Solid State Physics

Sem-5, Sub: PHSA (H), paper- CC-12

Band Theory of Solids:

Introduction:-

The free electron theory of solids explains various electronic and thermal properties of metals such as specific heat, thermal conductivity and electrical conductivity etc. However, there are various other properties which could not be explained by the free electron theory. For example, this theory could not explain why certain solids have a large number of free electrons and thus behave as good conductors while certain others have hardly any electrons and are therefore insulators. This theory could not explain the properties of semiconductors.

The failure of the free electron model is due to the oversimplified assumption that a conduction electron in a metal experiences a constant or zero potential due to the ion cores and hence is free to move about in a crystal and the motion being restrained only by the surface of the crystal. In fact, the potential due to ion cores is not constant and may change with position of the electron in the crystal. Some contribution to potential may also arise because of the other electrons present in the crystal. Thus the actual nature of the potential under which an electron moves in a crystal is very complicated. To some approximation, The ion cores may be considered at rest and The potential experienced by an electron in a crystal is assumed to be periodic with The period equal to The lattice constant as shown in Fig-2 for a one dimensional case. This assumption is based on The fact That The ion cores in a crystal are distributed periodically on The lattice sites. It is also assumed That This type of periodic potential extends upto infinity in all directions except at The surface of The crystal due to irregular periodicity of The lattice may be ignored.

This periodic potential forms The basis of The energy band Theory of solids. We describe The behaviour of The electron in This periodic potential and it is done by finding The electron wave function.

Periodic Potential in a Crystalline Solid :-

The potential energy of an electron at a distance r from a nucleus of charge Ze is given by

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} \quad \text{---(1)}$$

where ϵ_0 is The permittivity of The free space. The graphical variation of V with r is shown in Fig-1

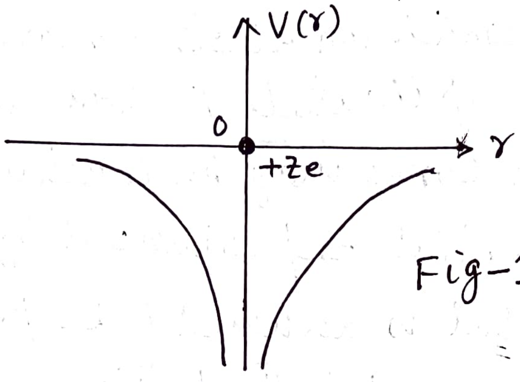


Fig-1.

In a solid a large number of such nuclei are brought together. So the P.E of an electron is the sum total of all the potential energies due to individual nuclei. Under such condition the P.E will be a periodic function of r in an infinite one dimensional lattice as shown in Fig-2

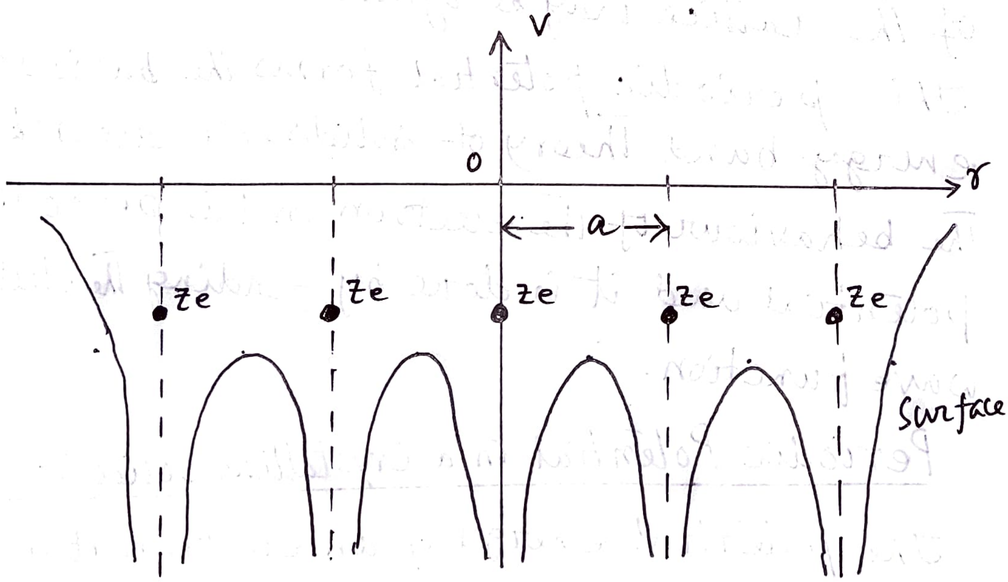


Fig-2

Energy of an electron from free electron theory :-

From free electron theory, an electron is assumed to move in a constant potential V_0 and hence for one dimensional case the Schrödinger's wave equation is given by

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V_0)\psi = 0 \quad \text{---(1)}$$

$$\Rightarrow \frac{d^2\psi}{dx^2} + K^2\psi = 0 \quad \text{-----(2)}$$

where $K = \frac{\sqrt{2m(E-V_0)}}{\hbar}$

The solution of equation (2) is

$$\psi(x) = e^{\pm iKx}$$

$$\therefore \frac{d^2\psi}{dx^2} = -K^2 e^{\pm iKx}$$

From (1)

$$-K^2 e^{\pm iKx} + \frac{2m}{\hbar^2}(E - V_0)e^{\pm iKx} = 0$$

$$\Rightarrow -K^2 + \frac{2m}{\hbar^2}(E - V_0) = 0 \text{ as } e^{\pm iKx} \neq 0.$$

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

$$\Rightarrow E - V_0 = \frac{\hbar^2 K^2}{2m}$$

$$\Rightarrow \text{K.E } E_{kin} = E - V_0 = \frac{\hbar^2 K^2}{2m} = \frac{p^2}{2m}$$

where K = wave number or wave vector

$$= \frac{p}{\hbar} = \frac{\text{momentum of an electron}}{\hbar}$$

$$= 2\pi/\lambda$$

Statement of Bloch Theorem:

The Schrödinger equation for an electron of total energy E and mass m, moving in a one-dimension periodic potential is given by

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]\psi = 0 \quad \text{---- (1)}$$

where $V(x) = V(x+a)$ and 'a' is the lattice Constant.

Bloch Theorem states that the solution of the Schrödinger equation for a periodic potential must be of the form

$$\psi(x) = e^{\pm ikx} u_k(x) \quad \text{---- (2)}$$

where $u_K(x) = u_K(x+a)$ ---- (3)

Thus the solutions are plane waves of the type $e^{\pm ikx}$ modulated by the function $u_K(x)$ having the same periodicity as the lattice

The wave function $\psi(x) = e^{\pm ikx} u_K(x)$ is called Bloch function and the wave vector $\vec{K}$ represents the direction of Bloch wave.

