

Unit 2 Band theory of Solids

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- Introduction
- Formation of bands and energy gap- A quantum Mechanical Approach
- Kronig –Penny Model and E- K Diagram, Energy band Formation
- Fermi Dirac Distribution Function and Fermi level
- Classification of Solids : conductors, semiconductors and insulators
- Concept of Effective mass

Band Theory of Solids



Developed by
Felix Bloch in
1928 as Zome
theory

Formation

In the case of any isolated atom the electrons in any orbit has a definite energy. So they occupy discrete energy levels. And wide regions of forbidden energies separate the allowed energy levels.

Formation

Consider a large number of identical atoms, which are far enough apart such that their interactions are negligible. So each atom has the same energy level diagram.

In order to define any electronic state
4 quantum numbers are required:

- 1) Principle q. no. n : determines
size of electron orbit. It can have
only integral values
 $n = 1, 2, 3, \dots$

The corresponding electron orbits are denoted by K,L,M,N Respectively.

No. of electron that any orbit can accommodate is $2n^2$.

2) Orbital q. no. l : determines shape of electron orbit. It can have values $l = 1, 2, 3, \dots, (n-1)$.

the corresponding subshells are denoted as s, p, d, f.

No. of electrons contained in a subshell are $2(2l+1)$

- 3) Magnetic q. no. m : determines the orientation of electron orbit. It can have values $-l$ to $+l$ including zero. So for a given l , m has $(2l+1)$ values.
- 4) Spin q. no. s : *gives the direction of the spin or self rotation. It can have values $\pm 1/2$.*

These four quantum numbers define completely the state of electron in an atom. Different physical and chemical properties of various elements are due to different configuration of electrons in their atoms.

Now as per Pauli's exclusion principle, no two electrons can have the same set of quantum no. Hence an energy level cannot have more than two electrons. Thus the energy level occupied by an electron is discrete in an atom.

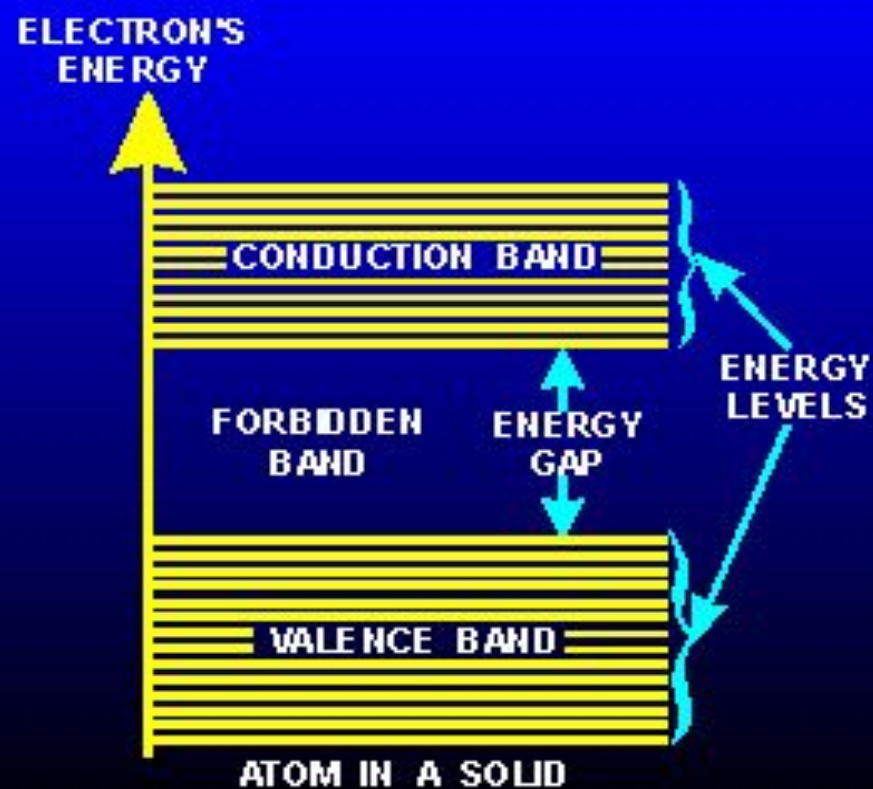
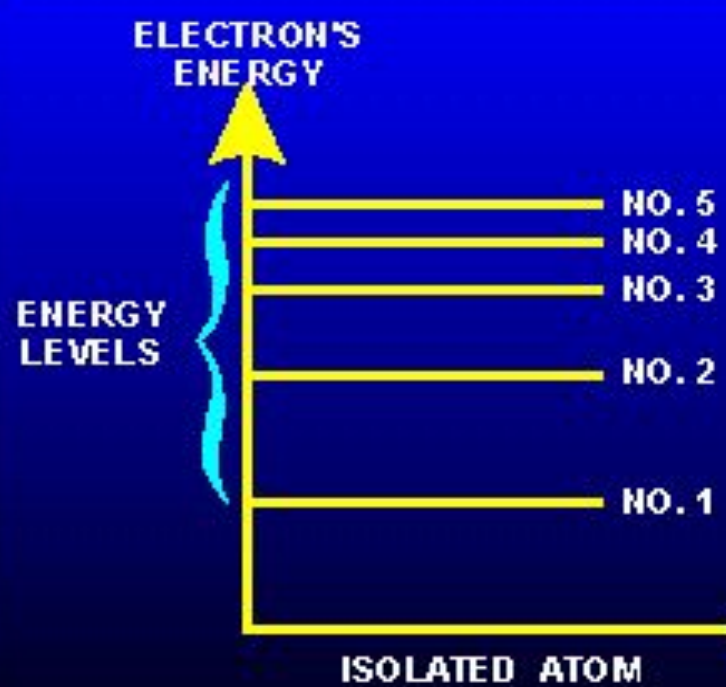
Now if two atom come closer to each other, they interact and there are significant changes in their energy levels. i. e. positive nucleus of one atom attracts the electrons and repels the nucleus of the adjacent atom.

