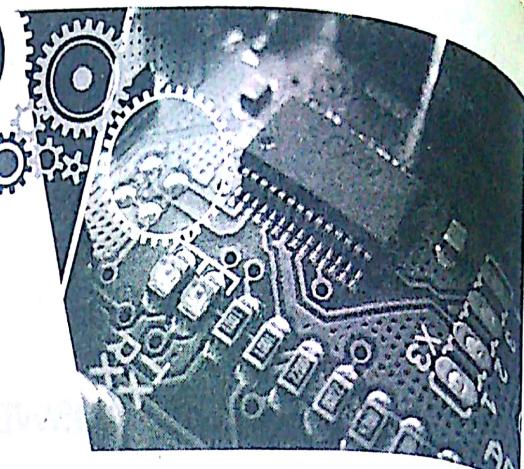


## BAND THEORY



3.1



### INTRODUCTION

With the help of the free electron theory, we cannot explain why certain solids have large number of free electrons and thus behave as good conductors. It cannot also explain why some are good electrical insulators and others are semiconductors. *The reason behind the failure of free electron theory is due to the oversimplified assumption that the conduction electrons in a metal move in a constant potential (conventionally taken as zero potential) of positive ion cores and hence is free to move about in a crystal.* To realise the difference in electrical conductivity at metal (good conductor), semiconductor and insulator, **the free electron theory was further modified by taking into account the interaction of free electron with the residual positive ions in the metal.** This indicates the potential energy of an electron due to ion cores is not constant, but it may change with position of the electron within the crystal.

In band theory, a periodic potential energy of an electron within the crystal has been considered.

3.2



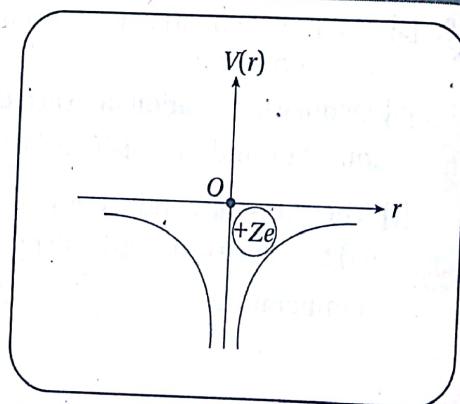
### PERIODIC POTENTIAL IN A CRYSTALLINE SOLID

Consider an electron in the vicinity of an atomic nucleus of charge  $Ze$ . So the potential energy of the electron at a distance  $r$  from this atomic nucleus is

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} \quad \dots (3.2.1)$$

where  $\epsilon_0$  is the permittivity of free space. The variation of potential energy [ $V(r)$ ] with the distance  $r$  for an isolated atom is shown in Fig. 1.

When the number of atoms is increased, the shape of the graph is modified. If a number of such atomic nuclei are brought to close each other to form a crystal, the potential of an electron is the sum of the potentials due to individual nuclei. The variation of potential with



**Fig. 1** Variation of potential energy with distance for an isolated atom

- ① Between the neighbouring positive ion cores, the potential energy variation of valence electron is shown. At smaller distance from the ions, the potential energy of valence electron will be low and of course kinetic energy is high. But the potential energy increases with the increase of distance of the electron from the ion cores.

distance for an infinite one dimensional crystal is shown in Fig. 2 (by considering one dimensional representation of potential experienced by an electron in a periodic crystal lattice).

The electrostatic potential energy of an electron in the field of positive charges of nuclei is attractive in nature i.e. negative. Due to this reason, the potential is shown along the  $-V(x)$  axis. Here the nuclei (or ion cores) are considered at rest and the potential experienced by an electron inside a metallic crystal is periodic in nature with the periodicity of the lattice (i.e. lattice constant  $a$ ). The potential near the surface of the crystal is interrupted and is shown on the right-hand edge of the figure. This is because there are no ions to reduce the potential again. The periodicity character of the potential extends to infinity in all directions inside the crystal. We shall now discuss the behaviour of the electron in this potential using a single electron approximation. *The behaviour of an electron in periodic potential can be described by Bloch theorem and by the Kronig-Penny model.* This can be done by finding the electron wave function.

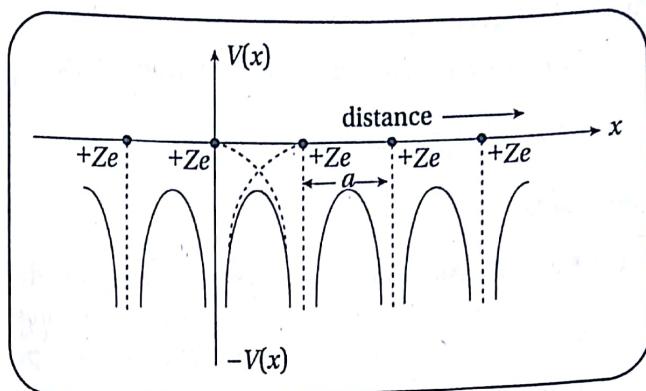


Fig. 2 ▷ Variation of potential energy of an electron with distance ( $x$ ) in a one dimensional periodic crystal with lattice constant  $a$

### 3.3 BLOCH THEOREM

In realistic approach, the potential inside a metallic crystal is periodic in nature due to the periodicity of the lattice [Fig. 2]. If the electron is supposed to move in an one dimensional periodic potential with a period equal to the lattice constant  $a$ , the periodic potential is given by

$$V(x) = V(x + a)$$

... (3.3.1)

The corresponding one dimensional Schrödinger equation for an electron moving in this one dimensional periodic potential is

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} [E - V(x)]\psi = 0 \quad \dots (3.3.2)$$

The solution of this equation are plane waves of the type  $e^{\pm ikx}$  modulated by a periodic function  $u_k(x)$  having the same periodicity as that of the lattice. Therefore, the solutions are in the form

$$\psi(x) = e^{\pm ikx} u_k(x) \quad \dots (3.3.3)$$

with  $u_k(x) = u_k(x + a)$  and  $u_k(x)$  is the periodic function in  $x$ .

The wave function of the type  $\psi(x) = e^{\pm ikx} u_k(x)$  is called Bloch function. The wave vector  $\vec{k}$  gives the direction of Bloch wave.

With reference to this solution of equation (3.3.3), there is an important theorem known as **Bloch theorem** or **Floquet's theorem**. Thus, the **Bloch theorem** is a

Although the character functions for the regions are defined and As we define and Now we can see that the wavy lines represent the periodic potential wells and the solid lines represent the barriers.

mathematical statement regarding the form of the one electron wave functions in a perfectly periodic potential where the solutions (i.e. wave functions) are plane waves of the type  $e^{\pm ikx}$  modulated by a periodic function  $u_k(x)$  having the same periodicity as the lattice.

The three dimensions Bloch function is given by

$$\psi_k(r) = e^{i(\vec{k} \cdot \vec{r})} u_k(r)$$

... (3.3.4)

#### Special Note

- ① **Periodic potential of the crystal:** In a crystal, the positively charged nucleus along with the remaining electrons forms the positive ion cores. The positive ion cores are arranged in a regular periodic manner depending on the type of the crystal. The conduction electrons experience the attractive periodic potential, such that  $V(r) = V(r + a)$ , where  $r$  is the distance of the conduction electron from the positive ion cores and the periodicity is equal to the lattice constant  $a$ .
- ② **Wave vector ( $\vec{k}$ ):** It gives the direction of the waves. Its magnitude is  $= \frac{2\pi}{\lambda} = \frac{p}{\hbar}$ . Each electron will have its own  $k$  and its own energy.

3.4



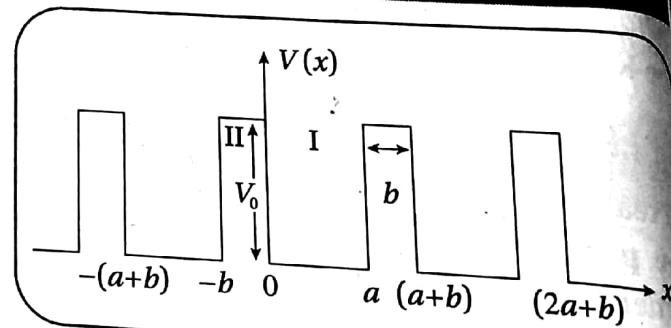
#### THE KRONIG-PENNEY MODEL

In 1930, R. de L. Kronig and W. G. Penney proposed a model that illustrates the behaviour of electrons in a periodic potential. In this model, it is assumed a relatively simple one dimensional periodic square potential wells as shown in Fig. 3. Each well represents an approximation to the potential produced by one positive ion. The potential energy of an electron is assumed to be a linear array of square potential wells of depth  $V_0$  and width  $a$  separated by barriers of width  $b$  [Fig. 3]. Here  $(a + b)$  is the period of potential.

It is assumed that the potential energy is zero when  $x$  lies between 0 to  $a$  (i.e., at the bottom of the well) and it is  $V_0$  when  $x$  lies between  $-b$  to 0 (i.e. outside a well).

i.e.

$$\begin{aligned} V(x) &= 0, 0 < x < a \\ &= V_0, -b < x < 0 \end{aligned}$$



**Fig. 3** ▷Kronig-Penney model of one dimensional periodic potential well

- Since the periodicity of the potential is  $(a + b)$ ,  $V(x) = V(x + a + b)$ . Here,  $x$  is the distance of the conduction electron from the positive ion cores of the crystal.
- The potential well corresponds to the vicinity of the ion core whereas the barrier corresponds to the region between two ion cores.