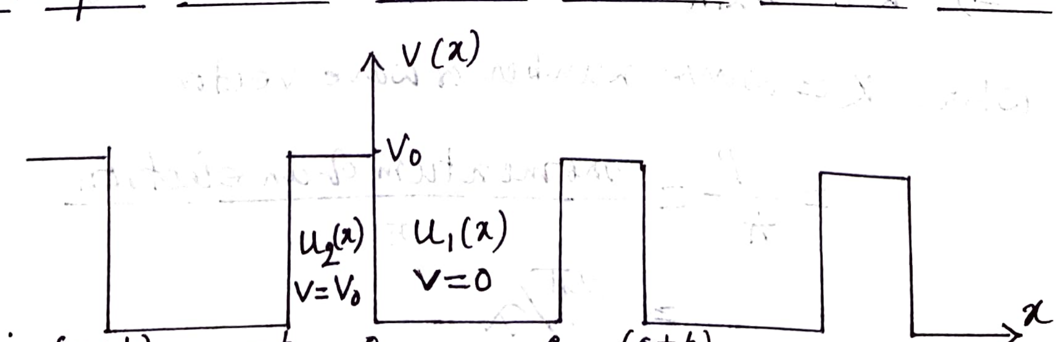


Fig-3: Kronig-Penney Model.

6.4. KRONIG-PENNEY MODEL

The properties of the behaviour of electrons in one dimensional periodic potential is given by Kronig and Penney.

It is assumed that the potential energy remains zero in the region $0 < x < a$ and the potential energy remains V_0 in the region $-b < x < 0$. The Schrodinger equation for two regions are

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E\psi = 0 \quad \text{for} \quad 0 < x < a \qquad \text{... (1)}$$

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

Let the energy E of the electron is less than V_0. Now putting

$$\left.\begin{aligned} \alpha^2 &= 2mE/\hbar^2 \\ \beta^2 &= \frac{2m(V_0 - E)}{\hbar^2} \end{aligned}\right\} \qquad \text{... (3)}$$

Now (1) and (2) can be written as

$$\frac{d^2\psi}{dx^2} + \alpha^2\psi = 0 \quad \text{for} \quad 0 < x < a \qquad \text{... (4)}$$

and

$$\frac{d^2\psi}{dx^2} - \beta^2\psi = 0 \quad \text{for} \quad -b < x < a \qquad \text{... (5)}$$

The solutions of (4) and (5) should be Bloch functions of the form

$$\psi(x) = e^{ikx}\, u_k(x)$$

$$\therefore \quad \frac{d\psi}{dx} = ike^{ikx}\, u_k(x) + e^{ikx}\frac{du}{dx}$$

$$\frac{d^2\psi}{dx^2} = -k^2 e^{ikx}\, u_k(x) + ik\, e^{ikx}\frac{du}{dx} + ik\, e^{ikx}\frac{du}{dx} + e^{ikx}\frac{d^2u}{dx^2}$$

or,

$$\frac{d^2\psi}{dx^2} = -k^2 e^{ikx}\, u_k(x) + 2ik\, e^{ikx}\frac{du}{dx} + e^{ikx}\frac{d^2u}{dx^2}$$

Putting these values in (4) and (5), we get

$$-k^2 e^{ikx}\, u_k(x) + 2ike^{ikx}\frac{du}{dx} + e^{ikx}\frac{d^2u}{dx^2} + \alpha^2 e^{ikx}\, u_k(x) = 0$$

or,

$$\frac{d^2u}{dx^2} + 2ik\frac{du}{dx} + (\alpha^2 - k^2) = 0 \quad \text{for} \quad 0 < x < a \qquad \text{... (6)}$$

and

$$\frac{d^2u}{dx^2} + 2ik\frac{du}{dx} - (\beta^2 + k^2)\, u = 0 \quad \text{for} \quad -b < x < 0 \qquad \text{... (7)}$$

The solutions of these equations are

$$u_1 = Ae^{i(\alpha - k)x} + Be^{-i(\alpha + k)x} \qquad \text{for} \quad 0 < x < a \qquad \text{... (8)}$$

$$u_2 = Ce^{(\beta - ik)x} + De^{-(\beta + ik)x} \quad \text{for} \quad -b < x < 0 \qquad \text{... (9)}$$

where A, B, C and D are constants which can be determined by applying boundary conditions.

$$u_1(0)=u_2(0);\ u_1(a)=u_2(-b)$$

$$\left.\begin{array}{l}\left(\dfrac{du_1}{dx}\right)_{x=0}=\left(\dfrac{du_2}{dx}\right)_{x=0};\left(\dfrac{du_1}{dx}\right)_{x=a}=\left(\dfrac{du_2}{dx}\right)_{x=-b}\end{array}\right\} \quad \text{... (10)}$$

Applying these conditions to (8) and (9), we get

$$A+B=C+D \quad \text{... (11a)}$$

$$\frac{du_1}{dx}=iA(\alpha-k)e^{i(\alpha-k)x}-iB(\alpha+k)e^{-i(\alpha+k)x}$$

$$\frac{du_2}{dx}=C(\beta-ik)e^{(\beta-ik)x}-D(\beta+ik)e^{-(\beta+ik)x}$$

$$iA(\alpha-k)-iB(\alpha+k)=C(\beta-ik)-D(\beta+ik) \quad \text{... (11b)}$$

$$Ae^{i(\alpha-k)a}+Be^{-i(\alpha+k)a}=Ce^{-(\beta-ik)b}+De^{(\beta+ik)b} \quad \text{... (11c)}$$

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

$$=C(\beta-ik)e^{-(\beta-ik)b}-D(\beta+ik)e^{(\beta+ik)b} \quad \text{... (11d)}$$

The equations (11a), (11b), (11c) and (11d) have non-vanishing solutions for A, B, C and D only if the determinant of their coefficients vanishes *i.e.*

$$\begin{vmatrix} 1 & 1 & 1 & 1 \\ i(\alpha-k) & -i(\alpha+k) & (\beta-ik) & -(\beta+ik) \\ e^{i(\alpha-k)a} & e^{-i(\alpha+k)a} & e^{-(\beta+ik)b} & e^{(\beta+ik)b} \\ i(\alpha-k)e^{i(\alpha-k)a}, & -i(\alpha+k)e^{-i(\alpha+k)a}, & (\beta-ik)e^{-(\beta-ik)b}, & -(\beta+ik)e^{(\beta+ik)b} \end{vmatrix}=0 \quad \text{... (12)}$$

After solving the determinant we get

$$\frac{\beta^2-\alpha^2}{2\alpha\beta}\sinh\beta b\sin\alpha a+\cosh\beta b\cos\alpha a=\cos k(a+b) \quad \text{... (13)}$$

In order to get more appropriate equation, Kronig and Penny assumed that V_0 tends to infinity and b approaches zero, but the product $V_0 b$ remains finite.

$\because$ $b\to 0$, $\sinh\beta b\to\beta b$ and $\cosh\beta b\to 1$

$$\therefore \quad \frac{\beta^2-\alpha^2}{2\alpha\beta}\times\beta b\sin\alpha a+\cos\alpha a=\cos ka \quad \text{... (14)}$$

From (3), $\beta^2=\dfrac{2m}{\hbar^2}(V_0-E)$ and $\alpha^2=\dfrac{2mE}{\hbar^2}$

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

If $V_0>>E$, $2E$ can be neglected in comparison to V_0 and hence

$$\beta^2-\alpha^2=\frac{2mV_0}{\hbar^2} \quad \text{... (15)}$$

Using (15) in (14),

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

or, $$\frac{mV_0 ba}{\hbar^2 \alpha a} \sin \alpha a + \cos \alpha a = \cos ka$$

Let us put $\frac{mV_0 ba}{\hbar^2} = P$

$$\therefore \quad \frac{P}{\alpha a} \sin \alpha a + \cos \alpha a = \cos ka \qquad \text{... (16)}$$

A graph is plotted between $\frac{P}{\alpha a} \sin \alpha a + \cos \alpha a$ and αa as shown in fig. (6.3).

