5.5 Band theory of solids (Zone theory)

The free electron theory explains the properties like thermal conductivity, electrical conductivity and specific heat of most of the metals.

But, it fails to explain why some solids are conductors, some are insulators and others are semiconductors.

A solution to this problem was given by band theory of solids and is called zone theory.

Postulates

1. According to band theory, potential energy of electron within the crystal is periodic due to periodicity of the crystal i.e., free electrons move inside periodic lattice field.
2. The potential energy of the solid varies periodically with the periodicity of space lattice ' a ' which is nothing but interatomic spacing.

5.5.1 BLOCH'S THEOREM FOR PARTICLES IN A PERIODIC POTENTIAL

The motion of electron inside the lattice is not free as expected, but the electron experiences a periodic potential variation. The potential energy on the electron is maximum between adjacent ions and gradually decrease as the electron moves towards ions as shown in fig.

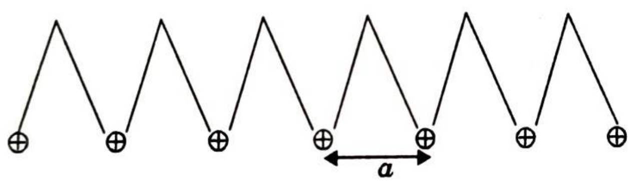

Fig. One-dimensional periodic potential distribution on electron in crystal lattice

Bloch Theorem

It is a mathematical statement regarding the form of one electron wave function for a perfectly periodic potential.

Statement

If an electron in a linear lattice of lattice constant 'a' characterised by potential function $V(x) = V(x + a)$ satisfies the Schrodinger equation

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]\Psi(x) = 0$$

then the wave functions $\Psi(x)$ of electron (with energy E) is obtained as a solution of Schrodinger equation are of the form

$$\Psi(x) = u_k(x)e^{ikx} \text{ where } u_k(x) = u_k(x + a)$$

Here $u_k(x)$ is also periodic with lattice periodicity.
The potential $V(x)$ is periodic as $V(x) = V(x + a)$ where a is a lattice constant.

From the Block theorem, we can say that the free electron is modulated by the periodic function $u_k(x)e^{ikx}$

In other words the solutions are plane waves modulated by the function $u_k(x)$ which has the same periodicity as the lattice. This theorem is known as Bloch Theorem. The functions of the type (2) are called Bloch functions.

Proof

If equation (1) has the solution with the property of equation (2), we can write the property of the Bloch functions i.e., equation (3) as

$$\Psi(x + a) = e^{ik(x+a)}u_k(x + a)$$
$$\text{(or) } \Psi(x + a) = e^{ikx} \cdot e^{ika}u_k(x + a)$$

Since $u_k(x + a) = u_k(x)$, we can write the above equation as

$$\Psi(x + a) = e^{ikx}e^{ika} \cdot u_k(x)$$

Since $\psi(x) = e^{ikx}u_k(x)$, we can write the above equation as

$$\psi(x + a) = e^{ika} \cdot \psi(x)$$

$$(\text{or})\ \Psi(x + a) = Q\psi(x)$$
$$\text{where}\quad Q = e^{ika}$$

If $\psi(x)$ is a single-valued function, then

we can write

$$\psi(x) = \psi(x + a)$$

Thus Bloch theorem is proved.

5.5.2 . BASICS OF KRONIG PENNY MODEL

The behaviour of electronic potential is studied by considering a periodic rectangular well structure in one dimension. It was first discussed by Kronig and Penny in the year 1931.

The potential energy of an electron, when it moves in one dimensional perfect crystal lattice is assumed in the form of rectangular wells as shown in fig.

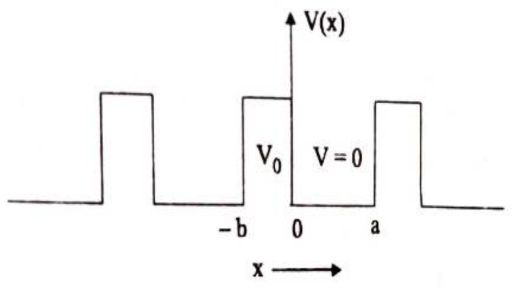

Fig. 5. 12 One dimensional periodic potential

(Kronig and Penny model)

In region where $0 < x < a$, the potential energy is zero and in the region $-b < x < 0$, the potential energy is V_o.