Although this model is highly artificial yet this model provides many of the characteristic features of the behaviour of electrons in a periodic lattice. The wave functions associated with this model can be calculated by solving Schrödinger equations for the regions I and II. The time independent Schrödinger wave equations for the two regions are

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

and  $\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} (E - V_0)\psi = 0 \quad \text{for } -b < x < 0$  ... (3.4.1)

Assuming that energy  $E$  of the electron under consideration is less than  $V_0$ , we define two quantities

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

and  $\beta^2 = \frac{2m}{\hbar^2} (V_0 - E)$  ... (3.4.3)

Now, we can write equation (3.4.1) and equation (3.4.2) as

$$\frac{d^2\psi}{dx^2} + \alpha^2\psi = 0 \quad \text{for } 0 < x < a \quad \dots (3.4.5)$$

and  $\frac{d^2\psi}{dx^2} - \beta^2\psi = 0 \quad \text{for } -b < x < 0$  ... (3.4.6)

Since the potential is periodic,  $V(x) = V(x + a + b)$ , we can write from Bloch theorem, the **solutions of the Schrödinger equations** are of the form of

$$\psi(x) = e^{ikx} u_k(x) \quad \dots (3.4.7)$$

where  $u_k(x)$  is the periodic function of  $x$  with periodicity  $(a + b)$ ; i.e.

$$u_k(x) = u_k(x + a + b) \quad \dots (3.4.8)$$

Substituting the value of  $\psi(x)$  in equation (3.4.5), we get

$$\frac{d^2u_1}{dx^2} + 2ik \frac{du_1}{dx} + (\alpha^2 - k^2)u_1 = 0 \quad \dots (3.4.9)$$

where  $u_1$  represents the value of  $u_k(x)$  in the interval  $0 < x < a$  and  $|k|$  is the propagation constant of each electron.

Similarly, substituting the value of  $\psi(x)$  from equation (3.4.7) in equation (3.4.6), we obtain

$$\frac{d^2u_2}{dx^2} + 2ik \frac{du_2}{dx} - (\beta^2 + k^2)u_2 = 0 \quad \dots (3.4.10)$$

where  $u_2$  represents the value of  $u_k(x)$  in the interval  $-b < x < 0$ .

The solutions of equations (3.4.9) and (3.4.10) are  
 $u_1 = Ae^{i(\alpha-k)x} + Be^{-i(\alpha+k)x}$  for  $0 < x < a$  ... (3.4.11)

and  
 $u_2 = Ce^{(\beta-ik)x} + De^{-(\beta+ik)x}$  for  $-b < x < 0$  ... (3.4.12)

where  $A, B, C$  and  $D$  are constants. These constants are determined in such a way that the wave function  $\psi$  and its derivative  $\frac{d\psi}{dx}$  are single valued and continuous at  $x = 0$ ,  $x = a$  and  $x = -b$ . So, the constants  $A, B, C$  and  $D$  are determined from the boundary conditions—

at  $x = 0$ ,  $u_1(x) = u_2(x)$  ... (3.4.13)

and  $\frac{du_1(x)}{dx} = \frac{du_2(x)}{dx}$  ... (3.4.14)

Similarly, at  $x = a$  and  $x = -b$ ,  $[u_1(x)]_{x=a} = [u_2(x)]_{x=-b}$  ... (3.4.15)

and  $\left[ \frac{du_1}{dx} \right]_{x=a} = \left[ \frac{du_2}{dx} \right]_{x=-b}$  ... (3.4.16)

By applying these boundary conditions in equations (3.4.11) and (3.4.12), we get the following four linear homogeneous equations:

$$A + B = C + D$$

$$Ai(\alpha - k) - Bi(\alpha + k) = C(\beta - ik) - D(\beta + ik) \quad \dots (3.4.17)$$

$$Ae^{i(\alpha-k)a} + Be^{-i(\alpha+k)a} = Ce^{-(\beta-ik)b} + De^{(\beta+ik)b} \quad \dots (3.4.18)$$

$$Ai(\alpha - k)e^{i(\alpha - k)a} - Bi(\alpha + k)e^{-i(\alpha + k)a} = C(\beta - ik)e^{-(\beta - ik)b} - D(\beta + ik)e^{(\beta + ik)b} \quad \dots (3.4.19)$$

and

These above four equations have a solution only if  $A, B, C$  and  $D$  vanish. ... (3.4.20)

The solutions of equations (3.4.9) and (3.4.10) are  
 $u_1 = Ae^{i(\alpha-k)x} + Be^{-i(\alpha+k)x}$  for  $0 < x < a$   
and  $u_2 = Ce^{(\beta-ik)x} + De^{-(\beta+ik)x}$  for  $-b < x < 0$

where  $A, B, C$  and  $D$  are constants. These constants are determined in such a way that the wave function  $\psi$  and its derivative  $\frac{d\psi}{dx}$  are single valued and continuous at  $x = a$  and  $x = -b$ . So, the constants  $A, B, C$  and  $D$  are determined from the boundary conditions—

$$\text{at } x = 0, u_1(x) = u_2(x)$$

$$\text{and } \frac{du_1(x)}{dx} = \frac{du_2(x)}{dx}$$

$$\text{Similarly, at } x = a \text{ and } x = -b, [u_1(x)]_{x=a} = [u_2(x)]_{x=-b}$$

$$\text{and } \left[ \frac{du_1}{dx} \right]_{x=a} = \left[ \frac{du_2}{dx} \right]_{x=-b}$$

By applying these boundary conditions in equations (3.4.11) and (3.4.12), we get the following four linear homogeneous equations :

$$A + B = C + D \quad \dots(3.4.17)$$

$$Ai(\alpha - k) - Bi(\alpha + k) = C(\beta - ik) - D(\beta + ik) \quad \dots(3.4.18)$$

$$Ae^{i(\alpha-k)a} + Be^{-i(\alpha+k)a} = Ce^{-(\beta-ik)b} + De^{(\beta+ik)b} \quad \dots(3.4.19)$$

$$\text{and } Ai(\alpha - k)e^{i(\alpha - k)a} - Bi(\alpha + k)e^{-i(\alpha + k)a}$$

$$= C(\beta - ik)e^{-(\beta - ik)b} - D(\beta + ik)e^{(\beta + ik)b} \quad \dots(3.4.20)$$

These above four equations have a solution only if the determinant of the coefficients of  $A, B, C$  and  $D$  vanish i.e.

$$\begin{vmatrix} 1 & 1 & 1 & 1 \\ i(\alpha - k) & -i(\alpha + k) & (\beta - ik) & -(\beta + ik) \\ e^{i(\alpha - k)a} & e^{-i(\alpha + k)a} & e^{-(\beta - ik)b} & e^{(\beta + ik)b} \\ i(\alpha - k)e^{i(\alpha - k)a} & -i(\alpha + k)e^{-i(\alpha + k)a} & (\beta - ik)e^{-(\beta - ik)b} & -(\beta + ik)e^{(\beta + ik)b} \end{vmatrix} = 0$$

After expanding and then simplifying this determinant,<sup>③</sup> we have  $\dots(3.4.21)$

$$\frac{\beta^2 - \alpha^2}{2\alpha\beta} \sin a\alpha \sinh b\beta + \cos a\alpha \cosh b\beta = \cos k(a+b) \quad \dots(3.4.22)$$

<sup>③</sup> To avoid detail calculations to get equation (3.4.21)

at  $x = 0$ ,  $u_1(x) = u_2(x)$

$$\text{and } \frac{du_1(x)}{dx} = \frac{du_2(x)}{dx}$$

Similarly, at  $x = a$  and  $x = -b$ ,  $[u_1(x)]_{x=a} = [u_2(x)]_{x=-b}$

$$\text{and } \left[ \frac{du_1}{dx} \right]_{x=a} = \left[ \frac{du_2}{dx} \right]_{x=-b}$$

By applying these boundary conditions in equations (3.4.11) and (3.4.12), we get the following four linear homogeneous equations:

$$A + B = C + D$$

$$Ai(\alpha - k) - Bi(\alpha + k) = C(\beta - ik) - D(\beta + ik)$$

$$Ae^{i(\alpha - k)a} + Be^{-i(\alpha + k)a} = Ce^{-(\beta - ik)b} + De^{(\beta + ik)b}$$

and

$$Ai(\alpha - k)e^{i(\alpha - k)a} - Bi(\alpha + k)e^{-i(\alpha + k)a} = C(\beta - ik)e^{-(\beta - ik)b} - D(\beta + ik)e^{(\beta + ik)b}$$

These above four equations have a solution only if the determinant of the coefficients of  $A$ ,  $B$ ,  $C$  and  $D$  vanish i.e.

$$\begin{vmatrix} 1 & 1 & 1 & 1 \\ i(\alpha - k) & -i(\alpha + k) & (\beta - ik) & -(\beta + ik) \\ e^{i(\alpha - k)a} & e^{-i(\alpha + k)a} & e^{-(\beta - ik)b} & e^{(\beta + ik)b} \\ i(\alpha - k)e^{i(\alpha - k)a} & -i(\alpha + k)e^{-i(\alpha + k)a} & (\beta - ik)e^{-(\beta - ik)b} & -(\beta + ik)e^{(\beta + ik)b} \end{vmatrix} = 0$$