From graph we conclude that

(i) The energy spectrum of the electrons consists of a number of allowed energy bands (shown thick) separated by intervals where there are no energy levels (marked dotted). These intervals are called forbidden regions.

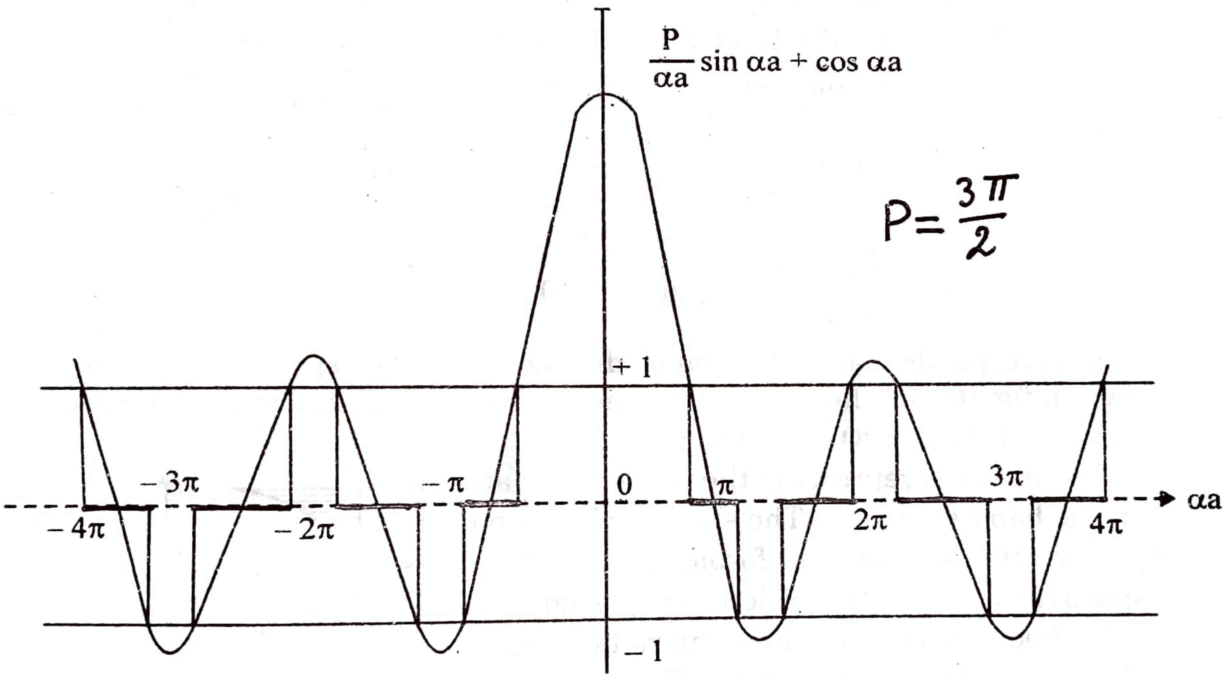


Fig. 6.3.

The allowed energy levels lies between the value +1 and –1 because boundaries of these levels correspond to the values of $\cos ka = \pm 1$ *i.e.*

$$ka = n\pi$$

(ii) The term $\frac{P \sin \alpha a}{\alpha a}$ on the left hand side of (16) decreases as αa increases and hence the width of allowed energy bands increass so that forbidden energy regions will become narrow.

(iii) The width of the allowed energy band decreases as P increases *i.e.* with increasing binding energy of the electrons. When $P \to \infty$, the allowed energy regions become infinitely narrow and the energy spectrum becomes a line spectrum.

In this case (16) has only solutions if

$$\sin \alpha a = 0$$

$$\therefore \quad \alpha a = n\pi$$

$$\therefore \qquad \alpha = \frac{n\pi}{a} \quad \text{where } n = 1, 2, 3, \ldots..$$

Using above result in (3), we get

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

$$\therefore \qquad E = \left(\frac{\pi^2\hbar^2}{2ma^2}\right)n^2 \quad \text{for } P \to \infty \qquad \ldots (17)$$

It is clear from (17) that E is not function of K. This equation gives the energy levels of a particle in a constant potential box of atomic dimensions. This is a physically expected result since the large P makes the tunneling through the barrier which is improbable.

When $P \to 0$, the form of (16) becomes

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

$$\therefore \qquad \alpha = k$$

$$\therefore \qquad \frac{2mE}{\hbar^2} = k^2$$

$$\therefore \qquad E = \frac{h^2k^2}{8\pi^2 m} = \frac{\hbar^2 k^2}{2m} \quad \text{for } P \to 0 \qquad \ldots (18)$$

which corresponds to free electron model and the energy spectrum is continuous as shown in fig. (6.4). When $P \to \infty$, the energy spectrum is line spectrum as shown in fig. (6.4) which is discussed above.

The fig. (6.4) represents the effect of variation of P on the band structure. The shaded and open parts represent the allowed and forbidden energy ranges respectively. The extreme left corresponds to $P = 0$ (*i.e.* for free electron) and extreme right corresponds to $P = \infty$ (*i.e.* for line spectrum). For any particular value of P, we can obtain the position and width of the allowed and forbidden bands by drawing a vertical line.

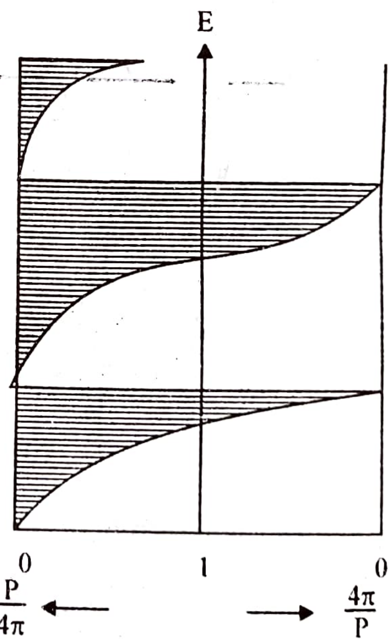


Fig. 6.4.

(iv) It is clear from (18) that the energy E is the function of wave number $K\left(\text{or } \frac{2\pi}{\lambda}\right)$. A graph is plotted between E and K as shown in fig. (6.5). In this curve discontinuities occurs at $K = \frac{\pi}{a}, \frac{2\pi}{a}, \frac{3\pi}{a} \ldots..$ $\frac{n\pi}{a}$ where $n = 1, 2, 3, \ldots$ These values of K represents the boundaries of the first, second, third, *etc.*, Brillouin zones. The fig. (6.5) gives only half of the complete E-K curve. Hence the first Brilliouin zone extends from $-\frac{\pi}{a}$ to

$+\frac{\pi}{a}$. The second Brillouin zone consists of two parts, one extending from $+\frac{\pi}{a}$ to $+\frac{2\pi}{a}$ and the second from $-\frac{\pi}{a}$ to $-\frac{2\pi}{a}$. The all portions of this curve are known as band. Following are the characteristics of the curves :

(i) Both at top and bottom of the curves are horizontal.