In these process the energy levels of the inner shell electrons are not much affected by the presence of neighbouring atoms , but the outer shell electrons change considerably.

In order to obey Pauli's principle, when two atoms come nearer, new energy levels must be established, which are discrete but infinitesimally different. This group of closely spaced levels is called *band*.

Thus the range of energies possessed by an electron in a solid is known as energy band.

Each energy level of an isolated atom becomes a band in solid.



Consequently the 2s band in a solid contain N discrete energy levels and $2N$ electron, two in each energy level. Similarly each of the 2p level contain N energy levels and $2N$ electrons. Hence a broad 2p band contain $3N$ levels and $6N$ electrons.

So in general each energy band has a total of N individual levels and each energy band can hold a maximum of $2(2l+1)N$ electrons.

In an atom the inner shell electrons are tightly bound to the nucleus. While the outermost shell electrons are loosely bound. So the inner shells are completely filled and do not participate in conduction.

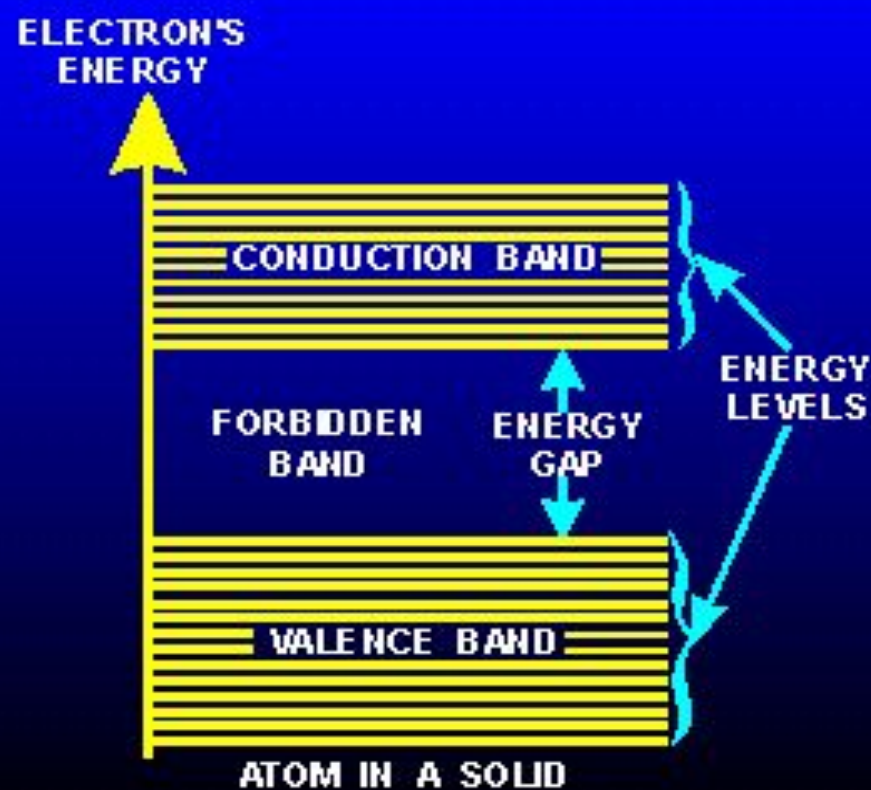
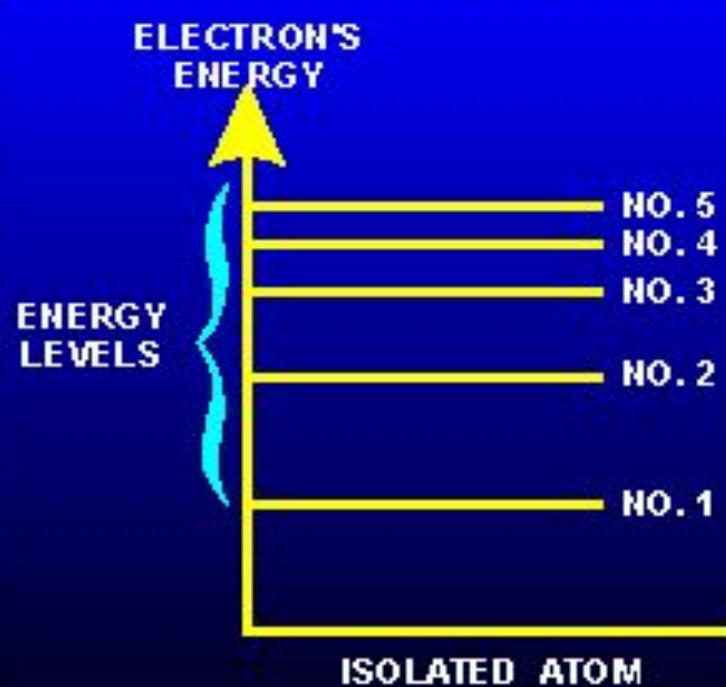
So during band formation the inner shells barely suffer any splitting. The outer shell levels are widely split and form wider bands.

The highest occupied band is called the **valance band** below which all the lower bands are occupied fully. The valalnce band may even be partially filled.

The empty band immediately above the valance band is the **conduction band**.

The gap between valance band and conduction band is called the energy band gap or forebidden band.

An energy band diagram is a graphic representation of energy levels associated with top energy band and the next lower energy band in a solid. The bottom of the conduction band show the smallest energy required by the electron to become free.