... (3.4.21)

After expanding and then simplifying this determinant, <sup>③</sup> we have

$$\frac{\beta^2 - \alpha^2}{2\alpha\beta} \sin a\alpha \sinh b\beta + \cos a\alpha \cosh b\beta = \cos k(a + b) \quad ... (3.4.22)$$

- <sup>③</sup> To avoid detail calculations to get equation (3.4.22) from equations (3.4.11) and (3.4.12), one can write directly after equation 3.4.12 as follows :

Using periodicity of the wave function and the boundary conditions satisfied by them at  $x = 0$ ,

$x = a$  and  $x = -b$ , we get

$$\frac{\beta^2 - \alpha^2}{2\alpha\beta} \sin a\alpha \sinh b\beta + \cos a\alpha \cosh b\beta = \cos k(a + b)$$



This equation is complicated. To simplify this equation, Kronig and Penney considered the case where  $V_0$  tends to infinity and  $b$  approaches to zero (i.e. for infinitely thin potential barriers of infinitely large potential) but the product  $bV_0$  remains finite. In this case, there is a finite possibility for an electron with energy ( $E$ ) less than  $V_0$  to tunnel from one potential well (cell) to the next.

Now, as  $b \rightarrow 0$ ,  $\sinh b\beta \rightarrow b\beta$ ,  $\cosh b\beta \rightarrow 1$  and  $\beta^2 - \alpha^2 = \beta^2$ . Hence, the equation (3.4.22) becomes

$$\frac{\beta^2}{2\alpha\beta} b\beta \sin \alpha\alpha + \cos \alpha\alpha = \cos ka$$

$$\beta^2 \frac{b}{2\alpha} \sin \alpha\alpha + \cos \alpha\alpha = \cos ka$$

$$\left(\beta^2 \frac{ab}{2}\right) \frac{\sin \alpha\alpha}{\alpha\alpha} + \cos \alpha\alpha = \cos ka$$

$$\text{or, } P \frac{\sin \alpha\alpha}{\alpha\alpha} + \cos \alpha\alpha = \cos ka$$

$$\text{where } P = \beta^2 \left( \frac{ab}{2} \right) = \frac{2mV_0}{\hbar^2} \frac{ab}{2} = \frac{mV_0 ab}{\hbar^2} \quad \dots(3.4.23)$$

$$\text{The term } V_0 b \text{ (product of the depth and the width of the barrier) is called strength of} \quad \dots(3.4.24)$$

**the potential barrier.** The term  $P \left( = \frac{mV_0 ab}{\hbar^2} \right)$  is sometimes referred as the scattering power of the potential barrier. The larger the value of  $P$ , the stronger is the binding energy of the electrons within the potential well. Thus, the physical significance of  $P$  is that, if  $P$  is increased, the electron gets bound more strongly to a particular potential well. If  $P$  tends to zero (i.e.  $P \rightarrow 0$ ), the potential barrier becomes very weak and then the electrons become free.

The RHS of equation (3.4.23) which is a cosine function (i.e.  $\cos ka$ ) must lie between +1 and -1. So, the LHS of equation (3.4.23) should have values between +1 and -1. It indicates that the LHS of this equation should take only those permissible or allowed values of  $\alpha\alpha$  for which its values lies in between +1 and -1. Other values of  $\alpha\alpha$  are not allowed.

In order to determine the range of allowed and forbidden energies, we plot  $P \frac{\sin \alpha\alpha}{\alpha\alpha} + \cos \alpha\alpha$  versus  $\alpha\alpha$ , for  $P = \frac{3\pi}{2}$  as shown in Fig. 4.

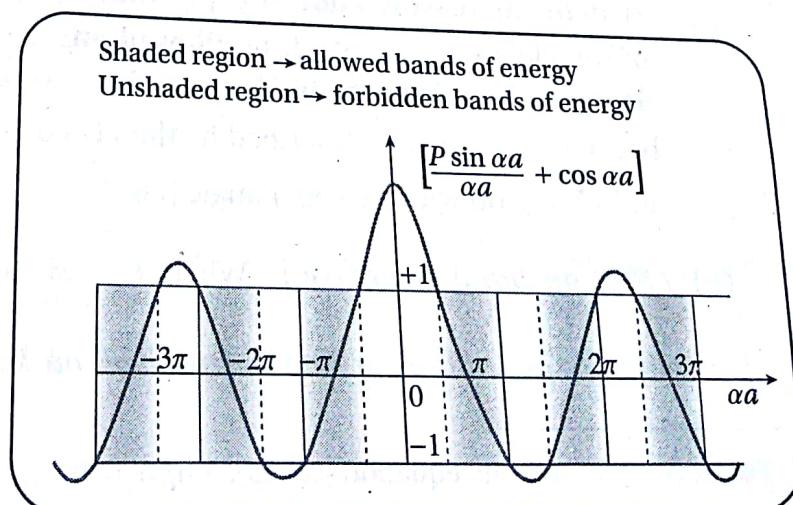


Fig. 4 ▷ Graph of  $P \frac{\sin \alpha\alpha}{\alpha\alpha} + \cos \alpha\alpha$  versus  $\alpha\alpha$  for  $P = \frac{3\pi}{2}$



**Observations from the curve:** The following conclusions may be drawn from the curve.

- ① **Existence of alternate allowed energy bands and forbidden gaps :** In the curve, the abscissa  $\alpha a$  (where  $\alpha = \frac{2mE}{\hbar^2}$ ) is a measure of the energy. The values of  $\alpha a$  for which the function  $P \frac{\sin \alpha a}{\alpha a} + \cos \alpha a$  lies within +1 and -1, are allowed. The values of  $\alpha a$  for which this function lies above +1 and below -1 are forbidden. Thus, the basic conclusion of the Kronig-Penney model is that the energy spectrum of the electrons consists of a number of allowed energy bands separated by forbidden regions. So, the energy spectrum of electrons consists of alternate allowed energy bands (shaded regions) and the forbidden energy gaps (unshaded regions). The boundaries of the allowed energy levels correspond to the values of  $\cos ka = n\pi$  i.e.  $k = \frac{n\pi}{a}$ ,  $n = \pm 1, \pm 2 \dots$ . The permitted values of the function are indicated by a solid line in Fig. 4.

- ② **Effect of  $\alpha a$  on the width of the allowed energy bands :** With the increase of  $\alpha a$ , the term  $P \frac{\sin \alpha a}{\alpha a}$  decreases. Thus, the width of the allowed energy bands increases (i.e. becomes wider) and the width of the forbidden bands decreases (i.e. becomes narrower) with the increase of  $\alpha a$  (i.e. the energy).

- ③ **Effect of  $P$  on the width of allowed energy band and band structure :**

(a) **Effect on width of allowed energy band :**

With the increasing value of  $P$  (i.e. with the increasing value of binding energy of the electron), the width of allowed energy bands becomes narrower (i.e. decreases) and the forbidden gap increases (i.e. becomes wider). This is because the function described by the LHS of equation (3.4.23) crosses the +1 and -1 region with a steeper angle [Fig. 5].

- (b) **Effect on band structure :** When  $P \rightarrow \infty$ ,  $E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$ . So the energy of electrons depends on  $n$  and independent on  $k$ . Thus, when  $P \rightarrow \infty$ , The energy

- ④ For  $P \rightarrow \infty$  we get from equation (3.4.23),  $\sin \alpha a = 0$

$$\text{or, } \alpha a = \pm n\pi, \text{ where } n = 1, 2, 3, \dots, \text{ or, } a \left( \frac{\sqrt{2mE_n}}{\hbar} \right) = \pm n\pi \text{ or, } E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$

Therefore energy depends on  $n$ . This indicates energy levels are discrete. These discrete energy levels exist for these electrons which are bound strongly to the nuclei as in single isolated atom.

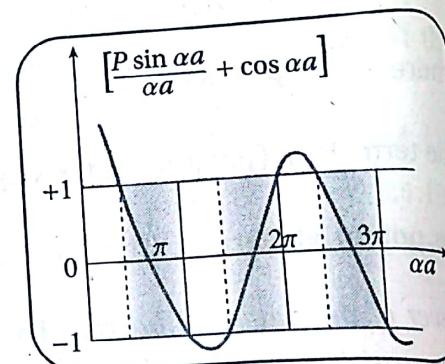


Fig. 5 ▷ The width of allowed energy bands decreases with the increasing value of  $P$ .

**Observations from the curve:** The following conclusions may be drawn from the curve.

① **Existence of alternate allowed energy bands and forbidden gaps:** In the curve, the abscissa  $\alpha a$  (where  $\alpha = \frac{2mE}{\hbar^2}$ ) is a measure of the energy. The values of  $\alpha a$  for which the function  $P \frac{\sin \alpha a}{\alpha a} + \cos \alpha a$  lies within  $+1$  and  $-1$ , are allowed. The values of  $\alpha a$  for which this function lies above  $+1$  and below  $-1$  are forbidden. Thus, the basic conclusion of the Kronig-Penney model is that the energy spectrum of the electrons consists of a number of allowed energy bands separated by forbidden regions, i.e., the energy spectrum of electrons consists of alternate allowed energy bands (shaded regions) and the forbidden energy gaps (unshaded regions). The boundaries of the allowed energy levels correspond to the values of  $\cos ka = n\pi$  i.e.  $k = \frac{n\pi}{a}$

$n = \pm 1, \pm 2, \dots$ . The permitted values of the function are indicated by a solid line in Fig. 4.