(ii) The curves are parabolic near the top and bottom.

(iii) In a particular energy band, the energy is a periodic function of K. For example, if K is replaced by $K + \frac{2\pi n}{a}$, where n is an integer, the right hand of (16) remains the same since $\cos\left(K + \frac{2\pi n}{a}\right)a = \cos(Ka + 2\pi n) = \cos Ka$. Thus K is not uniquely determined. Hence the 'reduced wave vector' is introduced which is limited in the region

$$-\frac{\pi}{a} \leq K \leq +\frac{\pi}{a} \qquad \text{... (19)}$$

The Fig. (6.6) represents the curve between energy and reduced wave vector.

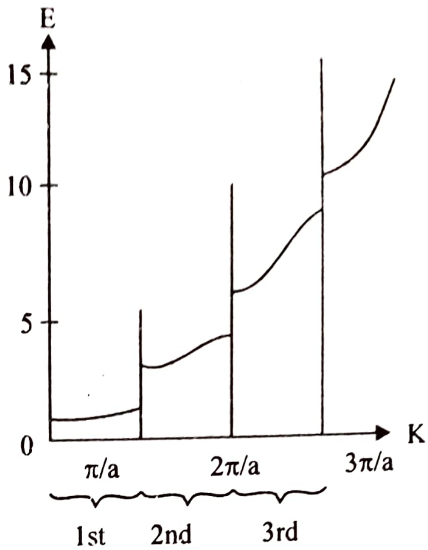


Fig. 6.5.

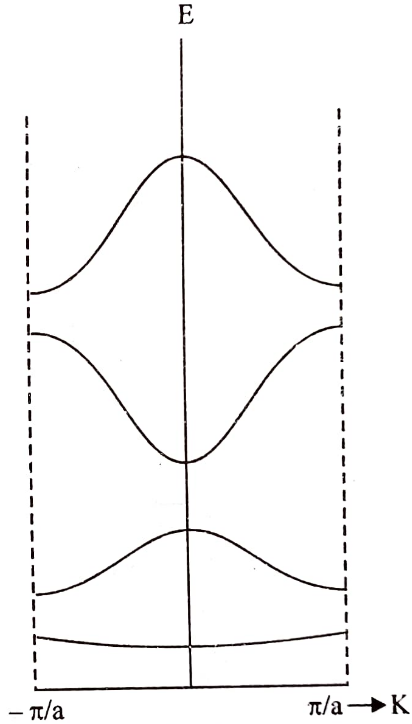


Fig. 6.6.

6.5. BRILLOUIN ZONES

In the case of Kronig-Penney model the energy discontinuities in a monoatomic one dimensional lattice occur if the wave number $K = \frac{n\pi}{a}$, where n is a positive or negative integer.

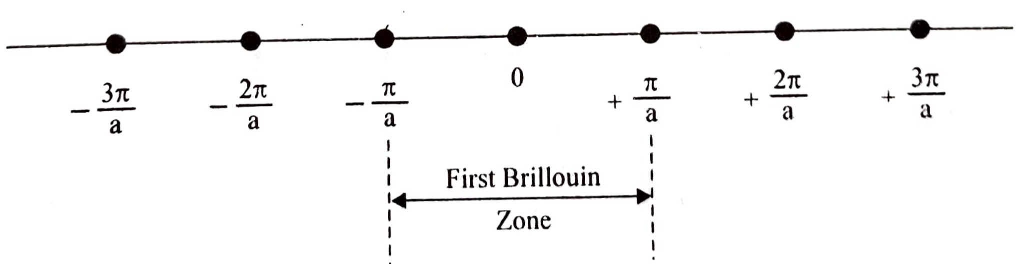


Fig. 6.7.

Fig. 6.7. represents a line showing the energy discontinuities into segments of length $\frac{\pi}{a}$ in a one dimensional monoatomic lattice. These line segments are called Brillouin zones. At $K = \pm\frac{\pi}{a}$, we get first reflection and first energy gap. As the wave reflected from one atom in the linear lattice interferes in the same phase with another wave reflected from a nearest neighbour atom, the reflection at $K = \pm\frac{\pi}{a}$ arises. Hence the region in the K-space between $-\frac{\pi}{a}$ and $+\frac{\pi}{a}$ is called the first Brillouin zone of the lattice.

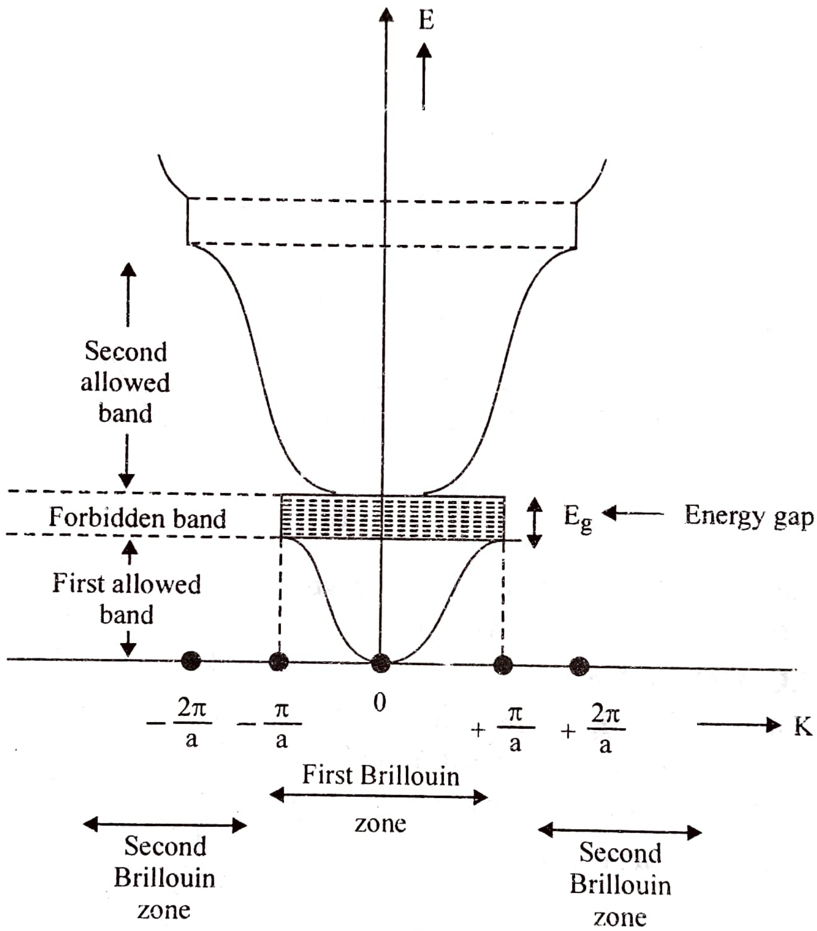


Fig. 6.8.

The second Brillouin zone contains electrons having K-values between $\frac{\pi}{a}$ and $\frac{2\pi}{a}$ for electrons moving in the $\pm K$ direction. At $K = \pm\frac{2\pi}{a}$, the second reflection and second energy gap occurs, hence the region in the K-space between $-\frac{2\pi}{a}$ to $-\frac{\pi}{a}$ and $+\frac{\pi}{a}$ to $+\frac{2\pi}{a}$ makes the Second Brillouin zone of the lattice. Similarly the formation of Brillouin zone of higher order can be explained.

