Unit 3

Band theory of solids.

(12) DENSITY OF STATES FOR AN ELECTRON IN A METAL

- Density of states is defined as number of available energy states per unit energy per unit volume.
- The density of states provides the information on how energy states are distributed in a given solid.
- It is typically denoted by as $g(E)$ or $Z(E)$.
- The density of states can be used to calculate the total no. of electrons in a band.
- If $Z(E)$ is the density of states, then the total number of e- in a band, $N(E)$ is given by;

$$\boxed{N(E) = \int_E Z(E)\, dE} \quad \text{—— (1)}$$

where the integration is performed over the entire band.

- Consider a three dimensional solid with uniform potential.
  For simplicity, the uniform potential is taken as zero.
- For this solid; the e- is defined by three quantum numbers (n_1, n_2, n_3) and its energy is given by.

$$\boxed{E = \frac{h^2}{8mL^2}\left(n_1^2 + n_2^2 + n_3^2\right)} \quad \text{—— (2)}$$

⇒ In eq (2); L is length of cubic of solid and 3 quantum numbers represent three axes (n_x, n_y, n_z), m is the mass of electron. We can replace the 3 quantum numbers by a single value n, so the eq. (2) modifies into

$$\boxed{E = \frac{n^2 h^2}{8mL^2}} \quad \text{—— (3)}$$

⇒ For small values of n these energy levels are quantized, but for large values of n the spacing between them are so close that the energy levels can be considered to be continuous.

⇒ So n represents the radius of a sphere, where the total number of states within the sphere is given by its volume.

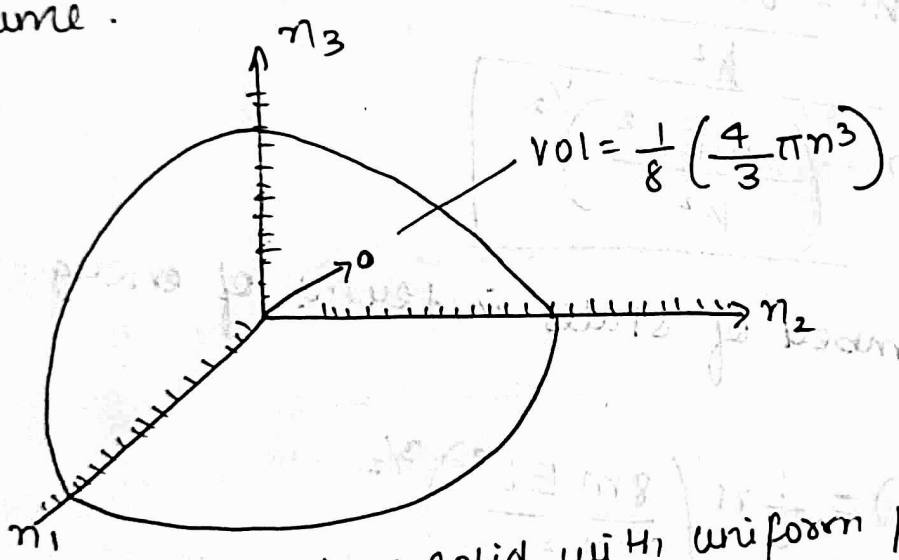

Fig: Energy states in a solid with uniform potential. The portion of the sphere corresponds to the constant energy surface

⇒ Since the quantum numbers can only be positive; we can only take the first quadrant of the sphere.

⇒ Here; the total number of states within the volume of the sphere with radius n in the first quadrant.

$$\boxed{S(E) = \frac{1}{8}\left(\frac{4}{3}\pi n^3\right) = \frac{\pi}{6} n^3} \quad \text{—— (4)}$$

- According to pauli's exclusion principle each state can take two electrons of opposite spin, the total number of energy states is given by;

$$S(E) = 2 \times \frac{\pi}{6} n^3$$

$$\boxed{S(E) = \frac{1}{3}\pi n^3} \quad \text{--- (5)}$$

- we know; $E = \frac{n^2 h^2}{8 m L^2}$.

- we can write quantum number n of electron in the solid interms of energy using eq(2);

$$n^2 = \frac{8 m E L^2}{h^2}$$

$$\boxed{n = \left(\frac{8 m E L^2}{h^2}\right)^{1/2}}$$

- The total number of states in terms of energy is given by.

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

$$\Rightarrow \boxed{S(E) = \frac{1}{3}\pi \left(\frac{8 m E}{h^2}\right)^{3/2} L^3} \quad \text{--- (6)}$$

- Now; dividing the total no. of states with volume of the cube (L^3) will give the density of energy states per unit volume.