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③ **Effect of  $P$  on the width of allowed energy band and band structure :**

(a) **Effect on width of allowed energy band :**

With the increasing value of  $P$  (i.e. with the increasing value of binding energy of the electron), the width of allowed energy bands becomes narrower (i.e. decreases) and the forbidden gap increases (i.e. becomes wider). This is because the function described by the LHS of equation (3.4.23) crosses the  $+1$  and  $-1$  region with a steeper angle [Fig. 5].

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④ For  $P \rightarrow \infty$  we get from equation (3.4.23),  $\sin \alpha a = 0$

or,  $\alpha a = \pm n\pi$ , where  $n = 1, 2, 3, \dots$ , or,  $a \left( \frac{\sqrt{2mE_n}}{\hbar} \right) = \pm n\pi$  or,  $E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$

Therefore energy depends on  $n$ . This indicates energy levels are discrete. These discrete energy levels exist for these electrons which are bound strongly to the nuclei as in single isolated atom.

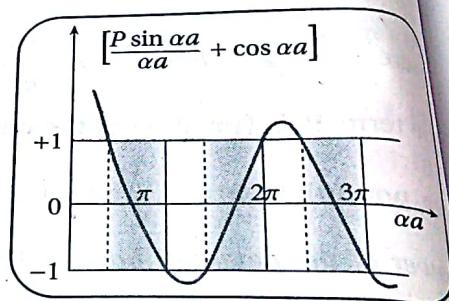
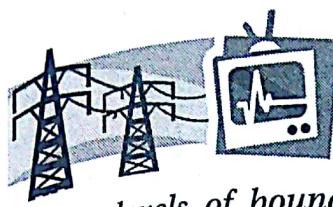


Fig. 5 ▷ The width of allowed energy bands decreases with the increasing value of  $P$ .



levels of bound electrons are discrete in nature (line spectrum) that exists in isolated system. In this case, all the electrons are tightly bound to their nuclei.

$$\text{When } P \rightarrow 0, E = \frac{\hbar^2 k^2}{2m} \text{ ⑤.}$$

This is the energy of a free electron. Thus, when  $P \rightarrow 0$ , all the electrons are free electrons and all energies are allowed for them, (i.e. the energy spectrum is called quasi continuous).

- ④  **$E$ - $k$  diagram, origins of allowed energy bands, forbidden gap from  $E$ - $k$  diagram and Brillouin zones :** For the boundaries of the allowed energy levels,

$$\cos ka = \pm 1 \quad \text{or, } \cos ka = \cos n\pi \quad \text{or, } k = \frac{n\pi}{a}, \quad \text{where } n = \pm 1, \pm 2, \pm 3, \dots$$

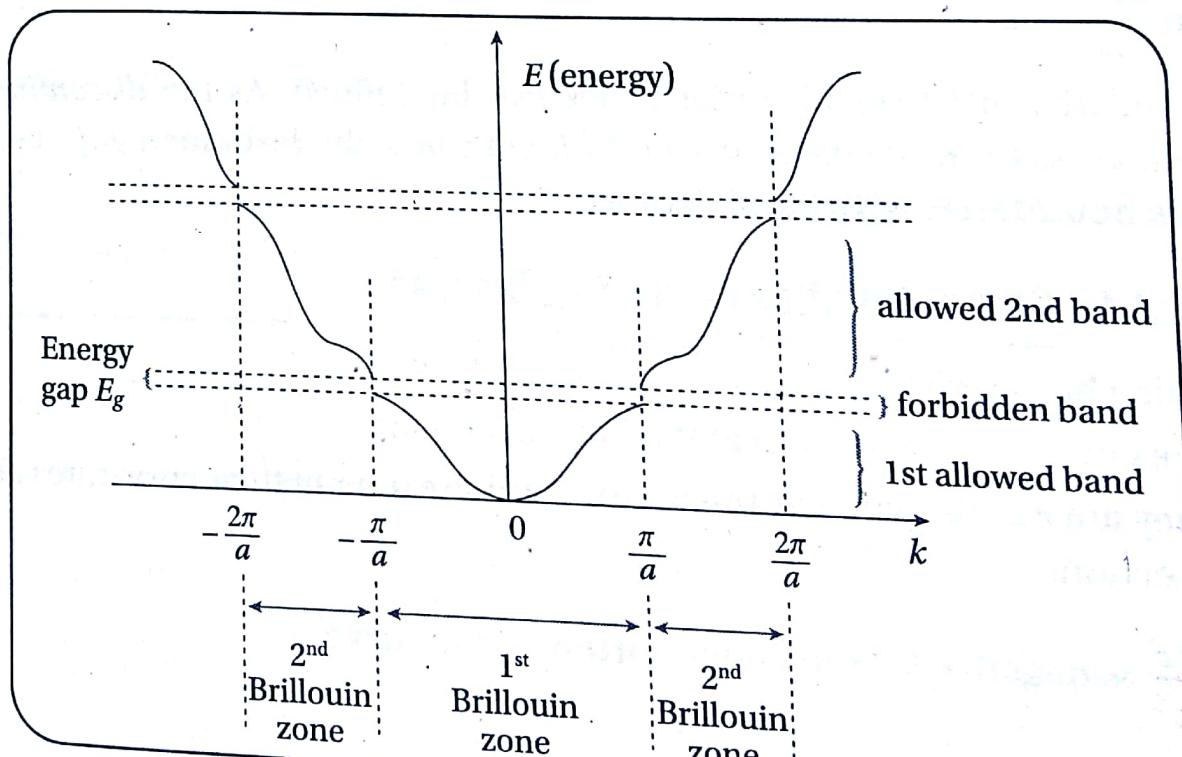


Fig. 6 ▷  $E$ - $k$  diagram and Brillouin zones

A plot of energy  $E$  of the electron

**E-k diagram, energy bands, forbidden gap from E-k diagram and Brillouin zones :** For the boundaries of the allowed energy levels,  $\cos ka = \pm 1$  or,  $\cos n\pi$  or,  $k = \frac{n\pi}{a}$ , where  $n = \pm 1, \pm 2, \pm 3, \dots$

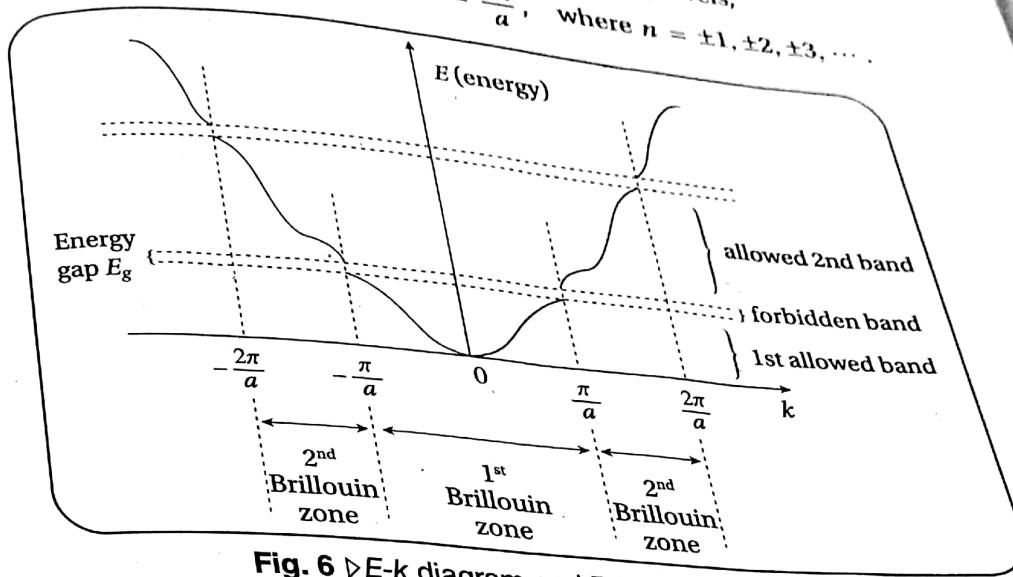


Fig. 6 ▷ E-k diagram and Brillouin zones

A plot of energy  $E$  of the electron versus wave number  $k$  [with the help of equation (3.4.23)] is called **E-k diagram** [Fig. 6].

It is observed from the figure that discontinuities in the energy curve occur at  $k = \pm \frac{\pi}{a}, \pm \frac{2\pi}{a}, \pm \frac{3\pi}{a}, \dots$ .