6.5. (a) BRILLOUIN ZONES FOR TWO DIMENSIONAL LATTICE

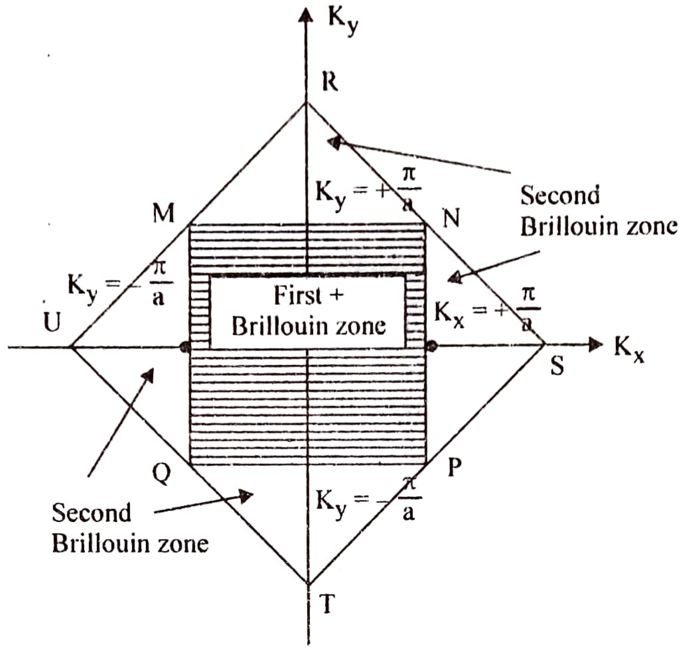


Fig. 6.8. (a)

The first Brillouin zone for two dimensional lattice in the *X-Y* plane is the square *MNPQ*. The boundaries of this zone can be written as

$$K_x = +\frac{\pi}{a};\ K_x = -\frac{\pi}{a};\ K_y = +\frac{\pi}{a};\ K_y = -\frac{\pi}{a}$$

The second zone for a two dimensional lattice in the *X-Y* plane is the square RSTU. The boundaries of this zone can be written as

$$K_x = \pm\frac{2\pi}{a} \text{ and } K_y = \pm\frac{2\pi}{a}$$

We have seen in Ewald's construction that a *K*-value is reflected only when Ewald's sphere intersects a point of reciprocal lattice. Let us construct a locus of all values of *K* that can be Bragg reflected.

Let us assume the simple square lattice having primitive translations vectors

$$\vec{a} = a\hat{i};\ \vec{b} = a\hat{j}$$

the corresponding reciprocal lattice translational vectors are

$$\vec{A} = \left(\frac{2\pi}{a}\right)\hat{i} \text{ and } \vec{B} = \left(\frac{2\pi}{a}\right)\hat{j}$$

Hence the reciprocal lattice vector *G* is given by

$$\vec{G} = h\vec{A} + k\vec{B} = h\left(\frac{2\pi}{a}\right)\hat{i} + k\left(\frac{2\pi}{a}\right)\hat{j}$$

$$= \left(\frac{2\pi}{a}\right)(h\hat{i} + k\hat{j}) \qquad \text{... (i)}$$

where *h* and *k* are integers.

Let us assume the wave-vector for an *X*-ray is

$$K = \hat{i}K_x + \hat{j}K_y$$

From Bragg's condition.

$$2\vec{K}.\vec{G}+G^2=0$$

$$2(K_x G_x + K_y G_y) + G_x^2 + G_y^2 = 0$$

$$2\left[K_x \frac{2\pi}{a} h + K_y \frac{2\pi}{a} K\right] + \left(\frac{2\pi}{a}\right)^2 h^2 + \left(\frac{2\pi}{a}\right)^2 K^2 = 0$$

or, $$\frac{4\pi}{a}(hK_x + KK_y) = -\left(\frac{2\pi}{a}\right)^2 (h^2 + K^2)$$

$\therefore$ $$hK_x + KK_y = -\frac{\pi}{a}(h^2 + K^2) \quad \text{.. (ii)}$$

The eq. (ii) represents straight lines in the K_x and K_y plane. The K_x and K_y can be written as

$$K_x = -\frac{\pi}{a}\frac{(h^2 + K^2)}{h}$$

$$K_y = -\frac{\pi}{a}\frac{(h^2 + K^2)}{k}$$

Hence Bragg's reflection will lake place

if $h = \pm 1$ and $K = 0$; $K_x = \pm\frac{\pi}{a}$, K_y = arbitrary

if $h = 0$ and $K = \pm 1$; $K_y = \pm\frac{\pi}{a}$, K_x = arbitrary

The four lines $K_x = \pm\frac{\pi}{a}$, $K_x = -\frac{\pi}{a}$, $K_y = +\frac{\pi}{a}$ and $K_y = -\frac{\pi}{a}$ are plotted in fig. (6.8b).

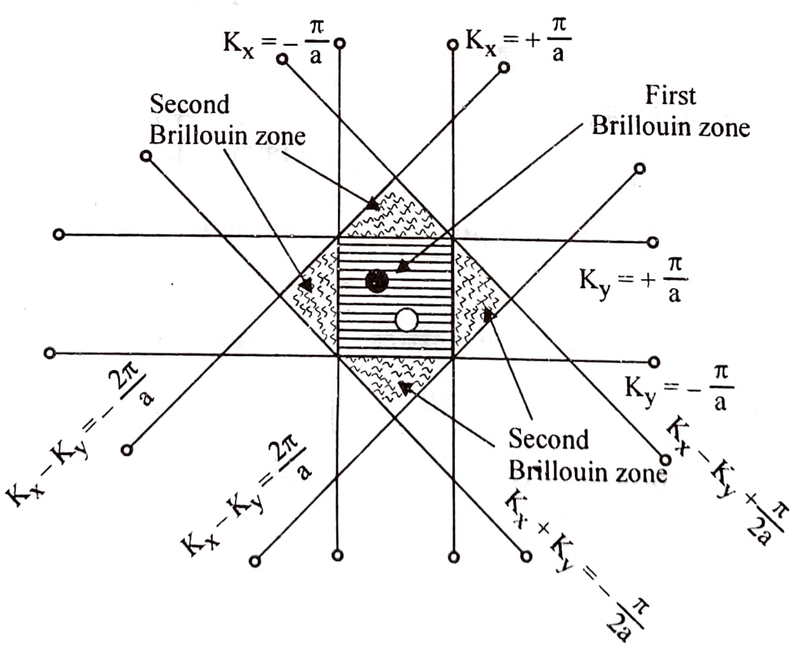


Fig. 6.8. (b)

All K-vectors originating at the origin O and terminating on these lines will produce Bragg reflection. The square bounded by $K_x = \pm\frac{\pi}{a}$ and $K_y = \pm\frac{\pi}{a}$ is the first

Brillouin zone. The additional area included by $\pm K_x, \pm K_y = \frac{2\pi}{a}$ is the second Brillouin zone. Similarly the third, fourth and other zones can be constructed.