- $$S_V(E) = \frac{\frac{1}{3}\pi \left(\frac{8 m E}{h^2}\right)^{3/2} L^3}{L^3}.$$

$$\Rightarrow \boxed{S_v(\epsilon) = \frac{1}{3}\pi\left(\frac{8mE}{h^2}\right)^{3/2}}$$

⇒ The density of states is the differential of total no. of states; so that $Z(\epsilon)$ is given by.

$$Z(\epsilon)\,d\epsilon = S_v(\epsilon)\,d\epsilon$$

$$= \frac{1}{3}\pi\left(\frac{8m}{h^2}\right)^{3/2} \cdot \frac{3}{2}E^{1/2}\,d\epsilon$$

$$\boxed{Z(\epsilon)\,d\epsilon = \frac{\pi}{2}\left(\frac{8m}{h^2}\right)^{3/2} E^{1/2}\,d\epsilon} \quad \text{— (7)}$$

⇒ Eq (7) gives the density of states (DOS) in a solid with a uniform potential.

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(13) (a). The structure and properties of solids are explained employing their electronic structure by the electron theory of solids. It has been developed in three main stages:

(1) Classical free electron theory
(2) Quantum free electron theory.

⇒ Classical free electron theory:

- The first theory was developed by Drude and Lorentz in 1900.
- According to this theory, metal contains free electrons which are responsible for the electrical conductivity and metals obey the laws of classical mechanics.

Assumptions:

i) Metal composed of atoms in which electrons revolve around the nucleus and many states available for occupation.

⇒ If the density of states is zero, no states can be occupied at that energy level.

(2) In metals, there are large number of free electrons. moving freely within the metal i.e the free e- or valence e- are free to move in the metal like gaseous molecules, because nuclei occupy only 15% metal space and remaining 85% space is available for the e- to move.

(3) the valence e- are freely moving about the whole volume of metals like the molecules of perfect gas in a container.

(4) The free e- moves in random directions and collide with either positive ions or other free e-. collision is independent of changes and is elastic in nature.

(5) The movements of free electrons obey the laws of classical kinetic theory of gases.

(6) Potential field remains constant throughout the lattice.

Advantages:

1. It explains the electrical conductivity and thermal conductivity of metals.
2. It verifies ohm's law.
3. It is used to explain the optical properties of metals.

Disadvantages:

1. It fails to explain the ~~electrical~~ specific heat and specific heat capacity of metals.
2. It fails to explain super conducting properties of metals.
3. It fails to explain new phenomena like photo-electric effect, Compton effect, Blackbody Radiation etc.

Quantum Free electron theory

In 1928; Sommerfield developed the quantum free e- theory. Acc. to sommerfield, the free e- moves with a constant potential. This theory obeys quantum laws.

Assumptions:

1. All the electrons are not present in the ground state at 0K, but the distribution obeys Pauli's exclusion principle. At 0K, the highest energy level filled is called the Fermi-level.
2. The potential remains constant throughout the lattice.
3. Collisions of e- with positive ion cores and other free e- is independent of charge and is elastic in nature.
4. Energy levels are discrete.

Advantages:

1. It was successful to explain not only conductivity, but also thermionic emission, paramagnetism and specific heat.

Drawbacks:

1. It fails to explain classification of solids as conductors, semiconductors and insulators.

(b) **Fermi Energy:** It is the energy of state at which the probability of electron occupation is 1/2 at any temperature above 0K. It separates filled energy states and unfulfilled energy states. The highest energy level that can be occupied by an electron at 0K is called Fermi Energy level.

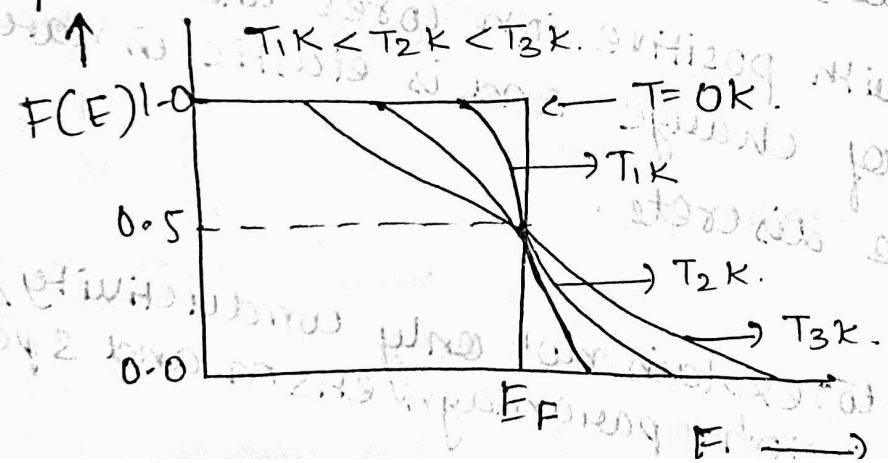
Fermi level: It is a level at which the electron probability is 1/2 at any temp above 0K (or) always it is 1 or 0 at 0K.