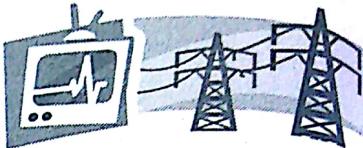
Each position of the curve may be called a band. The solid discontinuous curves indicates the allowed energy values of electrons in a periodic potential. The broken parabolic line represents the energy of free electrons. So, the **energy gaps occur** at

$$k = \pm \frac{\pi}{a}, \pm \frac{2\pi}{a}, \pm \frac{3\pi}{a}, \dots$$

⑤ For  $P = 0$ , we get from equation (3.4.23),  $\cos a\alpha = \cos ka$

$$\text{or, } \alpha = k \text{ or, } \frac{2mE}{\hbar^2} = k^2 \text{ or, } E = \frac{\hbar^2 k^2}{2m}$$

This is the **energy of a free electron**.



Thus, the origins of allowed energy bands and forbidden energy gaps can be explained with the help of  $E-k$  diagram.

##### ⑤ Brillouin zones :

We know from Kronig-Penney model, the discontinuities in energy occur at  $k = \frac{n\pi}{a}$ , where  $n = \pm 1, \pm 2, \pm 3, \dots$ . These  $k$  values define the boundaries of zone extending first, second, third, etc. Brillouin zones.

The region or zone extending from  $k = -\frac{\pi}{a}$  to  $k = \pm \frac{\pi}{a}$ , where the electron has allowed energy, is called first Brillouin zone. The region extending from  $k = -\frac{\pi}{a}$  to  $k = -\frac{2\pi}{a}$  and  $k = \frac{\pi}{a}$  to  $k = \frac{2\pi}{a}$  is called second Brillouin zone. Thus, the second Brillouin zone consists of two parts—one from  $\frac{+\pi}{a}$  to  $\frac{+2\pi}{a}$  and the second from  $\frac{-\pi}{a}$  to  $\frac{-2\pi}{a}$ .

Similarly, other higher order zones can be defined. As the discontinuity of energy values occur at the boundary of Brillouin zones, the forbidden gaps are observed at the boundaries of Brillouin zones.

#### 3.4.1 Characteristics of the $E-k$ Diagram

The main characteristics of the curves are as follows :

zone extending from  $k = -\frac{\pi}{a}$  to  $k = \pm \frac{\pi}{a}$ , where the electron allowed energy, is called **first Brillouin zone**. The region extending from  $k = -\frac{2\pi}{a}$  to  $k = \frac{2\pi}{a}$  is called **second Brillouin zone**. Thus, the second Brillouin zone consists of two parts—one from  $\frac{-\pi}{a}$  to  $\frac{+2\pi}{a}$  and the second from  $\frac{-2\pi}{a}$  to  $\frac{-\pi}{a}$ .

Similarly, other higher order zones can be defined. As the discontinuity of energy values occur at the boundary of Brillouin zones, the **forbidden gaps are observed at the boundaries of Brillouin zones**.

### 3.4.1 Characteristics of the E-k Diagram

The main characteristics of the curves are as follows :

- ① The curves are **horizontal at the bottom and top**.
- ② They are **parabolic near the bottom and the top** but their curvatures are in opposite directions.
- ③  $\frac{d^2E}{dk^2}$  is negative for the upper portion of the curve.
- ④  $\frac{d^2E}{dk^2}$  is positive for the lower portion of the curve.

#### PROBLEM

1 The side of a two dimensional square lattice is  $4\text{\AA}$ .

(i) Find the value of the momentum of electron for which the boundary of first Brillouin zone appears.

(ii) Calculate the corresponding energy of the free electron for that momentum.

#### Solution

- i We know the first Brillouin zone appears for wave number,  $k = +\frac{\pi}{a}$  to  $k = -\frac{\pi}{a}$  where  $a = \text{side of the lattice} = 4\text{\AA}$
- Now, the momentum of the electron for which the boundary of first Brillouin zone appear is

$$P = \hbar k = \hbar \left(\frac{\pi}{a}\right) = \frac{h}{2\pi} \left(\frac{\pi}{a}\right) = \frac{h}{2a} = \frac{6.62 \times 10^{-34}}{2 \times 4 \times 10^{-10}} = 0.8275 \times 10^{-24} \text{ kg} \cdot \text{m} \cdot \text{s}^{-1}$$

lowest band,  $E = \frac{P^2}{4\pi^2 m}$  meanings.

**Solution** We know from the

$$P \frac{\sin \alpha \alpha}{\alpha \alpha} + \cos \alpha \alpha = c$$

where  $P = \text{scattering power}$

We know, when  $k = 0$ ,

$$P \frac{\sin \alpha \alpha}{\alpha \alpha} + \cos \alpha \alpha = c$$

$$\text{or, } \frac{P}{\alpha \alpha} = \frac{1 - \cos \alpha \alpha}{\sin \alpha \alpha}$$

Now,  $\cos \alpha \alpha = 1$  —

and  $\sin \alpha \alpha = \alpha$

So, the equation

$$\frac{P}{\alpha \alpha} = 1$$

$$\text{or, } P =$$

$$\text{or, } P =$$

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ii The corresponding energy of the electron,

$$E = \frac{p^2}{2m} = \frac{(0.8275 \times 10^{-24})^2}{2 \times 9.1 \times 10^{-31}} = 0.0376 \times 10^{-17} \text{ J}$$

**PROBLEM**

**2** With the help of Kronig-Penney model with  $P \ll 1$ , prove that the energy of the lowest band,  $E = \frac{P\hbar^2}{4\pi^2 ma^2}$  at  $k = 0$ , where the symbols represent their usual meanings.

**Solution** We know from the condition of Kronig-Penney model,

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

where  $P = \text{scattering power of the potential barrier} = \frac{mV_0 ab}{\hbar^2}$  and  $\alpha = \sqrt{\frac{2mE}{\hbar^2}}$ .  
We know, when  $k = 0$ ,

$$P \frac{\sin a\alpha}{a\alpha} + \cos a\alpha = 1$$

$$\text{or, } \frac{P}{a\alpha} = \frac{1 - \cos a\alpha}{\sin a\alpha} \quad \dots(1)$$

$$\text{Now, } \cos a\alpha = 1 - \frac{(a\alpha)^2}{2!} + \frac{(a\alpha)^4}{4!} - \dots \approx 1 - \frac{(a\alpha)^2}{2!} \text{ (for small value of } a\alpha \text{)}$$

$$\text{and } \sin a\alpha = a\alpha - \frac{(a\alpha)^3}{3!} + \frac{(a\alpha)^5}{5!} - \dots \approx a\alpha \text{ (for small value of } a\alpha \text{)}$$

So, the equation (1) becomes

$$\frac{P}{a\alpha} = \frac{1 - \left[ 1 - \frac{(a\alpha)^2}{2!} \right]}{a\alpha}$$

$$\text{or, } P = \frac{(a\alpha)^2}{2}$$

$$\text{or, } P = \frac{a^2}{2} \left( \frac{2mE}{\hbar^2} \right) \left[ \because \alpha^2 = \frac{2mE}{\hbar^2} \right] \text{ or, } E = \frac{P\hbar^2}{a^2 m}$$

Substituting  $\hbar = \frac{h}{2\pi}$ , we get the energy of the lowest band, which is

$$E = \frac{Ph^2}{4\pi^2 ma^2} \quad (\text{Proved})$$



### 3.4.2 Number of Possible Wave Functions per Band

We have so far considered the crystal to be infinite. But now it is very essential to verify the consequences of imposing boundary conditions. For this purpose, let us consider a linear crystal of length  $L$  with the boundary condition

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

... (3.4.2.1)



Now using the Bloch functions, we can write

$$e^{ik(x+L)} \cdot U_k(x+L) = e^{ikx} U_k(x)$$

Since the function  $U_k(x)$  has the same periodicity as the lattice, we have

$$U_k(x+L) = U_k(x)$$

Substituting the value of  $U_k(x+L)$  from equation (3.4.2.3) in equation (3.4.2.2), we get

$$e^{ik(x+L)} = e^{ikx}$$

or,  $e^{ikL} = 1$  i.e.  $e^{ikL} = e^{i2n\pi}$

where  $n = \pm 1, \pm 2, \pm 3, \dots$

This equation implies

$$kL = 2n\pi \quad \text{or, } k = \frac{2n\pi}{L}$$

So, the number of possible wave functions in the range  $dk$  is

$$dn = \frac{L}{2\pi} dk$$

The total number of possible wave functions (or states) in a band is

$$n = \int dn = \frac{L}{2\pi} \int_{-\pi/a}^{\pi/a} dk = \frac{L}{2\pi} \left[ \frac{\pi}{a} + \frac{\pi}{a} \right] = \frac{L}{a}$$

$$L = na$$

If  $N$  is the number of unit cells, for  $b \rightarrow 0$  (i.e.  $a + b \approx a$ ) then the length of the crystal

$$L = N(a + b) \approx Na$$

Comparing equations (3.4.2.6) and (3.4.2.7), we have  $n = N$

Thus, the total number of possible wave functions in an energy band is equal to the number of unit cells  $N$ .

### 3.5



### VELOCITY OF AN ELECTRONS ACCORDING TO BAND THEORY

We know from quantum mechanical theory of particles, the velocity of the particle (i.e. particle velocity) is equal to the group velocity ( $v_g$ ) of the waves that represents the particle. So if an electron moves with a velocity  $v$ ,

$$v (= v_g) = \frac{d\omega}{dk} \quad \dots (3.5.1)$$

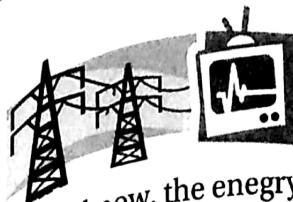
where  $\omega$  is the angular frequency of the de-Broglie wave.