The form of the Brillouin zone in three dimensions can be obtained from the following equation

$$hK_x + KK_y + lK_2 = -\frac{\pi}{a}(h^2 + K^2 + l^2)$$

6.6. NUMBER OF WAVE FUNCTIONS PER ENERGY BAND

Let us consider an infinitely long one dinensional crystal having certain allowed energy ranges in which distribution of energy is continuous. If L be the length of the crystal, the periodic boundary condition can be written as

$$\psi(x + L) = \psi(x) \qquad \ldots (1)$$

As the wave functions are Bloch functions, hence we may write

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

Due to the periodicity of u_K, we can write $u_K(x + L) = u_K(x)$

Hence $\quad e^{iK(x+L)} = e^{iKx}$ or $e^{iKL} = 1$

or, $\quad \cos KL + i \sin KL = 1$

$\therefore \quad \cos KL = 1$

$\therefore \quad KL = 2\pi n$

$\therefore \quad K = \frac{2\pi n}{L} \qquad \ldots (2)$

where $\quad n = \pm 1, \pm 2, \pm 3, \ldots$

or $\quad K = \pm \frac{2\pi}{L}, \pm \frac{4\pi}{L}, \ldots \qquad \ldots (3)$

From (2), we can write the number of possible wave function in the range dK,

$$dn = \frac{LdK}{2\pi} \qquad \ldots (4)$$

If we consider the first Brillouin zone, the maximum value of K is $\frac{\pi}{a}$ where a = length of the primitive cell. Let.

N = Number of primitive cells in the length L of the crystal.

Hence $a = \frac{L}{N}$ and thus the maximum value of K in the first zone is $\frac{N\pi}{L}$. Hence we can say that the series in (3) will end at $\frac{N\pi}{L}$. Therefore the total number of allowed K values in the first zone becomes equal to N. Thus it is clear that the total number of possible states or wave functions in an energy band becomes equal to the number of primitive unit cells N.

If we consider the spin of electrons and the Pauli's exclusion principle, each wave function can be occupied by at the most of two electrons. Hence each energy band provides place for a maximum number of electrons equal to the twice the number of unit cells. Thus if there are $2N$ electrons in a band, the band is completely filled.

6.7. MOTION OF ELECTRONS IN ONE DIMENSION ACCORDING TO BAND THEORY

In order to explain the motion of electrons in one dimension according to band theory let us first discuss the variation of velocity of an electron with wave vector K. According to the wave mechanical theory of particles, the particle velocity v is equal to the group velocity $\frac{d\omega}{dK}$ of the waves representing the particles. Hence

$$v = \frac{d\omega}{dK} \quad \text{... (1)}$$

where ω is the angular frequency of the de Broglie waves and K is the wave vector. Hence the energy of the particle is given by

$$E = \hbar\omega$$

$$\therefore \quad \omega = \frac{E}{\hbar} \quad \text{... (2)}$$

Using (2) in (1),

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

$$\therefore \quad v = \hbar^{-1}\frac{dE}{dK} \quad \text{... (3)}$$

We have for free electron,

$$E = \frac{\hbar^2 K^2}{2m} \quad \text{... (4)}$$

$$\therefore \quad \frac{dE}{dK} = \frac{\hbar^2}{m}K \quad \text{... (5)}$$

Using (5) in (3),

$$v = \frac{1}{\hbar}\frac{\hbar^2}{m}K = \frac{\hbar}{m}K \quad \text{... (6)}$$

$$\therefore \quad v = \frac{p}{m}$$

where p is the momentum of the particle.

According to band theory E is not in general proportional to K^2 as shown in fig. (6.5) but the variation of E with K is shown in fig. (6.9a). The variation of v with K according to (3) is shown in fig. (6.9b). For free electron v is proportional to K as clear from (6). At the top and bottom of the energy band $v = 0$, as from the periodicity of $(E - K)$ curve it is clear that $\frac{dE}{dK} = 0$ at that points. The value of velocity becomes maximum at $K = K_0$, where K_0, corresponds to the inflection point of the $(E - K)$ curve, Beyond this point the velocity decreases as energy increases, which is different from the behaviour of free electrons.

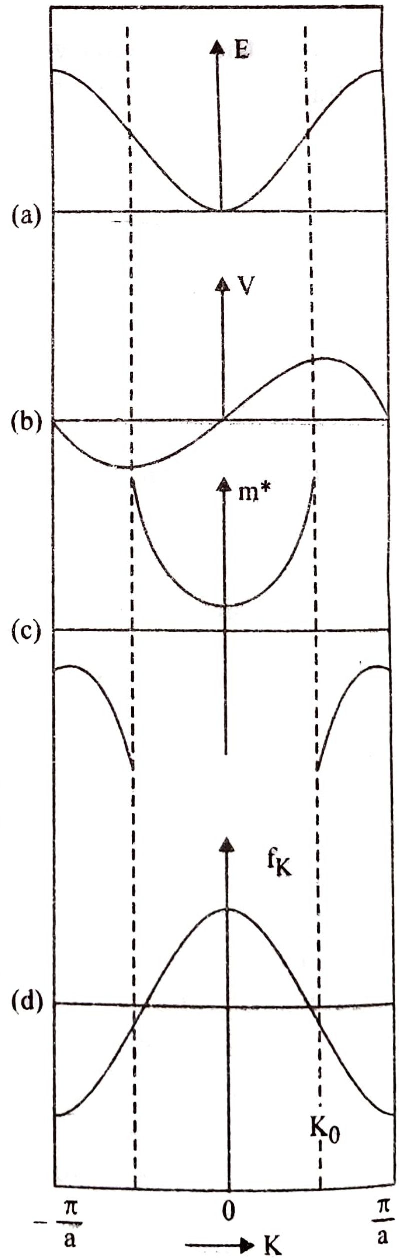


Fig. 6.9.

Effective mass of an electron : Let us assume the motion of an electron in a crystal when an external electric field F is applied. Let us consider the electron is initially in a state K. When the external field F is applied, the force acting on the electron will be eF, where e is the charge of an electron. Let the electron moves through a distance dx in time dt with force eF. Then

Work done = Gain in energy,

$$dE = eF\,dx$$

Let v = velocity of electron. Then can write

$$v = \frac{dx}{dt} \qquad \therefore \quad dx = v\,dt$$

Hence $\qquad dE = eF\,v\,dt \qquad \ldots (7)$

Using (3) in (7), we get

$$dE = eF\,\frac{1}{\hbar}\frac{dE}{dK}\,dt$$

or, $$\frac{dK}{dt} = \frac{eF}{\hbar} \qquad \ldots (8)$$

In order to obtain the acceleration, differentiating (3) with respect to t, we get

$$a = \frac{dv}{dt} = \frac{1}{\hbar}\frac{d}{dt}\left(\frac{dE}{dK}\right) = \frac{1}{\hbar}\frac{d^2E}{dK^2}\frac{dK}{dt} \qquad \ldots (9)$$

Using (8) in (9).

$$a = \frac{1}{\hbar}\frac{eF}{\hbar}\frac{d^2E}{dK^2}$$

$$\therefore \quad a = \left(\frac{eF}{\hbar^2}\right)\frac{d^2E}{dK^2} \qquad \ldots (10)$$

If m is the mass of a free electron, then its acceleration can be written as

$$a = \frac{eF}{m} \qquad \ldots (11)$$

From (10) and (11), we can say that the electron behaves as if it had an effective mass m^* which is equal to

$$m^* = \frac{\hbar^2}{\dfrac{d^2E}{dK^2}} \qquad \ldots (12)$$

Hence the value of effective mass can be determined by $\frac{d^2E}{dK^2}$ from $(E-K)$ curves from the motion of the electrons. The variation of effective mass with K is showin in fig. (6.9c). It is clear from the curve that m^* is positive in the lower half of the energy band and negative in the upper half. At the inflection points in $E-K$ curves, m^* becomes infinite. Let us consider $v-K$ curve. Let an electron starts at $K=0$. When an electric field is applied, the wave vector increases linearly with time. The electron is accelerated by the field until produces decrease in v and hence the mass becomes negative in the upper part of the band.