So according to the band theory, , a solid is characterized by the energy gap E_g separating the valance band and conduction band. The ability of conduction is decided by the order of magnitude of the energy gap E_g .

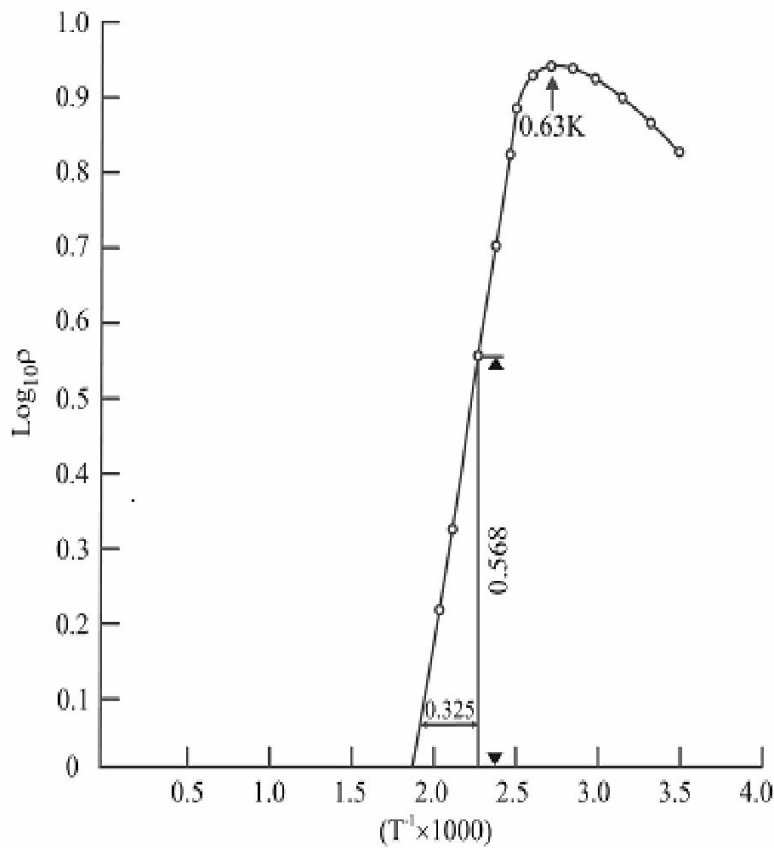
Band gap is proportional to the conductivity. $E_g = k_B T \ln \rho$

$$\rho = \frac{\rho_0}{G_7 \frac{W}{s}} \quad \rho_0 = \frac{V}{I} \times 2\pi s \quad G_7 \left(\frac{0.23}{2.0} \right) = G_7(0.115)$$

$$\rho = \frac{\rho_0}{12.36}$$

Where, Distance between probes (s) = 2.0mm,
Thickness of the crystal (w) = 0.23mm

Sr	Temperature T $^{\circ}\text{C}$	Voltage V (volt)	Temperature T_0 K	ρ_0	Resistivity ρ Ohm.cm	$\frac{10^3}{T}$ K	$\text{Log}_{10}\rho$



Now, Plot a graph for $\text{Log}_{10} \rho$ vs $10^3/T$

The slope of the curve is given by

$$\frac{\log_{10} \rho}{1/T} = \frac{E_g}{2k} \Rightarrow E_g = 2k \frac{\log_e \rho}{1/T^0 k}$$

k is Boltzmann's constant
 $= 8.6 \times 10^{-5} \text{ eV/K}$

CONDUCTION IN METALS

- Properties /Characteristics of metals :
 1. Metals have high thermal conductivity (K) and electrical conductivity(σ).
i.e. K and σ High

Ohm's law

- In the steady state, Ohm's law is obeyed.
i.e. current in the steady state is proportional to the electric field.
- $I \propto E$

- 3) Above Debye's Temperature, the resistivity is directly proportional to absolute temperature.
- $\rho \propto T$

- 4) At low temperature, resistivity is proportional to fifth power of absolute temperature.
- $\rho \propto T^5$

5) For almost all metals resistivity is inversely proportional to pressure.

- $\rho \propto 1/p$

Wiedemann-Frenzel law

6)“Above Debye’s temperature,
the ratio of thermal &
electrical conductivity is directly
proportional to absolute
temperature.”

$$K / \sigma = L T ; L = \text{Lorentz number}$$

SUPER CONDUCTIVITY

7)At absolute zero temperature, the resistivity tends to be zero and the specimen exhibits super conductivity phenomena.

MAGNETO- RESISTANCE EFFECT

8)The Conductivity of specimen varies with magnetic field.

Electrical Conductivity

- **Ohm's law:** “ The current through a conductor between two points is directly proportional to the potential difference across the two points.”

$$I=V/R$$

where

**I = current through the
conductor (amperes)**

V = potential

difference *across* the

conductor (volt),

R = resistance of the

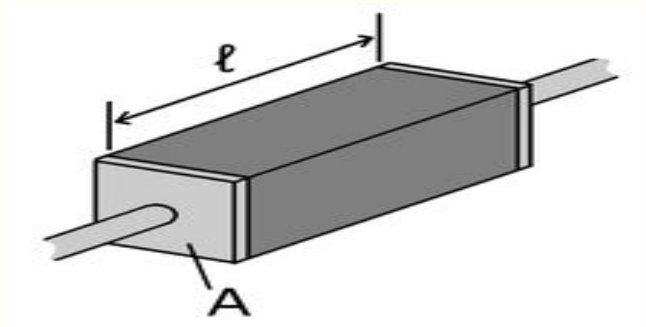
conductor (ohm).