Here the energy of the particle  $E = \hbar\omega$  or,  $\omega = \frac{E}{\hbar}$

$$\dots (3.5.2)$$

Now  $v = \frac{d\omega}{dk}$  or,  $v = \frac{d}{dk} \left( \frac{E}{\hbar} \right)$  or,  $v = \frac{1}{\hbar} \left( \frac{dE}{dk} \right)$

$$\dots (3.5.3)$$



but we know, the energy of free electrons

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

$$\text{i.e. } \frac{dE}{dk} = \frac{\hbar^2 k}{m}$$

so, the velocity of free electrons,  $v = \frac{1}{\hbar} \frac{dE}{dk}$

$$\text{or, } v = \frac{1}{\hbar} \frac{\hbar^2 k}{m} \quad \text{or, } v = \frac{\hbar k}{m} \quad \dots (3.5.4)$$

Thus, the velocity of a free electron is proportional to wave number  $k$ . The variations of energy ( $E$ ) and velocity ( $v$ ) of an electron against  $k$  on the basis of equations  $E = \frac{\hbar^2 k^2}{2m}$

and  $v = \frac{1}{\hbar} \frac{dE}{dk}$  are shown in Fig. 7(a) and Fig. 7(b) respectively.

It has been seen from the curve,  $v$  is maximum at  $k = k_0$  and  $k = -k_0$  corresponding to inflection points  $M$  and  $N$  respectively of the  $E-k$  diagram. Beyond these points, the velocity of electron decreases with increasing of energy, which is not observed in the free electron model.

The velocity of electron is zero at  $k = 0$ ,  $k = +\frac{\pi}{a}$  and  $k = -\frac{\pi}{a}$ . Thus, the velocity of electron is zero at the bottom and at the top of the Brillouin zone.

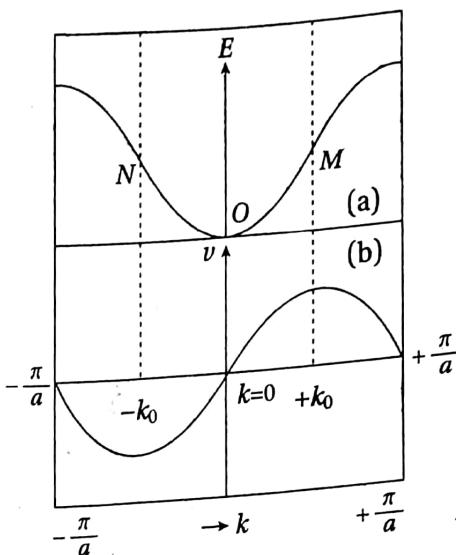


Fig. 7(a) ▷ Energy ( $E$ ) versus  $k$  diagram

(b) ▷ Velocity ( $v$ ) versus  $k$  diagram

### 3.6



### EFFECTIVE MASS OF AN ELECTRON

In a crystal, the electrons are not completely free. They interact with the crystal lattice. So, when an electron is accelerated by an electric field (external force) inside the crystal, its behaviour becomes different from that of a free electron. In general, the mass of an electron in a crystal appears to be different from the free electron mass (i.e. the nominal mass of an electron in free space). The altered (or changed) value of mass of an electron inside the periodic potential of the crystal under the influence of external field (electric field or magnetic field) is called effective mass of electron. It is represented by a symbol  $m^*$ .

Let us consider an electron is moving along  $X$  axis inside a crystal under the influence of an external uniform electric field  $E'$ . The external force acting on the electron  $= qE'$ ,  $q$  is the charge of the electron. If the electron gains velocity  $v$  over a distance  $dx$  in time  $dt$  due to this external force, the gain in energy (i.e., work done by the force) of the electron in this time interval

$$dE = (qE')vdt$$

$\dots (3.6.1)$

But we know from quantum mechanical theory, the velocity of the electron inside a lattice is equal to the group velocity ( $v_g$ ) of the wave representing the particle. The velocity of electron is given by from equation (3.5.3)



$$v = v_g = \frac{1}{\hbar} \frac{dE}{dk}$$

Substituting the value of  $v$  in equation (3.6.3), we get

$$dE = (qE') \frac{1}{\hbar} \frac{dE}{dk} dt$$

or,  $\frac{dE}{dk} dk = qE' \frac{1}{\hbar} \frac{dE}{dk} dt$

or,  $dk = qE' \frac{1}{\hbar} dt$

or,  $\frac{dk}{dt} = \frac{qE'}{\hbar}$

Differentiating equation (3.6.2), w.r.t time, we get the acceleration of the electron

$$f \left( = \frac{dv}{dt} \right) = \frac{1}{\hbar} \frac{d}{dt} \left( \frac{dE}{dk} \right)$$

or,  $f = \frac{1}{\hbar} \frac{d^2 E dk}{dk^2 dt}$

or,  $f = \frac{1}{\hbar} \frac{d^2 E}{dk^2} \left( \frac{qE'}{\hbar} \right) \left[ \because \frac{dk}{dt} = \frac{qE'}{\hbar} \right]$

or,  $f = \left( \frac{qE'}{\hbar^2} \right) \frac{d^2 E}{dk^2}$  ... (3.6.4)

This is the *acceleration of the electron due to the force  $qE'$* . Thus, the **effective mass of the electron is**

$$m^* = \frac{qE'}{f}$$

or,  $m^* = \frac{\hbar^2}{\frac{d^2 E}{dk^2}}$  ... (3.6.5)

**This is the expression of effective mass of a charged particle.**

This relation indicates that the value of effective mass ( $m^*$ ) depends on  $\frac{d^2 E}{dk^2}$  (i.e. on the shape of the  $E$ - $k$  diagram).

The effective mass ( $m^*$ ) of an electron for a metal does not vary greatly from its free mass (i.e. free electron mass)  $m_0$ . So if we use  $m_0$  in place of  $m^*$  for metals, no great error occurs. But in case of semiconductor,  $m^*$  can differ significantly from its free mass ( $m_0$ ). So, we must use effective mass to get accurate results for a semiconductor.

**Special Note**

① Free electrons do not contradict  $E$ - $k$  diagram:  
For a free electron, we have

$$E = \frac{\hbar^2 k^2}{2m_0}, \text{ where } m_0 = \text{mass of free electron.}$$

$$\therefore \frac{dE}{dk} = \frac{2\hbar^2 k}{2m_0} \quad \text{or, } \frac{d^2 E}{dk^2} = \frac{\hbar^2}{m_0}$$

Substituting the value of  $\frac{d^2 E}{dk^2}$  in equation (3.6.5), we get the effective mass of a free electron.

$$m^* = \frac{\hbar^2}{\frac{d^2 E}{dk^2}} = \frac{\hbar^2}{\frac{\hbar^2}{m_0}} = m_0$$

$$\text{or, } m^* = m_0$$

Thus, the effective mass of a free electron must be equal to its free mass.

② For a three dimensional periodic potential, the expression of effective mass can be written as  $\frac{1}{m^*} = \frac{1}{\hbar^2} \operatorname{grad}_k \operatorname{grad}_k E(k)$ , where  $\operatorname{grad}_k \operatorname{grad}_k E(k)$  is a tensor with nine components of the general form  $\frac{\partial^2 E}{\partial k_i \partial k_j}$ .

### 3.6.1 Importance of Effective Mass : Concept of Hole

The effective mass ( $m^*$ ) can differ significantly from its mass ( $m_0$ ) in free space.

The variation of effective mass  $m^*$  of an electron against  $k$  from  $k = -\frac{\pi}{a}$  to  $+\frac{\pi}{a}$  has been shown in [Fig. 8] on the basis

$$\text{of equation } m^* = \frac{\hbar^2}{\left(\frac{d^2 E}{dk^2}\right)}.$$

It has been seen from the curve, the effective mass  $m^*$  is negative at the top i.e. at the upper half of the energy band (i.e.  $k = +k_0$  to  $+\frac{\pi}{a}$  and  $k = -k_0$  to  $-\frac{\pi}{a}$ ) and  $m^*$  is positive at the lower half of the energy band (i.e.  $k = -k_0$  to  $k_0$ ). At the inflection points (i.e.  $k = 0$ ) of the  $E$ - $k$  diagram  $m^*$  becomes infinite.

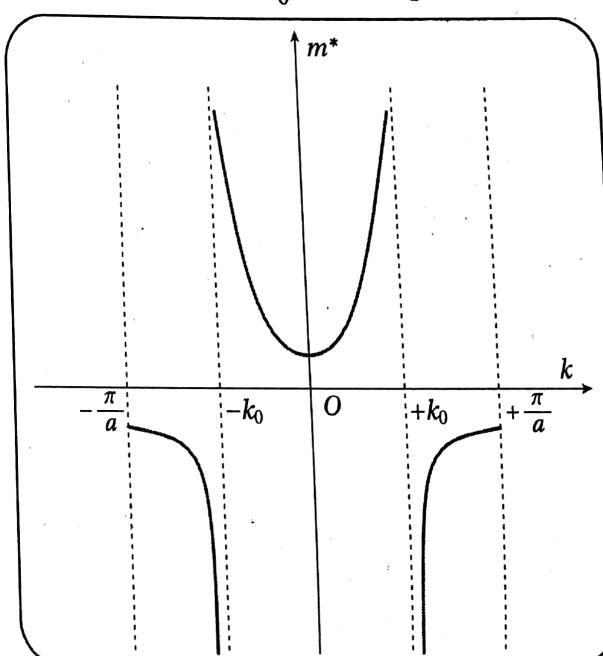


Fig. 8 ▷ Effective mass ( $m^*$ ) vs  $k$  curve



This means that in the upper half of the energy band, electron behaves as a negative mass. This idea of negative effective mass of an electron introduces the concept of new particle, called 'hole'.