Now let us introduce a factor f_K. It is the ratio of the rest mass of a free electron m to its effective mass m^* in the crystal in the K-state. hence

$$f_K = \frac{m}{m^*} = \left(\frac{m}{\hbar^2}\right)\left(\frac{d^2E}{dK^2}\right) \qquad \text{... (13)}$$

This expression is a measure for the extent to which an electron in the K-state is free. If $f_K = 1$ *i.e.*, $m^* = m$, the electron in the crystal treated as a free electron. It is clear from fig. (6.9d) that f_K is positive in the lower half of the band and negative in the upper half of the band.

6.8. CLASSIFICATION OF SOLIDS

The electrons in a solid are distributed in different energy bands which are sepearted from each other by forbidden regions. The band consists of large number of energy levels. The width of the band is very small and is nearly equal to few electron volts. The two electrons having opposite spins can occupy each energy level in a band. Generally lower energy bands will be filled by electrons. Thus solids can be classified into conductors, semiconductors and insulators on the basis of band occupation by electrons and on the width of forbidden regions.

Conductors : It is found that in a certain solids above the completely filled lower bands there is partially filled band. Figures (6.10a) and (6.10b) represent the simplified diagram of energy bands of Sodium and Beryllium respectively. A single valence electron is found in 3*s*-level of the sodium atom. Hence if there are N atoms

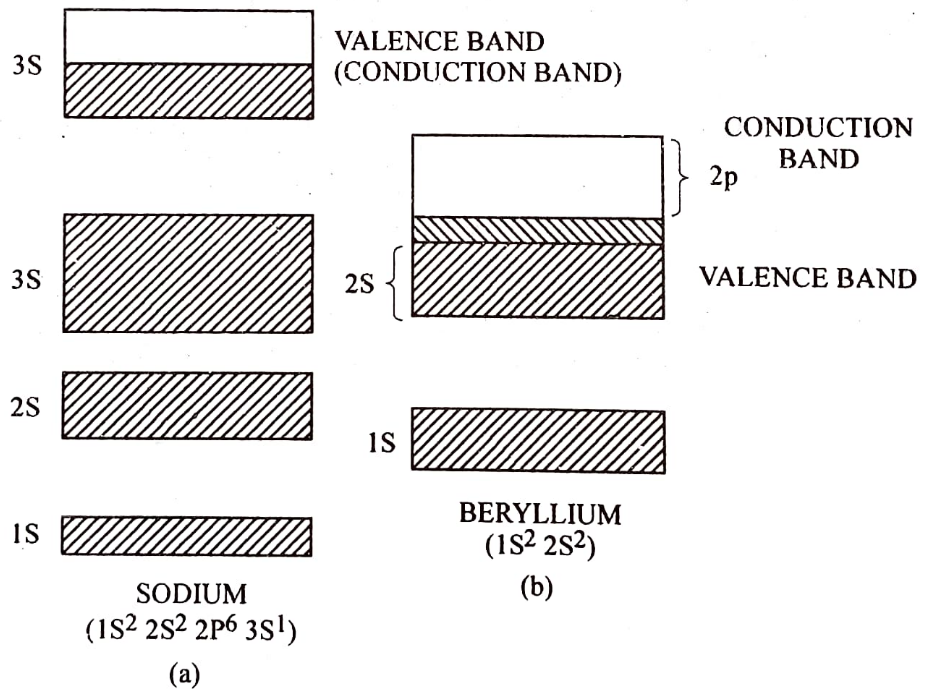


Fig. 6.10.

in a solid sodium the energy levels contained by 3*s* velence band will be N. Hence the valence-band may be defined as the band formed from energy-levels having valence electrons. The cause of the formation of partially filled band is the overlappling of completely filled and empty bands. In beryllium there is overlapping of the lower energy levels of the empty 2*p*-band with the upper energy levels of the completely 2s-band. Hence the electrons occupying the highest energy levels in the 2s-band will go into the lowest energy levels of the overlapping 2p-band. Hence the upper part of the 2s-band become unoccupied and hence the band is partially filled.

When an electric field is applied across a solid sodium, the electrons in the valence band gain some energy to go to the higher unoccupied energy level within the band. These electrons form an electric current. So we can say that sodium metal is a good conductor of electricity.

Conduction band is defined as an unoccupied band into which the electrons can pass.

Insulators : The valence band is completely filled and the higher band seperated by a large energy gap is empty in the case of few solids as shown in fig. (6.11). These solids are called insulators (or dielectrics). In these solids electric current will not flow.

When an electric field is applied across the solid, the electron in the valence band would not move within the band as there are no unoccupied levels in the band. The electrons can move to the higher band only if they gained energy E_g to cross the forbidden gap. This amount of energy can't be produced by an electric field. The examples of insulators are Diamond. NaCl etc. The both diamond and NaCl have forbidden gap $E_g \approx 6\text{eV}$.

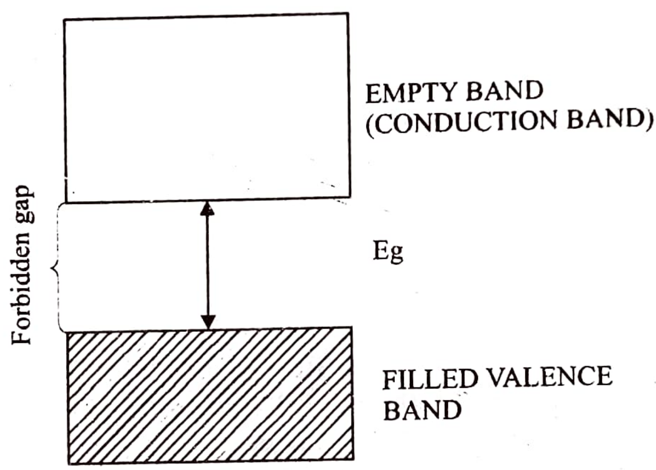


Fig. 6.11.

Semiconductors : A semiconductor is a solid substance whose electrical conductivity lies between the very high conductivity of conductors and very low conductivity of insulators. Germanium, Silicon etc are the examples of semiconductors. In this substance the width of the forbidden gap is very small as shown in fig. (6.12). In this substance a small portion of its electrons in the valence band have sufficient kinetic energy to cross the forbidden region and enter the empty band (conduction band).

