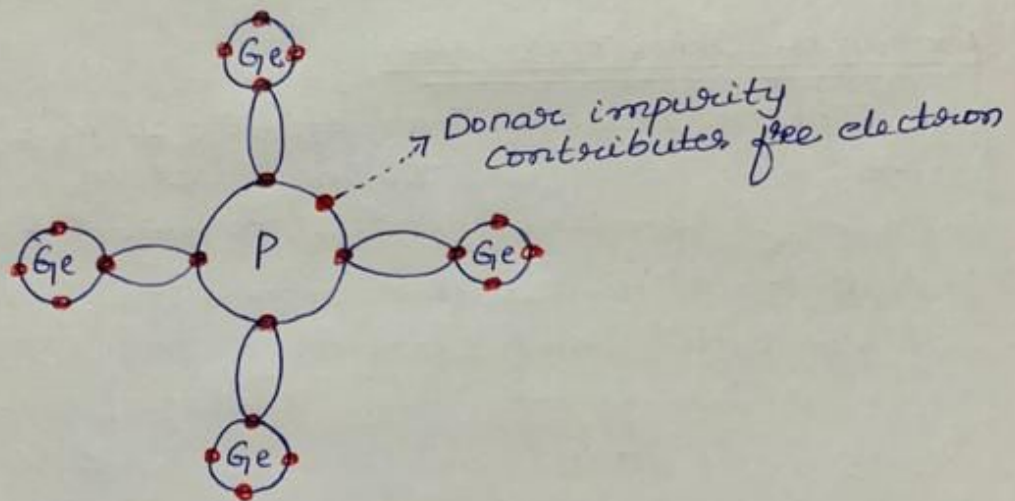
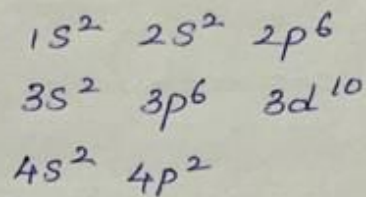
n-type Semiconductor

If a pentavalent impurity like phosphorus is introduced in the intrinsic semiconductor like Germanium, n-type semiconductor is obtained.

At no of phosphorus = 15



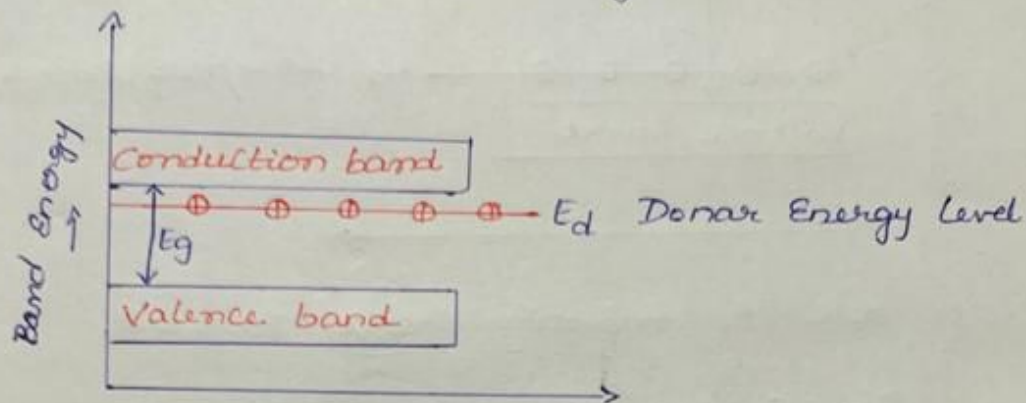
At no of Germanium = 32



out of 5 electrons of phosphorus, the 4 will form the covalent bond with the 4 electrons of Germanium, and 5th electron will be almost free. Thus every impurity atom contributes almost free electrons without creating a hole & these free electrons acts as carrier of current. A small amount of energy of Germanium is required to free the 5th electron from the impurity atom.

As these impurities donate excess electrons, so are called as donor impurities (n-type)

When donor impurities are added, the additional discrete levels are introduced just below the conduction band in the forbidden region (Energy gap). Electrons are the majority charge carriers.



Ex: Sb, P, Bi and As

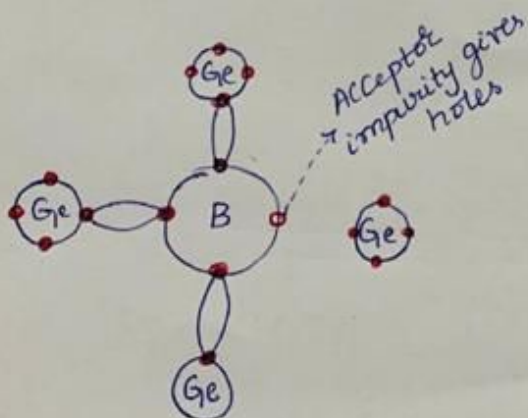
p-type Semiconductors

When trivalent impurity like Boron is added to the pure Germanium, results in p-type semiconductors. Here only 3 of the covalent bonds can be filled up and the vacancy that exists in the fourth bond contributes a hole.

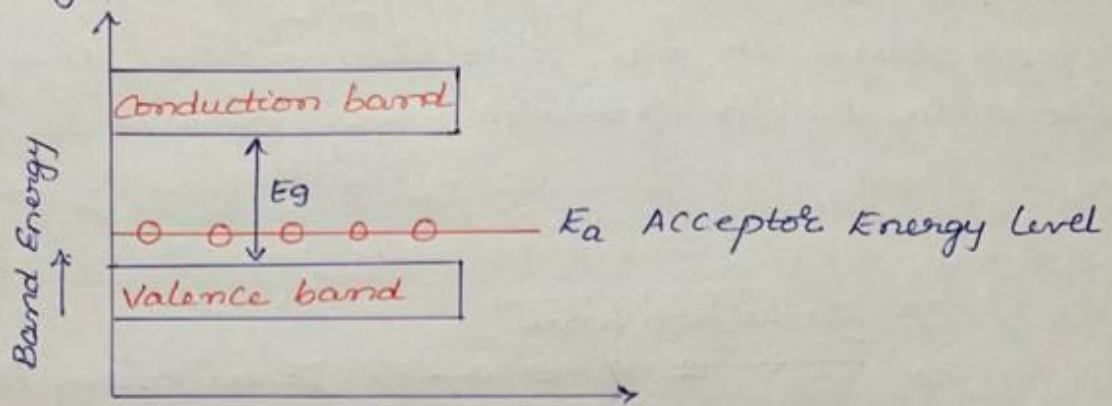
At no of Boron = 5
 $1s^2 2s^2 2p^1$

At no of Germanium = 32

$1s^2 2s^2 2p^6$
 $3s^2 3p^6 3d^{10}$
 $4s^2 4p^2$



Trivalent impurity creates a hole called as acceptor impurity.



Holes are the majority charge carriers.

Ex: Ga, B, In, Al