The concept of hole is of great importance in the theory of conductivity of semi conductor and Hall effect.

### Special Note

The extent of freedom of an electron at the state  $k$  is determined by factor

$$f_k = \frac{\text{free mass} (m_0)}{\text{effective mass} (m^*)} = \frac{m_0}{\frac{\hbar^2}{\frac{d^2 E}{dk^2}}} = \left( \frac{m_0}{\hbar^2} \right) \frac{d^2 E}{dk^2}$$

$$\therefore f_k = \frac{m_0 d^2 E}{\hbar^2 dk^2} \quad \dots (3.6.1.1)$$

If  $f_k$  is small, the particle behaves as a heavy particle.

If  $f_k = 1$ , the particle behaves as a free particle.

### PROBLEM

- 1 The effective mass of an electron =  $0.3 m_0$ . Taking the origin at the bottom of the conduction band, find the momentum of the free electron with energy 0.03 eV.

**Solution** We know the energy of a free electron,  $E = \frac{\hbar^2 k^2}{2m^*}$  ... (1)

where  $m^* = \text{effective mass of electron} = 0.3 m_0$

But the momentum of the free electron,  $p = \hbar k$

$\therefore$  We get from equation (1),  $E = \frac{p^2}{2m^*}$

or,  $p = (2m^* E)^{1/2}$

$$= (2 \times 0.3 \times 9.11 \times 10^{-31} \times 0.03 \times 1.6 \times 10^{-19})^{1/2} = 5.12 \times 10^{-26} \text{ kg} \cdot \text{m} \cdot \text{s}^{-1}$$

### PROBLEM

- 2 The energy wave vector dispersion relation for a one-dimensional crystal of lattice constant  $a$  is given by

$E(k) = E_0 - \alpha - 2\beta \cos ka$ , where  $E_0$ ,  $\alpha$ ,  $\beta$  are constants.

- Find the value of  $k$  at which the velocity of an electron is a maximum.
- Find the difference between the top and the bottom of the energy band.
- Obtain the effective mass  $m^*$  of the electron at the bottom and at the top of the band.

[C.U. 2003]

### Solution

- i According to band theory, the velocity of an electron is,

$$v = \frac{1}{\hbar} \frac{dE}{dk}$$

$$= \frac{1}{\hbar dk} (E_0 - \alpha - 2\beta \cos ka)$$

$$= \frac{2\beta a}{\hbar} \sin ka$$

$\therefore$  For maximum velocity ( $v$ ) of the electron,

$$\sin ka = 1 \quad \text{or, } \sin ka = \sin \frac{\pi}{2} \quad \text{or, } k = \frac{\pi}{2a}$$

$\therefore$  The velocity of electron is maximum at  $k = \frac{2\pi}{a}$

iii From band theory, we know  $E(k)$  is maximum at the top of the band. But  
 $E(k) = E_0 - \alpha - 2\beta \cos ka$

So, when  $E(k)$  is maximum,  $\cos ka$  is minimum, i.e.  $\cos ka = -1$

$$\therefore E_{\text{top}} = E_0 - \alpha + 2\beta$$

At the bottom of the band,  $E(k)$  is minimum. But,  $E(k) = E_0 - \alpha - 2\beta \cos ka$

So, when  $E(k)$  is minimum,  $\cos ka$  is maximum i.e.  $\cos ka = 1$

$$\therefore E_{\text{bottom}} = E_0 - \alpha - 2\beta$$

Thus, the difference between the top and the bottom of the energy band

$$E_d = E_{\text{top}} - E_{\text{bottom}}$$

$$\text{or, } E_d = E_0 - \alpha + 2\beta - (E_0 - \alpha - 2\beta)$$

$$\text{or, } E_d = 4\beta$$

iii The effective mass ( $m^*$ ) of an electron

$$m^* = \frac{\hbar^2}{\frac{d^2 E}{dk^2}} = \frac{\hbar^2}{\frac{d}{dk} \left( \frac{dE}{dk} \right)}$$

$$= \frac{\hbar^2}{\frac{d}{dk} (2\beta a \sin ka)}$$

$$= \frac{\hbar^2}{2\beta a^2 \cos ka}$$

Since, at the top of the band  $\cos ka = -1$ , so

$$m^* = -\frac{\hbar^2}{2\beta a^2}$$

Again, at the bottom of the band,  $\cos ka = \pm 1$ , so

$$m^* = \frac{\hbar^2}{2\beta a^2}$$

**PROBLEM**

- 3.** The  $E-k$  relation for a particular crystal is given by  $E(k) = Ck^2 + Dk^3$ , where  $C$  and  $D$  are two positive constants.
- Find the wave vectors for which the electron group velocity is zero.
  - Calculate values of the effective mass and the phase velocity of electron waves for these values of wave vector calculated above!

**Solution**

- i** From band theory we know, the group velocity of an electron is

$$v_g = \frac{1}{\hbar} \frac{dE}{dk} = \frac{1}{\hbar} \frac{d}{dk}(Ck^2 + Dk^3) = \frac{1}{\hbar} (2Ck + 3Dk^2) = \frac{2k}{\hbar} \left( C + \frac{3}{2} Dk \right)$$

Thus, when  $v_g = 0$ ,  $k = 0$  and  $k = -\frac{2C}{3D}$

$$\text{ii} \quad \text{Effective mass, } m^* = \frac{\hbar^2}{\frac{d^2E}{dk^2}}$$

$$= \frac{\hbar^2}{\frac{d}{dk} \left( \frac{dE}{dk} \right)}$$

$$= \frac{\hbar^2}{\frac{d}{dk} (2Ck + 3Dk^2)}$$

$$= \frac{\hbar^2}{2C + 6Dk}$$

When  $k = 0$ , effective mass,  $m^* = \frac{\hbar^2}{2C}$ . (This implies  $k$  corresponds to the bottom of a band)

When  $k = -\frac{2C}{3D}$ , effective mass,  $m^* = -\frac{\hbar^2}{2C}$

(This implies that  $k$  corresponds to the top of the band). We know, phase velocity

$$v_p = \frac{\omega}{k} = \frac{\hbar\omega}{\hbar k} = \frac{E}{\hbar k}$$

$\therefore$  Substituting the value of  $E(k) = Ck^2 + Dk^3$ , we get

$$v_p = \frac{Ck^2 + Dk^3}{\hbar k} = \frac{(Ck + Dk^2)}{\hbar}$$

If  $k = 0$ ,  $v_p = 0$

If  $k = -\frac{2C}{3D}$ ,  $v_p = \frac{-2C^2}{9D\hbar}$

## 3.7

## CLASSIFICATION OF MATERIALS : METALS, SEMICONDUCTORS AND INSULATORS

Let us consider a particular energy band which is filled with electrons up to a certain value  $k_1$ , where  $k_1$  is less than  $\frac{\pi}{a}$  as shown in Fig. 9. The effective number of free electrons in the band is

$$N_{\text{eff}} = \sum f_k$$

where,  $f_k$  = degrees of freedom of an electron  $\dots (3.7.1)$

$= \frac{m}{m^*} = \left(\frac{m}{\hbar^2}\right) \frac{d^2 E}{dk^2}$  and the summation extends over all occupied states in the band.

Now for a one dimensional lattice of length  $L$ , the number of states in the interval  $dk$  is  $\frac{L}{2\pi} dk$ .

According to Pauli's principle, each of these states in the shaded region of Fig. 10 can be occupied by two electrons. So, the effective extent of freedom of the electrons populating the band within the limits  $-k_1$  to  $+k_1$  is

$$N_{\text{eff}} = 2 \frac{L}{2\pi} \int_{-k_1}^{k_1} f_k dk \dots (3.7.2)$$

Substituting the value of  $f_k$  from equation (3.6.1.1), we have

$$\begin{aligned} N_{\text{eff}} &= \frac{2L}{2\pi} \int_{-k_1}^{k_1} \frac{m_0 d^2 E}{\hbar^2 dk^2} dk \\ &= \frac{2L}{\pi} \int_0^{k_1} \frac{m_0 d^2 E}{\hbar^2 dk^2} dk \\ &= \frac{2m_0 L}{\pi \hbar^2} \int_0^{k_1} \left( \frac{d^2 E}{dk^2} \right) dk \\ &= \frac{2m_0 L}{\pi \hbar^2} \int_0^{k_1} \frac{d}{dk} \left( \frac{dE}{dk} \right) dk \\ &= \frac{2m_0 L}{\pi \hbar^2} \int_0^{k_1} d \left( \frac{dE}{dk} \right) \\ &= \frac{2m_0 L}{\pi \hbar^2} \left( \frac{dE}{dk} \right) \Big|_{k=k_1} \dots (3.7.3) \end{aligned}$$

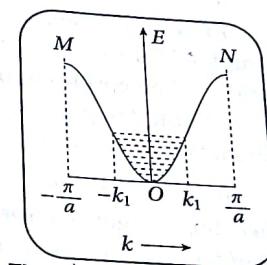


Fig. 9 ▷ Energy band filled up to states  $k_1$  (at  $T = 0$ )

Now, we can make the following conclusions from this result :

- When the band is filled up to the inflection points of the  $E-k$  curve, the value of  $\frac{dE}{dk}$  reaches a maximum. So, the effective number of free electrons ( $N_{\text{eff}}$ ) is maximum in an energy band in a solid.