-) Therefore, the probability function F(E) of an electron occupying an energy level E is given by.

$$F(E) = \frac{1}{1 + \exp\left[\frac{E - E_F}{KT}\right]} \quad \text{--- (1)}$$

where; E_F is known as Fermi Energy and it is constant for a system.

K is the Boltzmann constant and T is the absolute temperature.



⇒ Case 1: At $T > 0K$ if $E = E_F$; $F(E) = \frac{1}{2}$.

$$F(E) = \frac{1}{1 + e^{\left(\frac{E - E_F}{KT}\right)}} = \frac{1}{1 + e^{\left(\frac{0}{KT}\right)}} = \frac{1}{e^{0} + 1} = \frac{1}{1+1} = \frac{1}{2}.$$

Case 2: At $T = 0K$ if $E > E_F$. $F(E) = 0$.

$$F(E) = \frac{1}{1 + e^{\left(\frac{E - E_F}{0}\right)}} = \frac{1}{1 + e^{\infty}} = \frac{1}{1 + \infty} = \frac{1}{\infty} = 0$$

$$F(E) = 0.$$

[since $(E - E_F) = +ve$ value.
since $\frac{+ve \text{ value}}{0} = \infty$.]

Case 3: At $T = 0K$ if $E < E_F$; $F(E) = 1$

$$F(E) = \frac{1}{1 + e^{\left(\frac{E - E_F}{0}\right)}} = \frac{1}{1 + e^{\frac{-ve \text{ value}}{0}}} = -ve \text{ value}.$$

$$= \frac{1}{e^{-\infty} + 1} = \frac{1}{0 + 1} = \frac{1}{1} = 1$$

$$\left[e^{-\infty} = \frac{1}{e^{\infty}} = \frac{1}{\infty} = 0 \right]$$

$$= F(E) = 1$$

⇒ Hence; there are three probabilities namely;

1. $F(E) = 1$ 100% probability to occupy the energy level by e-

2. $F(E) = 0$ No probability to occupy the energy levels by e- and hence; it is empty.

3. $F(E) = 0.5$ 50% probability of finding the e- in the energy level.

(14) (a) Acc. to this theory, the electrons moves in a ~~particular~~ periodic Potential produced by the positive ion cores. KRONIG PENNY MODE

- The potential of e- varies periodically with periodicity of ion core and potential energy of the e- is zero near nucleus of positive ion core.
- It is maximum when it is lying between the adjacent nuclei which are separated by inter-atomic spacing.
- The variation of potential of e- while it is moving through ion core is shown;

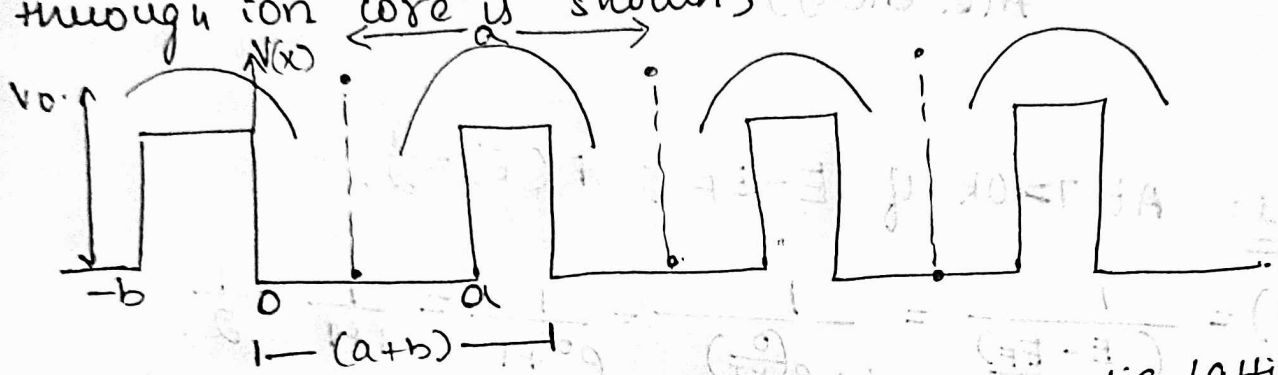


Fig: Variation of potential energy in a periodic lattice.

$$V(x) = \begin{cases} 0, & \text{for the region } 0 < x < a \\ V_0, & \text{for the region } -b < x < 0 \end{cases} \quad \text{— (1)}$$

⇒ Schrödinger's time-independent wave equation:-

$$\left[\frac{\partial^2 \psi}{\partial x^2} + \frac{2m(E-V)}{\hbar^2}\psi = 0 \right]$$