Resistance (R)

- The Resistance R is a geometry dependent factor of the material used.

$$R = \frac{\rho l}{A}$$

$$R = \frac{l}{\sigma A}$$



Current density(J)

- Current density : the current per unit area of cross section of an imaginary plane held normal to the direction of flow of current in current carrying conductor.

(A/m²)

$$J = \frac{I}{A}$$

Electric Field(E)

- Electric field E : the potential drop (voltage) V per unit length.

$$(Vm^{-1})$$

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

Electrical

conductivity(σ)

$$V=IR \Rightarrow$$

$$R = \frac{l}{\sigma A}$$

$$V = \frac{Il}{\sigma A}$$

$$\frac{I}{A} = \sigma \frac{V}{l}$$

$$J = \sigma E$$

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

- **Electrical conductivity:** It is the rate of charge flow across unit area per unit potential gradient within a conductor.

$$J = \sigma E \Rightarrow \frac{I}{A} = \frac{1}{\rho} \frac{V}{l}$$

$$I = \frac{A}{\rho l} V$$

$$I = \frac{1}{R} V$$

$$\Rightarrow V = IR$$

Current Density J , Drift velocity V_d and mobility μ

- The current density J :

If n is the number of charge carriers per unit volume in a conductor of length l with cross sectional area A then $I = neAv_d$;

$$I = \frac{neAl}{t}$$

Drift velocity: It is the average velocity gained by the charge carriers in the presence of an electric field.

But we know $J = \frac{I}{A}$

$$\therefore J = \frac{neAv}{A} = nev_d$$

$$\therefore \sigma E = nev_d$$

$$\therefore \sigma = nev_d / E \quad \therefore \sigma = ne\mu$$

- $\mu = v_d / E$ is called the mobility of the charge carrier .
- It is the drift velocity per unit electric field. ($\text{m}^2\text{V}^{-1}\text{s}^{-1}$)

- In the case of metals, this μ is the mobility of the electrons.
- Thus, the electrical conductivity can be controlled by controlling no. of charge carriers per unit Potential difference V .

- The mobility is important in metals .But in semiconductors and insulators, the no. of charge carrier ' n ' is important.

• In semi conductors, since electrons and holes are both involved in conduction, the expression for conductivity becomes

$$\sigma = n_e e \mu_e + n_h e \mu_h$$

Electron theory of metals

1. Classical free electron theory / Drude-Lorentz theory.
2. Quantum free electron theory / Sommerfeld theory.
3. Zone theory / band theory of solids.

Assumptions of free electron theory

1. A metal is composed of positive metal ion fixed in the lattice.
2. All the valence electrons are free to move among the ionic array. Such freely moving electrons contribute towards conduction in metals.

3. Free electrons in metals have large energies & velocities.

4. There are a large number of free electrons in a metal and they move about the whole volume like the molecules of gas.

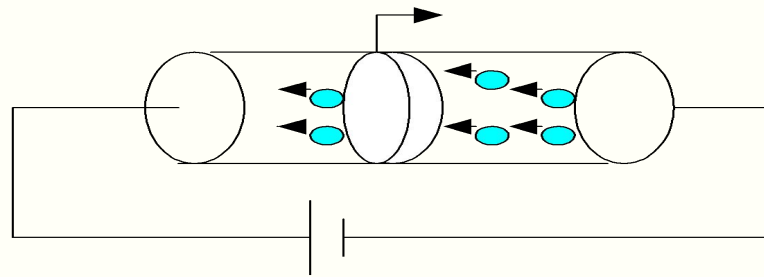
5. The electrostatic force between free electrons and the metallic ions are neglected i.e. the total energy of free electrons is equals to its kinetic energy.

6. The free electrons collide with the positive ions in the lattice and also among themselves. All the collisions are elastic.

7. In the absence of the electric field, the random motion of free electrons is equally probable in all directions. So the net current flow is zero.

8. When an electric field is applied the electrons gain a velocity called drift velocity v_d and moves in opp. direction to the field resulting in current flow in the direction of the field.

- Thus, drift velocity is the average velocity acquired by an electron on applying an electric field.



9. Relaxation Time

- It is defined as the time required for the drift velocity to reduce $(1/e)$ times of its initial value just when the field is switched off.

- It is also defined as the time taken by the free electron to reach its equilibrium position from its disturbed position just when the field is switched off.

10. Mean collision time(t_c)

- The average time between two consecutive collisions of an electron with the lattice points is called collision time.

11. Mean free path(λ)

- It is the average distance travelled by the conduction electron between successive collisions with the lattice ions.

Electrical conductivity

- It is defined as the rate of charge flow across a unit area in a conductor per unit potential(voltage) gradient.

$$\sigma = \frac{J}{E} \quad (\Omega^{-1}\text{m}^{-1})$$

Electrical

conductivity

- Electrical conductivity of a conductor is the property by which it allows the flow electric current. In metal, the valence electrons are not attached to individual atoms & are free to move about within the lattice. Hence the valence electrons are also called free electrons or conduction electrons.

- In the absence of electric field, motion of the free electrons are random like those of the molecules of a gas in container. But, when an electric field is applied, the electrons modify their random motion so that they drift slowly in opp. direction to that of applied field with an average velocity called drift velocity.

- When an electric field E is applied, the free electrons in a metal experiences a force eE . Due to this force, the acceleration 'a' gained by the electron is

$$F = eE$$

$$\therefore ma = eE$$

$$\therefore a = \frac{eE}{m}$$

- Consider an electron that has just collided with an iron core. The collision momentarily destroys the tendency to drift and the electron will have truly random direction after this collision.