The one dimensional Schrodinger wave equations for two regions are written as

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}[E - 0]\psi = 0 \text{ for } 0 < x < a$$

$$\text{(or) } \frac{d^2\psi}{dx^2} + \alpha^2\psi r = 0$$

$$\text{where } \alpha^2 = \frac{2mE}{\hbar^2}$$

and

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V_0)\psi = 0 \text{ for } -b < x < 0$$

$$\text{(or) } \begin{aligned} \frac{d^2\psi}{dx^2} - \beta^2\psi &= 0 \\ \text{where } \beta^2 &= \frac{2m}{\hbar^2}(V_0 - E) \end{aligned}$$

For both the regions, the appropriate solution suggested by Bloch is of the from

$$\Psi = e^{ikx}U_K(x)$$

Differentiating equation (5) and substituting in equations (2) and (4), then further

$$\frac{P\sin\alpha a}{\alpha a} + \cos\alpha a = \cos ka$$

$$\frac{Psin\alpha a}{\alpha a} + cos\alpha a = coska$$

$$\text{where } \alpha = \frac{\sqrt{2mE}}{\hbar} \text{ and } P = \frac{mV_o ba}{\hbar^2}$$

The term P is ealled as Seattering power of the potential barrier. It is a measure of strength with which potential bax'ier. It is a measure of strength with the electrons are attracted by the positive ions.

The equation is analysed by drawing a plot between αa and $\left[\frac{P\sin\alpha a}{\alpha a} + \cos\alpha\alpha\right]$.

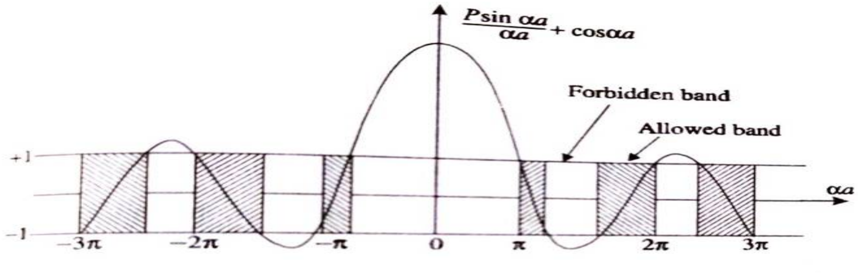

Fig. 5. 13 A plot of αa versus $\left(\frac{P\sin\alpha a}{\alpha a} + \cos\alpha a\right)$

From the graph, we conclude that

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

2 The width of allowed energy band (shaded portion) increases with increase of energy values i.e., increasing the values of αa.

This is because the first term of equation $\frac{P\sin\alpha a}{\alpha a}$ decreases with increase of αa.

3 In the limit $P \to \infty$ the allowed energy band reduces to one single energy level corresponding to the discrete energy level of an isolated atom. (ie., $a \to \infty$)

4 In the other extreme case, when $P \to 0$

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

Thus, $\alpha = k$

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

$$\frac{2mE}{\hbar^2} = h^2$$

$$E = \frac{\hbar k^2}{2mE}$$

$$\boldsymbol{E} = \frac{h^2 k^2}{8\pi^2 m}$$

which corresponds to free electron model.

This indicates that the particle is completely free and no energy levels exist. Thus by varying P from 0 to ∞ we find that the completely free electron becomes completely bound.

$E - K$ curve

The energy of the electron in the periodic lattice is given by

$$E = \frac{h^2 k^2}{8\pi m} \cdot h^2$$

From the above equation as h changes, the corresponding energy (E) also changes. For a free electron, the energy curve is continuous as shown by dotted parabola.

But for the electron in the periodic lattice, the energy curve is not a continuous parabola and discontinuity occur at $k = \frac{n\pi}{a}$.

The zone between $+\frac{\pi}{a}$ and $-\frac{\pi}{a}$ is known as first Brillouin ocne and the second zone has two parts from $+\frac{\pi}{a}$ to $+\frac{2\pi}{a}$, and -$\frac{\pi}{a}$ to $-\frac{2\pi}{a}$. These zones are the allowed energy bands separated by forbidden energy bands as shown in fig. 7.23

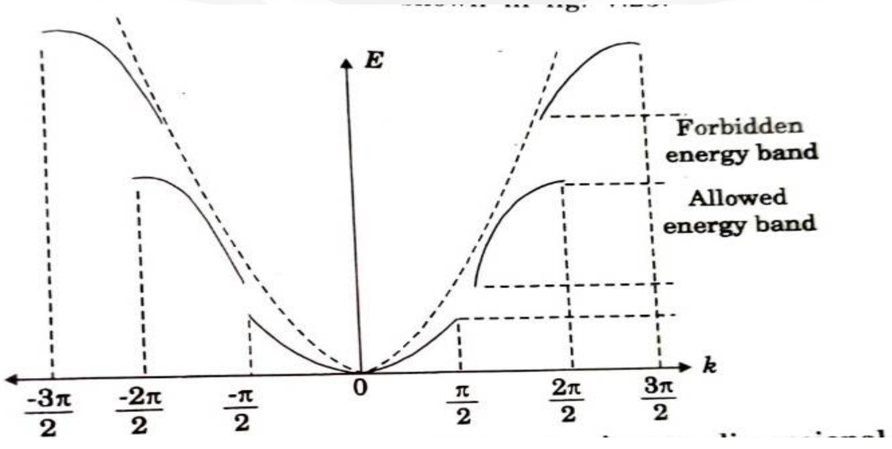

Fig5.14 Plot of energy Vs. wave vector in one dimensional lattice