⇒ Applying S.T.I.W.E ~~to the two~~ regions.

$$\Rightarrow \boxed{\frac{\partial^2 \psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0 \quad (\text{for region } 0 < x < a)} \quad \text{— (2)}$$

$$\Rightarrow \boxed{\frac{\partial^2 \psi}{\partial x^2} + \frac{2m(E-V_0)}{\hbar^2}\psi = 0 \quad (\text{for region } -b < x < 0)} \quad \text{— (3)}$$

Substituting: $\boxed{\alpha^2 = \frac{2mE}{\hbar^2}}$ — (4)

$$\beta^2 = \frac{2m(E-V_0)}{\hbar^2}$$

$$\boxed{\beta^2 = -\frac{2m(V_0-E)}{\hbar^2}} \text{ — (5)}$$

$$\Rightarrow \left[\begin{array}{ll} \frac{\partial^2\psi}{\partial x^2} + \alpha^2\psi = 0 & \text{(for region } 0<x<a) \text{ — (6)} \\ \frac{d^2\psi}{dx^2} - \beta^2\psi = 0 & \text{(for region } -b<x<0) \text{ — (7)} \end{array}\right]$$

⇒ The solution for the equation (6) and (7) can be written as.

$$\boxed{\psi(x) = U_k(x)\, e^{ikx}} \text{ — (8)}.$$

⇒ The above solution consists of a plane wave e^{ikx} modulated by the periodic function $U_k(x)$ where $U_k(x)$ has the periodicity of the ion such that

$$\boxed{U_k(x) = U_k(x+a)} \text{ — (9)}.$$

where k is propagating vector along x-direction and is given by $\boxed{k = \frac{2\pi}{\lambda}}$. k is also known as wave vector.

⇒ Differentiating eq (8) twice w.r.to x, and substituting in eq (6) and (7); two independent second order linear differential equations can be obtained for the regions $0<x<a$ and $-b<x<0$.

⇒ Applying the boundary conditions, the solution of above equations can be obtained for linear equations in terms of A, B, C, D (where A, B, C, D are constants)

The solution for these equations can be determined only if the determinant of the co-efficients of A, B, C and D vanishes, on solving the determinant.

$$\boxed{\left(\frac{\beta^2-\alpha^2}{2\alpha\beta}\right)\sinh\beta b \sin\alpha a + \cosh\beta b \cos\alpha a = \cos k(a+b)} \quad \text{—— (10)}$$

⇒ The above eq is complicated and kronig and penny tried to modify this equation as follows.

⇒ Let V_0 is tending to infinite and b is approaching to zero. such that $V_0 b$ remains finite.

Therefore $\boxed{\sinh\beta b \to \beta b}$ and $\boxed{\cosh\beta b \to 1}$

$$\beta^2-\alpha^2 = \left(\frac{2m}{\hbar^2}\right)(V_0-E) - \left(\frac{2mE}{\hbar^2}\right)$$

$$= \left(\frac{2m}{\hbar^2}\right)[V_0-E-E]$$

$$= \left(\frac{2m}{\hbar^2}\right)(V_0-2E).$$

$$\boxed{\beta^2-\alpha^2 = \frac{2mV_0}{\hbar^2}} \quad (\text{since } V_0 >> E)$$

Substituting all these values in (10), it can be written as

$$\left(\frac{\cancel{2}mV_0}{\hbar^2 \cdot \cancel{2}\alpha\beta}\right)\sinh\beta b \sin\alpha a + \cos\alpha a \cdot \cosh\beta b = \cos k(a+b)$$

⇒ Applying all conditions; $\sinh\beta \to \beta b$ $\quad \cosh\beta \to 1$

$b \to 0$.

$\Rightarrow \frac{mV_0}{\alpha\beta\hbar^2}(\beta b)\sin\alpha a + \cos\alpha a = \cos ka.$