In the next collision, the electron velocity would have changed to an average value v_d given by

$$v_d = at, \quad \tau = \text{mean free time}$$

- On solving, we get

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

- The current density is given by

$$J = nev_d \quad \text{where } n = \text{no. of free electrons per unit volume}$$

$$\therefore J = ne \frac{eE\tau}{m} \Rightarrow J = ne^2 \frac{E\tau}{m}$$

- But J is also expressed as

$$J = \sigma E$$

Therefore, $\sigma E = ne^2 \frac{E\tau}{m}$

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

- Thus, the above expression relates the electrical conductivity to the number of free electrons per unit volume

Expression for σ in terms of $K_B T$

- The mean free time τ in terms of mean free path λ and average thermal velocity \bar{v} is given by

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

- The kinetic energy of an electron based on kinetic theory is given by

$$\frac{1}{2} m v^2 = \frac{3}{2} K_B T$$

- Substituting value of m

$$\sigma = ne^2 v^2 \frac{\tau}{3KBT}$$

$$\sigma = ne^2 \frac{v\lambda}{3KBT}$$

- The electrical conductivity of a metal decreases with increase in temperature

Thermal conductivity

- It is defined as the rate of heat flow across a unit area of a conductor per unit temperature gradient.

- Thus $K = - \frac{Q' \frac{dt}{dx}}{A \frac{dT}{dx}}$
=temp.gradient

- The –ve sign is optional, which indicates that the heat flows from higher to lower temperature side.
- Unit- $\text{W m}^{-1} \text{K}^{-1}$.

- In solids, heat transfer takes place by conduction. In the process of heat transfer both electrons and photons take part.

Hence total thermal conductivity

$$K_{\text{total}} = K_{\text{electron}} + K_{\text{photon}}$$

- Since thermal conductivity due to electrons is greater than the thermal conductivity due to photons in the case of pure metals, the total thermal conductivity is given by

$$K_{\text{total}} = K_{\text{electron}}$$

Thermal Conductivity

- Consider a uniform metallic rod AB. Let the surface A be at a higher temperature T , and the surface B at a lower temp. $T - dt$, as in fig. Let the dist. of separation between the surface be λ . The electrons conduct heat from A to B. During collision, the electrons near A lose their K.E while the electrons near B gain energy.

Let;

The density of electrons= n

The average thermal velocity= v

Based on kinetic theory,

the average kinetic energy of an electron at $A=3k_B T/2$

- Similarly, the average kinetic energy of an electron at $A=3k_B T/2$
- Similarly, at $B=3k_B (T-dT)/2$

- Therefore, the excess kinetic energy carried by electrons from A to B = $(3k_B T)/2 - 3k_B (T - dT)/2$
$$= (3k_B dT)/2$$
- There is equal probability for the electrons to move in all six directions (x, y, z) and (-x, -y, -z).

- The no. of electrons crossing unit area in unit time from A to B = $(nv)/6$.
- Therefore, the excess energy transferred from A to B per unit area in unit time

$$= (nv)/6 * (3k_B dT)/2$$

$$= (nvk_B dT)/4$$

- Similarly, the deficiency of energy = - $(n v k_B dT)/4$

- Since, the net energy transferred from A to B per unit area per unit time is the rate of Q. Then,

$$\begin{aligned} Q &= (nvk_B dT)/4 - (-nvk_B dT)/4 \\ &= (nvk_B dT)/2 \end{aligned}$$

But, from the definition of K ,

$$K = \frac{Q}{\frac{dt}{dx}}$$

Here $dx = \lambda$ $sc_K = \frac{Q}{\frac{dt}{\lambda}}$

Therefore,

$$K = \frac{\left(\frac{1}{2}\right) n v k dT}{\frac{dt}{\lambda}}$$

$$K = (n v k_B \lambda) / 2$$

- This expression can be verified experimentally and the free electron theory is found to be successful in explaining the thermal conductivity.

Wiedemann-Franz Law

- Statement: This law states the ratio of thermal conductivity to the electrical conductivity is directly proportional to the absolute temperature.

Thus, $\frac{K}{\sigma} \propto T$

$$=LT \quad L=\text{constant}=\text{Lorentz no.}=2.44 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$$

Derivation

- The electrical conductivity is

$$\sigma = \frac{ne * e\lambda v}{3kBT}$$

- The K is given by

$$K = (nvk_B \lambda)/2$$

$$\frac{K}{\sigma} = \frac{nvkB\lambda}{2 \frac{ne * e\lambda v}{3kBT}} = \frac{nvkB\lambda. 3kBT}{2ne * e\lambda v} = \frac{3kB * kBT}{2e * e}$$

$$\frac{K}{\sigma} = \frac{3}{2} \left(\frac{kB}{e} \right)^2 T = LT, \text{ where } L = \frac{3}{2} \left(\frac{kB}{e} \right)^2$$

$L = 1.12 / 10^8 \text{ W}\Omega / \text{k}^2$ is known as Lorentz no.

- The above value of Lorentz no. based on classical concept does not agree with the experimental value.

- Hence, the assumption that all the free electrons of a metal participate in the thermal conductivity isn't correct.
- The actual experimental value of the Lorentz no. is $2.44 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$.
- Thus, there is a discrepancy in the L.

- This discrepancy gets eliminated on applying quantum theory.

Success of free electron theory

1. It verifies ohm's law.
2. It explains the thermal and electrical conductivities of metals .
3. It is used to deduce Wiedermann-Franz law.
4. It explains the optical properties of metals.

Drawbacks of free electron theory

1. The theoretical value obtained for specific heat and electronic specific heat of metals based on this theory is not in agreement with the experimental value.

2. The classical free electron theory is not able to explain the electrical conductivity of semiconductors and insulators.
3. According to classical theory $k/\sigma T$ is constant at all temperature but not constant at low temperature.

4. The theoretical value of paramagnetic susceptibility is greater than the experimental value; also, ferromagnetism cannot be explained.