- 2** When the band is completely filled,  $\frac{dE}{dk}$  is zero at the top of the band. As a result,  $N_{\text{eff}} = 0$ . This indicates the effective number of free electrons in a completely filled band is zero. So, there are no free electrons in a completely filled band. As a result, they cannot contribute to electrical conductivity.
- 3** We can distinguish among metal, semiconductor and insulator on the basis of the above discussion.

In case of insulators, a certain number of energy bands (called valence band) are completely filled up by the electrons. Above these bands there exist a series of empty bands, called **conduction bands**. The gap between conduction band and valence band is called **forbidden gap**. The **forbidden gap of insulator is so large that electrons cannot reach conduction band from valence band at ordinary temperature**.

In case of metals (conductors), valence band and conduction band overlap to each other. So, we get a **large number of free electrons in metal**. In semiconductors, the **forbidden gap is small**. Because this, **a moderate number of electrons are present in conduction band even at room temperature**.



## EXERCISE

### MULTIPLE CHOICE QUESTIONS

- 1. Bloch function is used for a**
  - (A) perfectly periodic potential
  - (B) non-periodic potential
  - (C) none of themAns. (A)
- 2. The one dimension Bloch function is expressed as**
  - (A)  $\psi(x) = e^{\pm ikx} U_k(x)$
  - (B)  $\psi(x) = \frac{1}{e^{ikx}} U_k(x)$
  - (C)  $\psi(x) = \frac{1}{e^{-ikx}} U_k(x)$Ans. (A)

where the symbols are as their usual meanings.
- 3. The electrical conductivity of an insulator is zero due to the presence of**
  - (A) free electrons
  - (B) bound electrons
  - (C) protonsAns. (B)
- 4. The energy spectrum of an electron in a crystal consists of**
  - (A) alternate allowed energy bands
  - (B) alternate forbidden energy gap
  - (C) alternate allowed energy bands and the forbidden energy gapAns. (C)
- 5. The solutions to Bloch functions are not exist in**
  - (A) Brillouin zones
  - (B) forbidden regions
  - (C) allowed energy bandsAns. (B)
- 6. The energy of a free electron is given by**
  - (A)  $E = \frac{\hbar^2 k^2}{2m}$
  - (B)  $E = \frac{\hbar k}{m}$
  - (C)  $\frac{4\hbar^2 k^2}{m}$Ans. (A)



of the band. As a result, in a completely filled band. As a result, on the basis of the d valence band) are a series of empty and valence band is overlap to each miconductors, the ns are present in

filled band. As a result, tor on the basis of the d valence band) are a series of empty and valence band is

electrons cannot reach

overlap to each miconductors, the ns are present in

initial

Ans. (A)

Ans. (A)

Ans. (B)

Ans. (C)

Ans. (B)

Ans. (A)

7. The region extending from  $k = -\frac{\pi}{a}$  to  $k = +\frac{\pi}{a}$  is called  
 (A) the first Brillouin zone  
 (B) the second Brillouin zone  
 (C) the third Brillouin zone

8. The region extending from  $k = \frac{\pi}{a}$  to  $\frac{2\pi}{a}$  and  $k = \frac{\pi}{a}$  to  $\frac{2\pi}{a}$  is known as  
 (A) the fourth Brillouin zone  
 (B) the second Brillouin zone  
 (C) the third Brillouin zone

9. The forbidden gaps are observed in a periodic potential of a crystal is observed  
 (A) at the boundaries of Brillouin zone  
 (B) at the middle of the Brillouin zone  
 (C) within the Brillouin zone

10. The electron has allowed energy  
 (A) at the boundaries of Brillouin zone  
 (B) at the middle of the Brillouin zone  
 (C) within the Brillouin zone

11. The group velocity ( $v_g$ ) of an electron in a lattice is given by  
 (A)  $v_g = \frac{1}{\hbar^2} \frac{dE}{dk}$       (B)  $v_g = \frac{1}{\hbar} \frac{dE}{dk}$       (C)  $v_g = \frac{p}{\hbar} \frac{dE}{dk}$

Ans. (A)

Ans. (B)

Ans. (A)

Ans. (C)

Ans. (B)

12. The mass of an electron inside a crystal appears to be  
 (A) different from the mass of a free electron  
 (B) equal of free electron mass  
 (C) the product of its mass and velocity

Ans. (A)

13. The effective mass ( $m^*$ ) of an electron inside a crystal is  
 (A)  $m^* = \frac{2\hbar^2}{d^2 E / dk^2}$       (B)  $m^* = \frac{\hbar}{d^2 E / dk^2}$       (C)  $m^* = \frac{\hbar^2}{d^2 E / dk^2}$

Ans. (C)

14. The idea of negative effective mass of an electron introduces the concept of new particle, is called  
 (A) muon      (B) mason      (C) hole

Ans. (C)

15. Conductors, semiconductors and insulators are identified only by  
 (A) Fermi levels      (B) the magnitude of their energy band gap  
 (C) their carrier concentrations

Ans. (B)

## ► SHORT ANSWER TYPE QUESTIONS

1. How does potential energy of an electron vary with distance in an one dimensional periodic crystal?  
 [See article 3.2]



2. State and explain the Bloch theorem.
3. What is an effective mass of an electron? Deduce the expression for effective mass an electron? [See article 3.6]
4. Derive the expression of velocity of free electron. [See article 3.5]
5. Mention the characteristics of the  $E-k$  diagram. [See article 3.4.1]
6. Explain the significance of effective mass of an electron. [See article 3.6.1]
7. [a] Define the term "effective mass of an electron". Is it different from the free electron mass? What is "crystal momentum"? [C.U. 1997] [See article 3.6]
- [b] What is the significance of negative effective mass of electrons? [Purvanchal Univ. 2003] [See article 3.6.1]

### ► LONG ANSWER TYPE QUESTIONS

1. Discuss the Kronig-Penney model for the motion of an electron in a periodic potential. How does this model lead to the concept of allowed and forbidden energy bands in solids? [See article 3.4; For 2nd part discuss the 1st part of observation of the graph of Fig. 4]
2. Give the observations form the graph of  $P \frac{\sin a\alpha}{a\alpha} + \cos a\alpha$  versus  $a\alpha$ , where  $P$  is the scattering power of the potential,  $a$  is the width of the potential well and  $a^2 = \frac{2mE}{\hbar^2}$ .  $m$  is the mass of the electron of energy  $E$ . [See last part of article 3.4 and discuss with help of Fig. 4]
3. What is  $E-k$  diagram? Explain the origin of allowed energy bands and forbidden gap from  $E-k$  diagram. [See the 4th point of observation of last part of article 3.4]
4. [a] What are Brillouin zones? Explain it with the help of  $E-k$  diagram. [See 4th point of observation of last part of article 3.4]  
[b] What are the characteristics of  $E-k$  diagram? [See article 3.4.1]
5. [a] What is barrier strength and scattering power of an potential barrier? [See article 3.4]  
[b] How does the band theory of solid help to classify solids into conductors, semiconductors and insulators. [See article 3.5]
6. [a] Define effective mass. Prove that effective mass of an electron,  $m^* = \frac{\hbar^2}{d^2 E / dk^2}$  [See article 3.6]  
[b] Give the physical significance of effective mass. [See article 3.6.1]
7. In the Kronig-Penney model for the motion of electron in a periodic potential, will the widths of the allowed energy bands change due to the increase of the height of the periodic potential? [See 2nd point of observation of the last part of article 3.4 and discuss with the help of Fig. 4]



8. Show that the effective number of free electrons is maximum in an energy band in a solid when the band is filled up to the inflection points of the E-k diagram.

[See article 3.7]

9. An electron moving in a potential is given by

$$V(x) = 0, \text{ when } 0 < x < a \\ = V_0, \text{ when } -b < x < 0.$$

If the period of this potential is  $(a + b)$ , prove that

$$\frac{\beta^2 - \alpha^2}{2\alpha\beta} \sin \alpha x \sinh \beta + \cos \alpha x \cosh \beta = \cos k(a + b)$$

$$\text{where } \alpha^2 = \frac{2mE}{\hbar^2} \text{ and } \beta^2 = \frac{2m(V_0 - E)}{\hbar^2}$$

[See article 3.4]

10. [a] Prove that the velocity of electron is zero at the bottom and the top of the Brillouin zone.

[See article 3.5]

[b] Prove that the effective mass of an electron is negative at the top of the energy band and positive at the lower half of the energy band.

[See article 3.6.1]