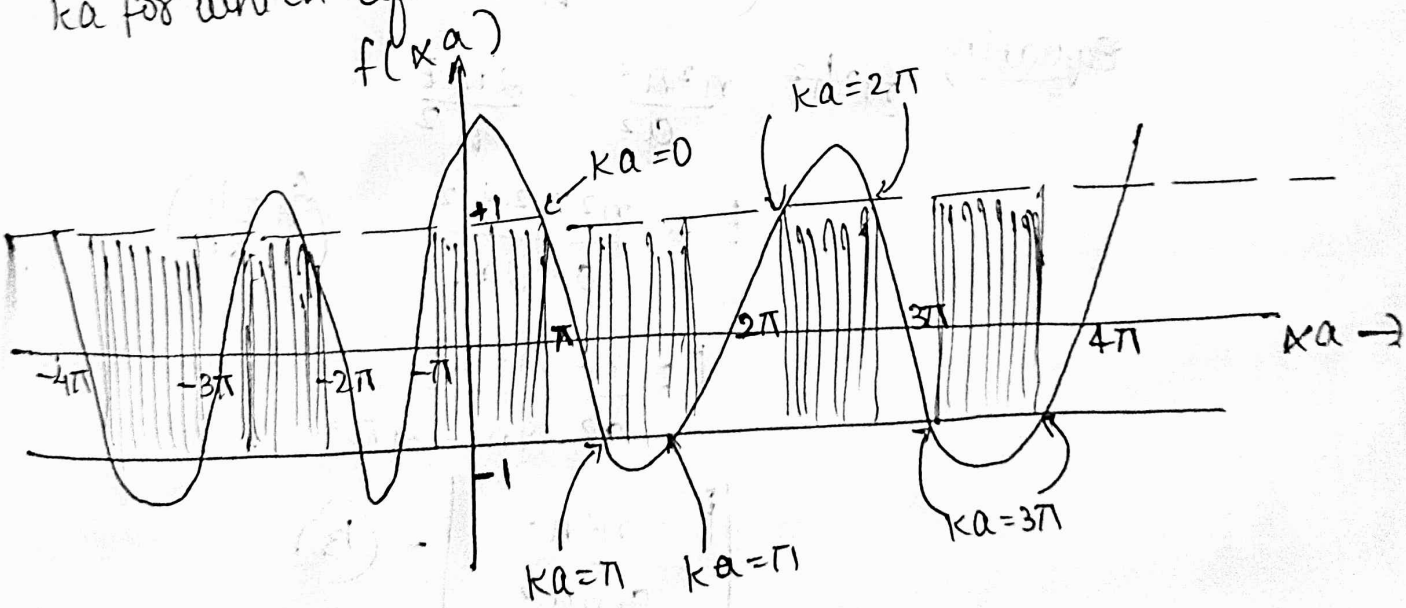
$\Rightarrow \frac{a \times mV_0 b}{a \times \alpha\hbar^2}\sin\alpha a + \cos\alpha a = \cos ka$

$\Rightarrow \left(\frac{mV_0 ba}{\hbar^2}\right)\cdot\frac{1}{\alpha a}\sin\alpha a + \cos\alpha a = \cos ka$

$\Rightarrow \boxed{\left(\frac{P}{\alpha a}\right)\sin\alpha a + \cos\alpha a = \cos ka}$ — (11)

where $\boxed{P = \frac{mV_0 ba}{\hbar^2}}$ — (12) is a measure of potential barrier strength.

$\Rightarrow$ The left hand side of eq (11) is plotted as a function of α for the value of $\boxed{P = \frac{3\pi}{2}}$ which is shown in figure, the right hand side one takes values between -1 to $+1$ as indicated by the horizontal lines in figure. Therefore the equation (11) is satisfied only for those values of ka for which left hand side lies between ± 1



Conclusions from the figure:-

① The energy spectrum of the electron consists of a number of allowed and forbidden energy bands.

② the width of the allowed energy band increases with increase of energy values. i.e increasing the values of

③ With increasing P, i.e with increasing potential barrier, the width of an allowed band decreases.

As $P \to \infty$, the allowed energy becomes infinitely narrow and the energy spectrum is a line spectrum.

→ If $P \to \infty$; then eq (11) has solution

$$\sin \alpha a = 0$$

$$\alpha a = \pm n\pi$$

$$\alpha = \pm \frac{n\pi}{a}$$

$$\alpha^2 = \frac{n^2\pi^2}{a^2}$$

But; we know; $\left(\alpha^2 = \frac{2mE}{\hbar^2}\right)$ from ④

Equating

$$\cancel{\pi^2\hbar^2} \quad \frac{n^2\pi^2}{a^2} = \frac{2mE}{\hbar^2}$$

$$E = \frac{n^2\pi^2\hbar^2}{a^2\, 2m} \qquad \left(\hbar = \frac{h}{2\pi}\right)$$

$$E = \frac{n^2\pi^2 h^2}{a^2 \cdot 2m \cdot 4\pi^2}$$

$$\boxed{E = \frac{n^2h^2}{8ma^2}} \quad \text{—} (13)$$

This expression shows that the energy spectrum of the e- contains discrete energy levels separated by forbidden regions.