5. The phenomena such as photoelectric effect, Compton effect & black body radiation cannot be explained.

Quantum free electron theory

- To overcome drawbacks of free electron theory ,in 1928 by applying quantum mechanical principles ARNOLD SOMMERFIELD proposed a new theory called quantum free electron theory or sommerfield theory.

- The electrons are assumed to obey pauli's exclusive principle.
- The assumptions are:

1. The energy levels of the conduction electrons are quantized.
2. The electrons are assumed to possess wave nature.

3. The distribution of electrons in the various allowed energy level occurs as per Pauli's exclusion principle.
4. The free electrons are assumed to obey Fermi-Dirac statistics.

5. The potential energy of the electron is uniform inside the metal.
6. The electrons are free to move inside the metal, but confined to stay within its boundaries.

7. The attraction between the electrons and the lattice ions, and the repulsion between the electrons themselves are ignored.

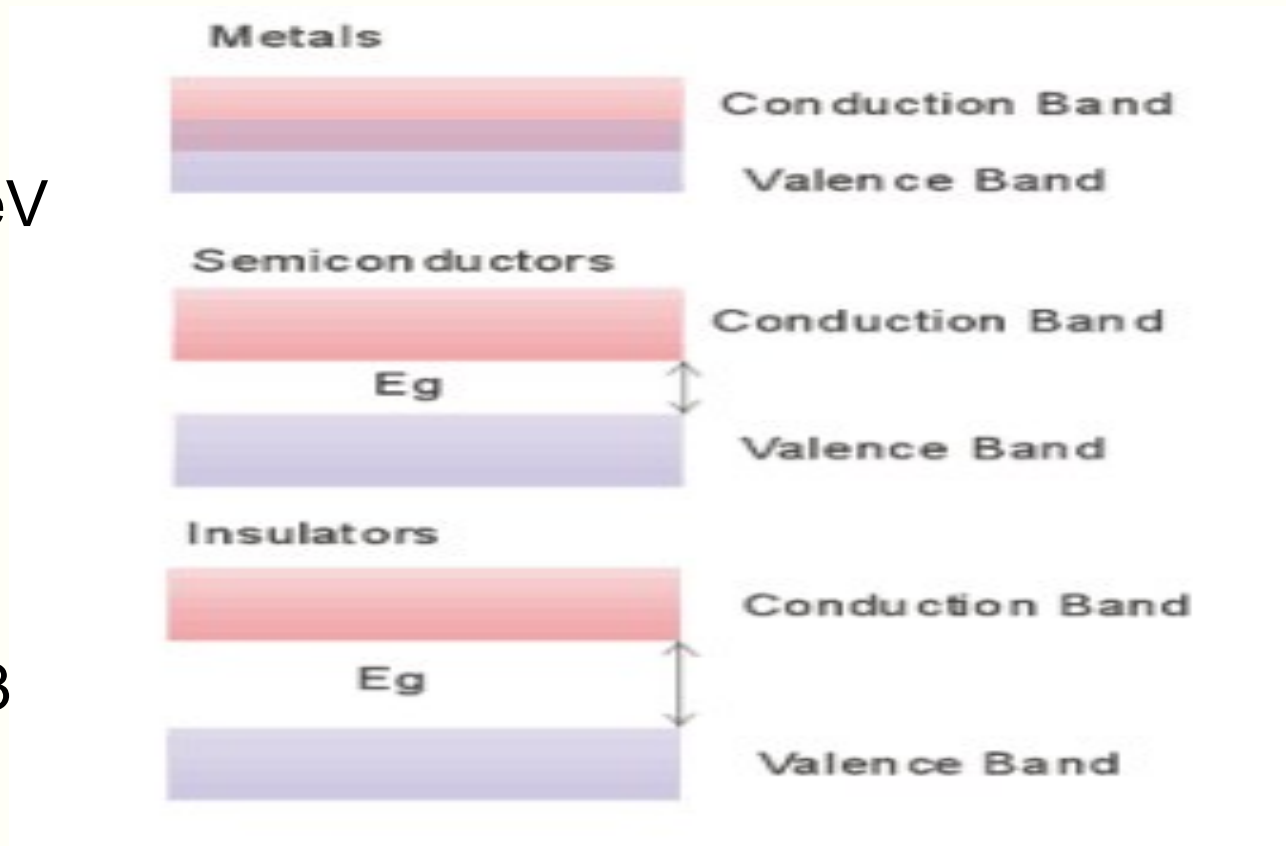
- Quantum free electrons theory provides explanation for electrical conductivity, thermal conductivity, specific heat capacity of metals, electronic specific heat capacity, Compton effect, photoelectric effect etc.

- This theory fails to make distinction between metals, semi conductors and insulators, also fails to explain the positive value of the hall coefficient and some pransport properties of metals.