(4) when $P \to 0$ then;

$$\left(\frac{P}{\alpha a}\right) \sin \alpha a + \cos \alpha a = \cos ka$$

$$\cos \alpha a = \cos ka$$

$$\alpha = k$$

$$\alpha^2 = k^2$$

but; $\left(\alpha^2 = \frac{2mE}{\hbar^2}\right)$ from (4)

equating:

$\Rightarrow$ $k^2 = \frac{2mE}{\hbar^2}$ we know $\left[\begin{array}{l} P = \hbar k \\ P^2 = \hbar^2 k^2 \end{array}\right]$.

$\Rightarrow$ $E = \frac{k^2 \hbar^2}{2m}$ we know; $(P = mV)$

$\Rightarrow$ $E = \frac{P^2}{2m}$

$\Rightarrow$ $E = \frac{m^2 V^2}{2m}$

$\Rightarrow$ $\boxed{E = \frac{1}{2} m V^2}$ —— (14)

$\Rightarrow$ the eq (14) shows that all the electrons are completely free to move in the crystal without any constraints.

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(5) A set of closely packed energy levels is called a band.

Valence Band:

) A band which is occupied by the valence electrons is called as valence band.

) the valence band may be partially or completely filled up depending on the nature of the material.

Conduction Band:

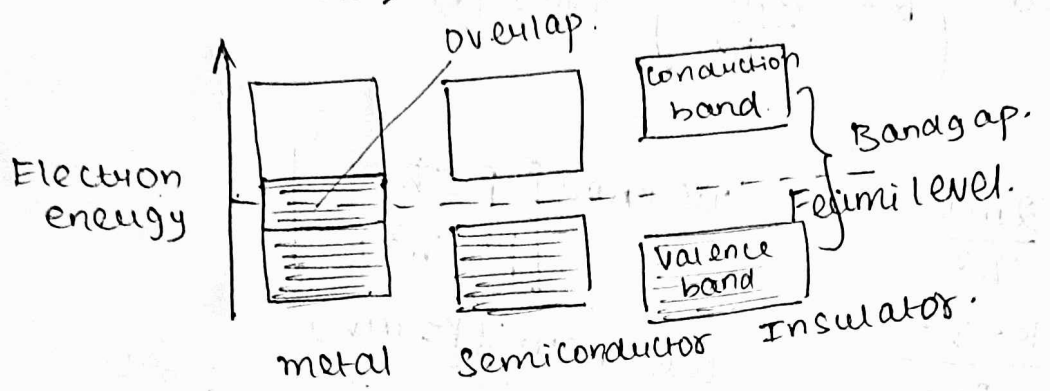
) the lowest unfulfilled energy band is called as conduction band. this band may be empty or partially filled. In conduction band the electrons can move freely named as free electrons.

Forbidden Energy gap (or) forbidden gap.

The energy gap between valence band and conduction band is called forbidden energy gap.

Classification of crystalline solids.

Based on forbidden band width, the solids are classified into conductors, semi conductors and Insulators.



Conductors:

⇒ The valence Band and conduction Bands are overlapped with each other and the energy gap Eg is zero.

⇒ At room temperatures, free electrons already exist in huge number at conduction band.

⇒ Hence; these solids are good electrical conductors as well as good thermal conductors.

⇒ The electrical resistivity increases at high temp by collisions among the free electrons.

Ex:- Al, Cu, Ag, Au etc.

Semi Conductors:

⇒ The valence band and conduction bands are separated ~~to~~ with a small energy band gap Eg ≈ 1 eV.

⇒ At low temp (0K), free e⁻ are not available in conduction band.

⇒ Hence; they behave like insulators at low temp.

⇒ The electrical conductivity increases at high temp. by the transition of free electrons from valence band to conduction band.

⇒ Thus, these solids behave like electrical conductors at high temperatures.

⇒ Ex: silicon Eg = 1.1 eV, Germanium Eg = 0.7 eV

Insulators: the valence band and conduction bands are separated by a very large energy gap.

⇒ At room temp; conduction band is empty and valence band is full of electrons.

⇒ Hence, these solids are electrical insulators.

⇒ Even at high temp; valence e- are unable to jump into conduction band.

⇒ Ex: Glass, mica, Ebonite, Rubber etc.

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(15) (a). CONCEPT OF EFFECTIVE MASS OF ELECTRON:

⇒ When an electron in a periodic potential of lattice is accelerated by an known electric field or magnetic field, then the mass of the electron is called effective mass and is represented by m^*.

⇒ To explain, let us consider an electron of charge 'e' and mass 'm' moving inside a crystal lattice of electric field E.

⇒ Acceleration $a = \frac{eE}{m}$ is not a constant in the Periodic lattice of the crystal.

⇒ It can be considered that its variation is caused by the variation of electron's mass when it moves in the crystal lattice.

Electrical force on the electron $F = m^* a$ —— (1).

Therefore acceleration $a = eE/m^*$

Considering the free e- as a wave packet, the group velocity V_g corresponding to the particle's velocity can be written as.