E_g
~ 0.01 eV

< 2 eV

> 3 eV



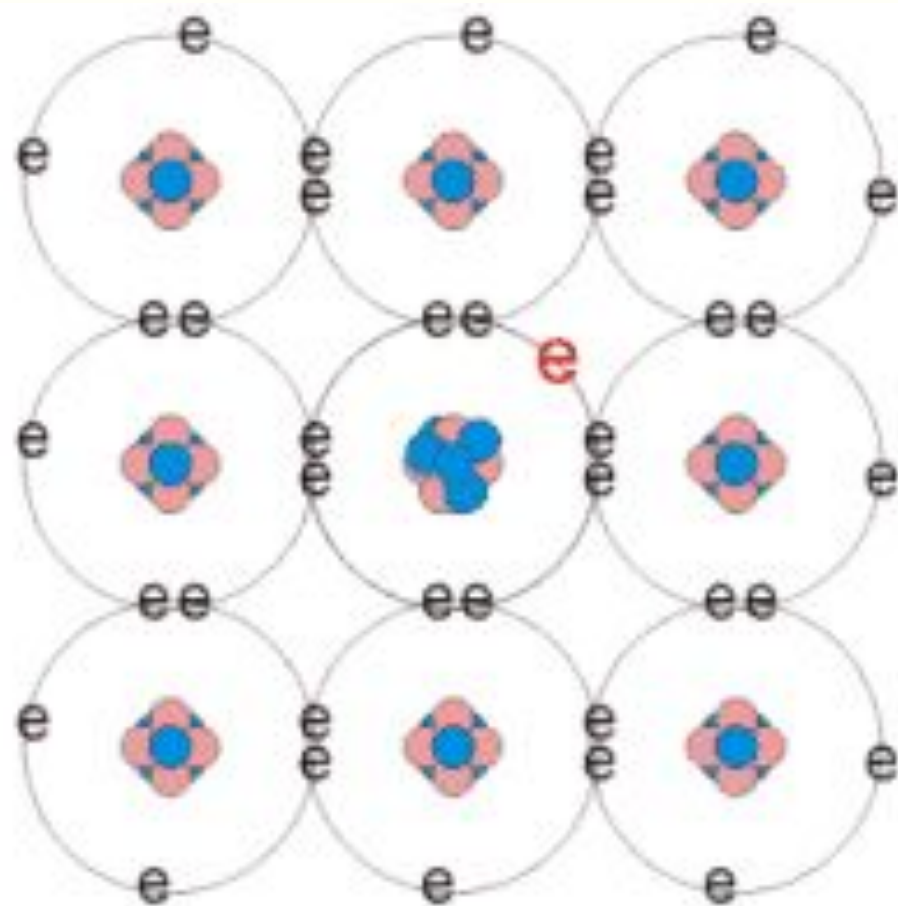
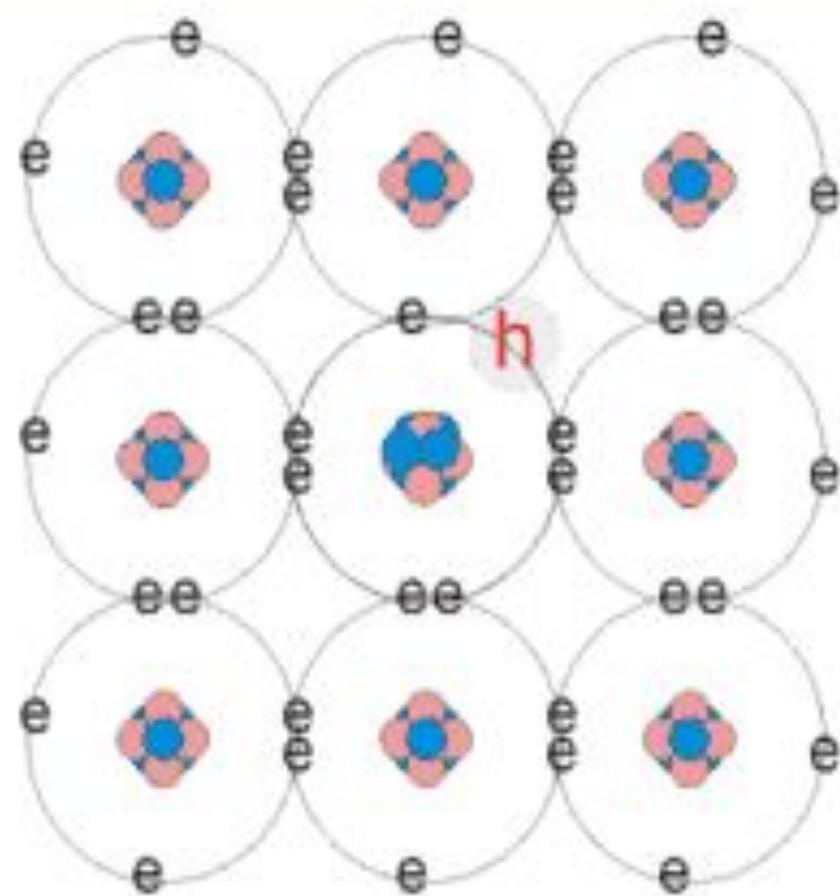
A semiconductor is considered to be pure when there is less than one impurity atom in a billion host atoms.

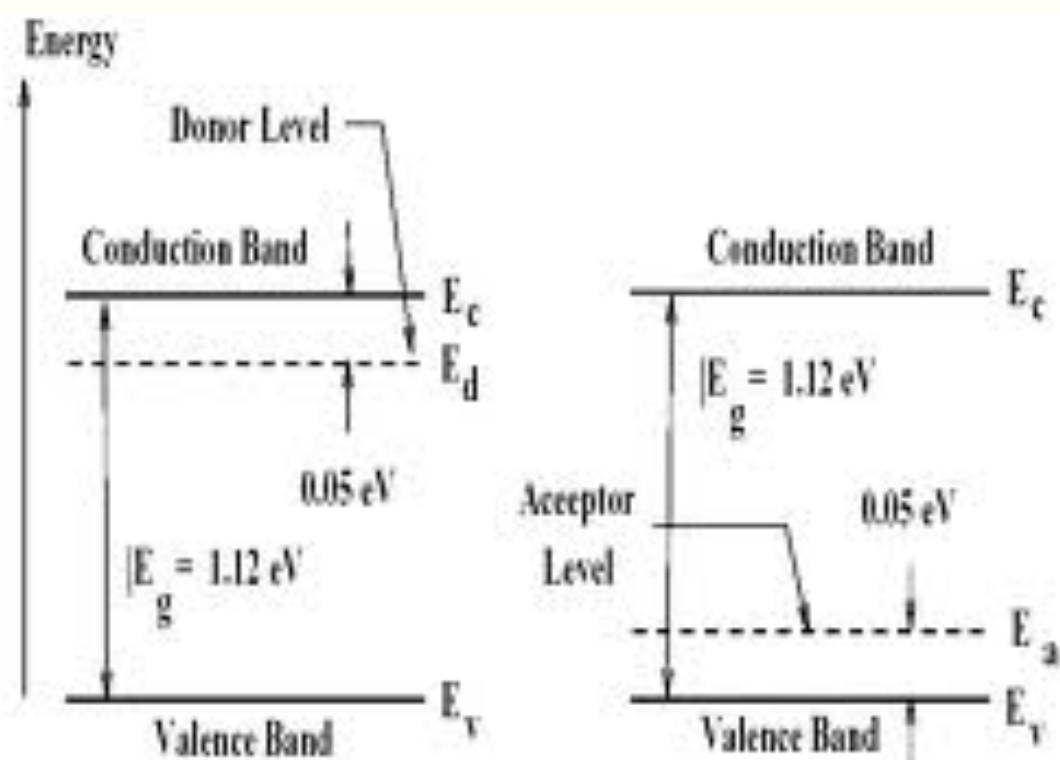
E.g. Silicon and germanium

They are intrinsic semiconductors, where the conduction arises due to thermally excited electrons and holes.

The process of intentional addition of controlled amount of impurity to an extrinsic semiconductor is known as doping.

A semiconductor doped with the impurity atoms is called an extrinsic semiconductor.

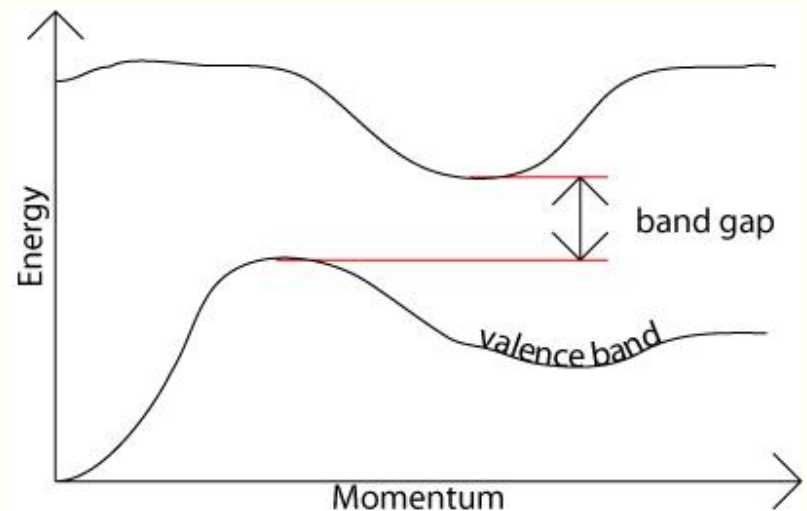
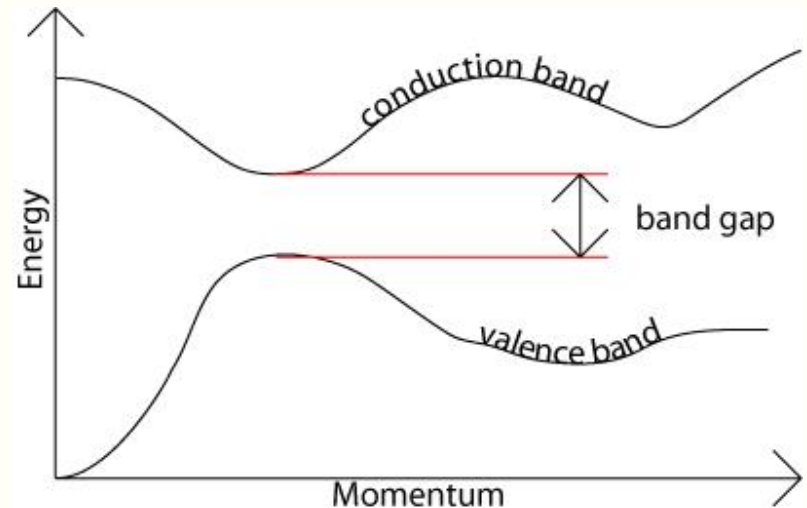




- The highest occupied band is called the **valance band** below which all the lower bands are occupied fully. The valance band may even be partially filled.
- The empty band immediately above the valance band is the **conduction band**.
- The gap between **valance band** and **conduction band** is called **the energy band gap or forbidden band**.

The top of the valence band and the bottom of the conduction band are not generally at the same value of the electron momentum. In a **direct band gap semiconductor**, the top of the valence band and the bottom of the conduction band occur at the same value of momentum, as in the schematic below.

In an **indirect band gap semiconductor**, the maximum energy of the valence band occurs at a different value of momentum to the minimum in the conduction band energy



At the highest energies of the valence band in many semiconductors (Ge, Si, GaAs, ...), and the lowest energies of the conduction band in some semiconductors (GaAs, ...), the band structure $E(\mathbf{k})$ can be locally approximated as

$$E(\mathbf{k}) = E_0 + \frac{\hbar^2 \mathbf{k}^2}{2m^*}$$

where $E(\mathbf{k})$ is the energy of an electron at wavevector \mathbf{k} in that band, E_0 is a constant giving the edge of energy of that band,

and m^* is a constant (the effective mass).

It can be shown that the electrons placed in these bands behave as free electrons except with a different mass,

as long as their energy stays within the range of validity of the approximation above.

As a result, the electron mass in models such as the Drude model must be replaced with the effective mass.