$\Rightarrow$ $V_g = \frac{d\omega}{dk}$.

$$\left[\begin{array}{l} \omega = 2\pi\nu \\ E = h\nu \qquad \nu = \frac{E}{h}. \\ \omega = 2\pi \cdot \frac{E}{h} \qquad \left[\hbar = \frac{h}{2\pi}\right] \\ \omega = \frac{E}{\hbar} \end{array}\right]$$

$\Rightarrow$ $V_g = \frac{d}{dk}\left(\frac{E}{\hbar}\right)$

$\Rightarrow$ $\boxed{V_g = \frac{1}{\hbar}\frac{dE}{dk}}$ — (1).

$\Rightarrow$ Differentiating eq (1) w.r.t 't'

$\Rightarrow$ $a = \frac{d}{dt}(V_g) = \frac{d}{dt}\left(\frac{1}{\hbar}\frac{dE}{dk}\right)$.

$\Rightarrow$ $a = \frac{1}{\hbar}\frac{d}{dt}\left(\frac{dE}{dk}\right)$.

$\Rightarrow$ $a = \frac{1}{\hbar}\frac{d}{dk}\left(\frac{dE}{dt}\right) = \boxed{\frac{1}{\hbar}\frac{d}{dk}\left(\frac{dE}{dk}\cdot\frac{dk}{dt}\right)}$ — (2)

$\Rightarrow$ we know; $\boxed{P = \hbar k}$. — (3)

Differentiating (2) w.r.t 't'

$\Rightarrow$ $\frac{dP}{dt} = \frac{d}{dt}(\hbar k)$. $\qquad \left(\frac{dP}{dt} = F\right)$.

$\Rightarrow$ $F = \hbar\frac{dk}{dt}$.

$\Rightarrow$ $\boxed{\frac{dk}{dt} = \frac{F}{\hbar}}$ — (4) substitute (4) in (2).

$\Rightarrow$ $a = \frac{1}{\hbar}\frac{d}{dk}\left(\frac{dE}{dk}\cdot\frac{F}{\hbar}\right)$.

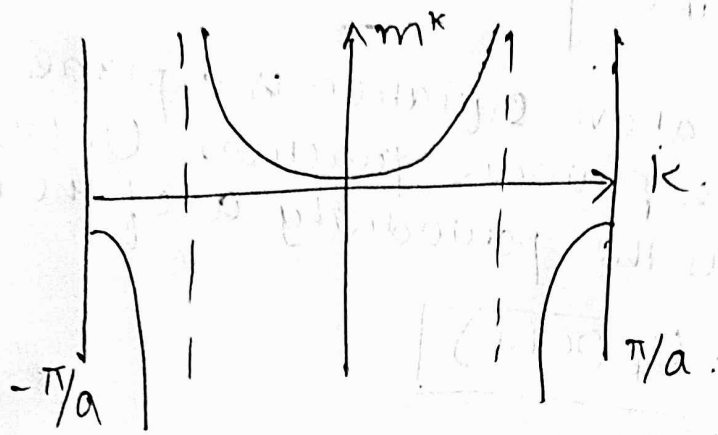
$\Rightarrow$ $a = \frac{F}{\hbar^2}\frac{d^2E}{dk^2}$.

$\Rightarrow$ $F = \left[\frac{\hbar^2}{\frac{d^2E}{dk^2}}\right]a$ — (5).

$$\Rightarrow \boxed{m^*_e = \frac{\hbar^2}{d^2E/dk^2}}$$

⇒ This equation indicates that the effective mass is determined by d^2E/dk^2.

⇒ Variation of effective mass m^* with k



⇒ This graph shows variation of m^* with k.

- Near k=0; effective mass approaches m. As the k values increases, m^* increases, reaching its maximum value known as infinite effective mass.
- Above the point of inflection, m^* is negative and as k tends to π/a, it decreases to a small negative value called negative effective mass in the lower region.

(b) Bloch theorem

⇒ Acc. to free electron model, a conduction electron in metal experiences constant potential.

⇒ But in real crystal, there exists a periodic arrangement of positively charged ions through which the electrons move.

⇒ As a consequence, the potential experienced by electrons is not constant but it varies with the periodicity of the lattice.

⇒ In Band theory, as per Bloch, potential energy of electrons considered as varying potential with respect to lattice parameter 'a'

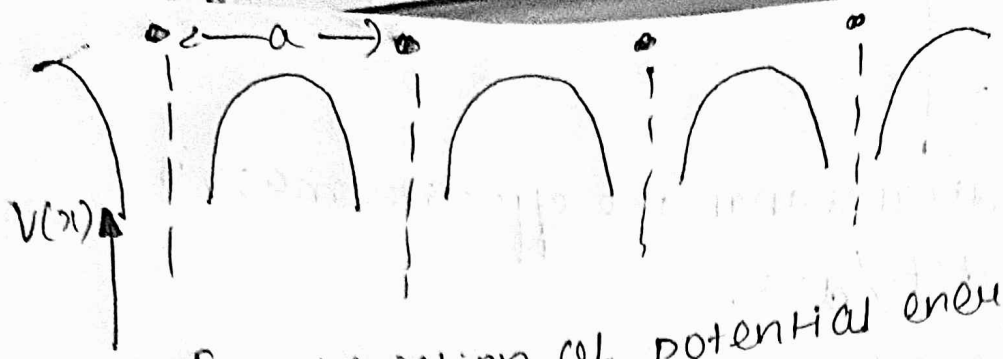


Fig: variation of potential energy in a period lattice.

$$\boxed{\psi(x) = U_k(x) e^{ikx}}$$

The above solution of above equation is a plane wave e^{ikx} modulated by the periodic function $U_k(x)$ where this $U_k(x)$ has the periodicity a of the ion such that

$$\boxed{U_k(x) = U_k(x+a)}$$

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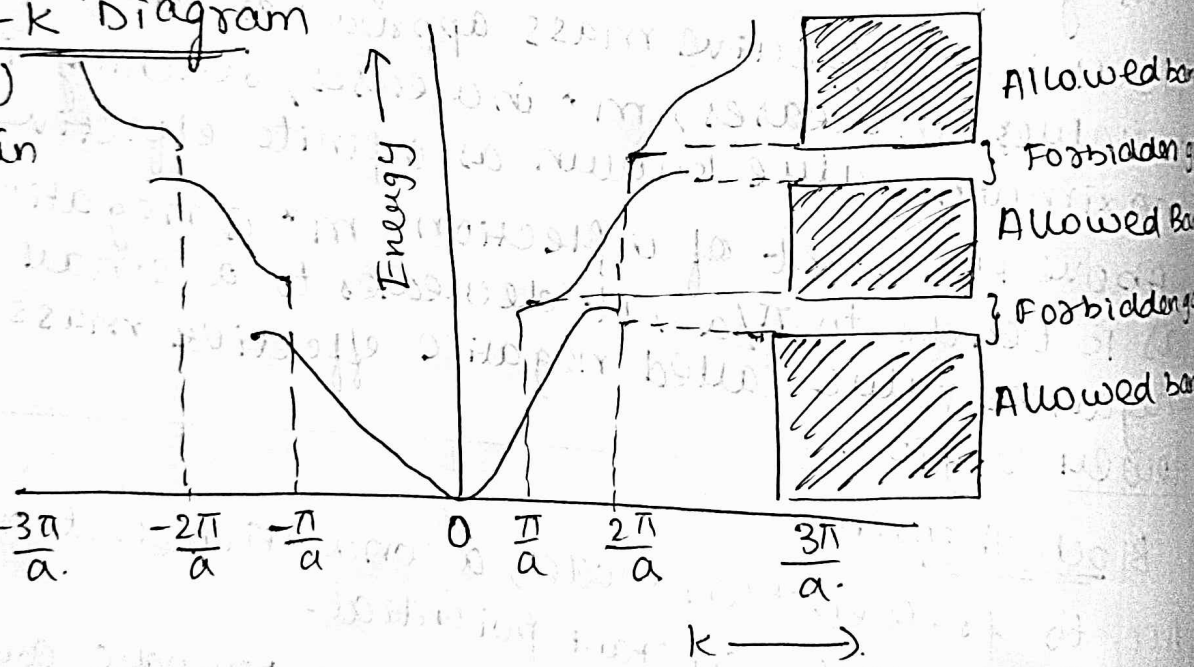
② E-K Diagram

(Q4)

Brillouin zone



=) the Brillouin zone are the boundaries that are marked by the values of wave vector k, in which electrons can have allowed energy values.

=) these represent the allowed values of k of the e- in 1D, 2D and 3D.

⇒ It is the energy spectrum of an e- moving in presence of a periodic potential field and is divided into allowed energy regions (allowed zones) or forbidden energy gaps (forbidden zones).

⇒ Allowed energy values lie in the region $\left[k = \frac{-\pi}{a} \text{ to } +\frac{\pi}{a}\right]$

⇒ This zone is called first Brillouin zone.

⇒ After a break in the energy values, called forbidden energy band, we have another allowed zone spread from $k = -\frac{\pi}{a}$ to $-\frac{2\pi}{a}$ and $+\frac{\pi}{a}$ to $+\frac{2\pi}{a}$.

⇒ This zone is called the second Brillouin zone.

⇒ Similarly, higher Brillouin zones are formed.