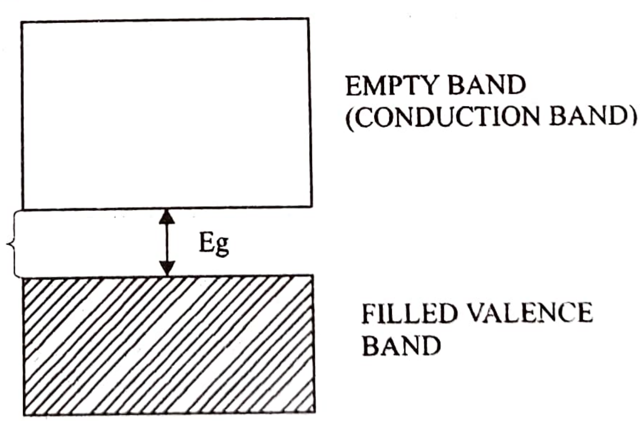


Fig. 6.12.

When an electric field is applied across the solid, few electrons in the valence band gain some energy to move towards the conduction band. The very small current is flowing in this case. The forbidden gap E_g for Germanium is 0.7eV and for Silicon is 1.1 eV.

6.9. DISTINCTION BETWEEN METALS, INSULATORS AND INTRINSIC SEMICONDUCTORS

The proper distinction between conductors, insulators and intrinsic semiconductors can be made with the help of band theory of solids. From eq. (13) of Art. 6.7. we can write

$$f_K = \frac{m}{m^*} = \frac{m}{\hbar^2} \frac{d^2E}{dK^2}$$

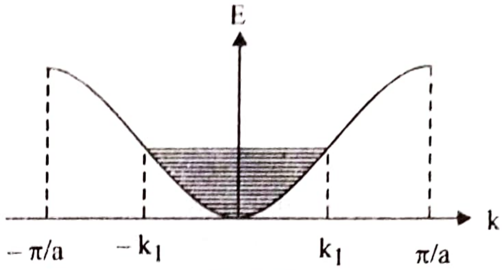


Fig.6.13.

where f_K is a measure for the extent to which an electron in the sate K is free to take part in electrical conduction. The number of free electrons effective for conduction in the band can be written as

$$N_{eff} = \Sigma f_K \quad \text{... (1)}$$

where the summation extends overall occupied states in the band.

Let the electrons be filled in a particular energy band up to fixed value K_1. If we assume one dimensional lattice of length L, the number of states in the interval dK is given by

$$dn = \frac{L}{2\pi} dK \quad \text{... (2)}$$

As two electrons occupy each of these states in the shaded region of fig. (6.13), we can write the effective number of free electrons in this region,

$$N_{eff} = 2\int_{-K_1}^{+K_1} f_K \, dn = 2\int_{-K_1}^{+K_1} \frac{m}{\hbar^2} \frac{d^2E}{dK^2} \frac{L}{2\pi} dK$$

$$= \frac{mL}{\pi\hbar^2} \int_{-K_1}^{+K_1} \frac{d^2E}{dK^2} dK$$

$$= \frac{2mL}{\pi\hbar^2} \int_{0}^{K_1} \frac{d^2E}{dK^2} dK$$

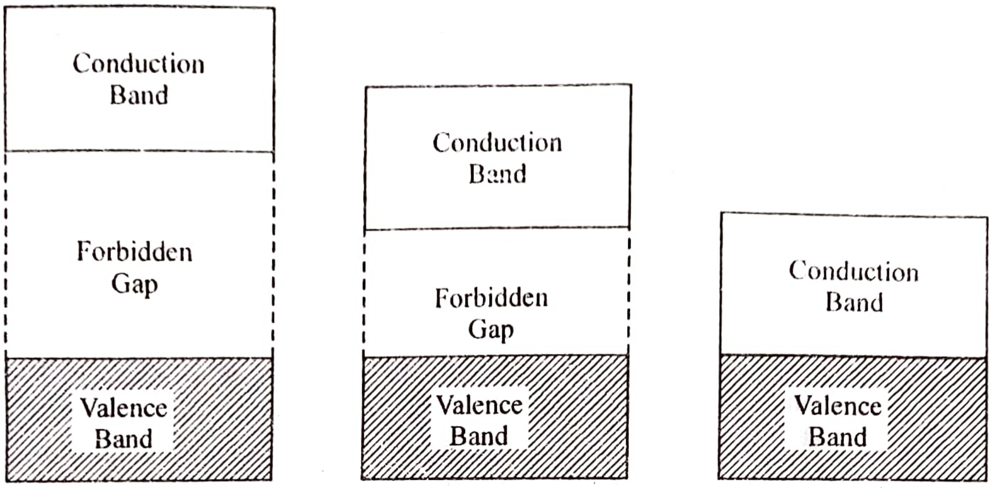
$$\therefore \quad N_{eff} = \frac{2mL}{\pi\hbar^2} \left[\frac{dE}{dK}\right]_0^{K_1} \quad \text{... (3)}$$

The following conclusions can be drawn from above results :

(i) At the top and bottom of the band *i.e.*, at $K = 0$ and $\frac{\pi}{a}$ for the $E - K$ curve, $\frac{dE}{dK} = 0$ and thus the effective number of electrons in a completely filled band will be zero *i.e.*, $N_{eff} = 0$.

(ii) Since $\frac{dE}{dK}$ becomes maximum at the point of inflection, the effective number becomes maximum for a band filled to the point of inflection.

Because no effective free electrons are found in the case of insulator, all bands up to valence band are completely filled and the upper band known as conduction band is completely empty (Fig. 6.14a). The forbidden energy region between the valence and conduction bands is so wide that no electrons can cross the forbidden gap.



(a) Insulator (a) Insulator (a) Insulator

Fig. 6.14.

If the forbidden gap between the filled (valence) band and empty (conduction) band is small say about 1.1eV, then there is some possibility that the electrons at room temperature will be excited from states near the top of filled band across the forbidden gap to the states near the bottom of the conduction band (Fig. 6.14b). If an electric field is applied, these electrons constitute a limited current. A substance of this type is known as intrinsic semiconductor.

If the substance has incompletely filled valence band, there are large number of electrons available for conduction which behaves as a free electrons (Fig. 6.14c). Such substance is called good conductor of electricity. All intrinsic semiconductors are insulators at $T = 0$ while all insulators may be treated as semiconductors at $T > 0$.

Example 1 : *Using Kronig Penny Model show that for $P << 1$, the energy of the lowest energy band is*

$$E = \frac{P\hbar^2}{ma^2}$$

[P.U. 2001]

Solution : From Kronig-Penny Model the solution of Schrodinger's equation for one dimensional periodic lattice can be written as

$$\frac{P \sin \alpha a}{\alpha a} + \cos \alpha a = \cos Ka \quad \text{... (i)}$$

where $\alpha^2 = \frac{2mE}{\hbar^2}, P = \frac{mV_0 ba}{\hbar^2}$ ... (ii)

and $Ka = \pm n\pi;\ n = 1,\ 2,\ 3, \ldots\ldots\ldots$

Hence the energy of the lowest band corresponds to $n = 1$. Thus

$$Ka = \pm \pi \quad \text{or,} \quad K = \pm \frac{\pi}{a}$$

Hence $\cos Ka = \pm \cos \pi = \pm 1$

Assuming only magnitude, we can write from (i),

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

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

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

$\because$ $$\cos \alpha a = 1 - 2\sin^2\left(\frac{\alpha a}{2}\right)$$

$\therefore$ $$1 - \cos \alpha a = 2\sin^2\left(\frac{\alpha a}{2}\right)$$

Also $$\sin \alpha a = 2\sin\left(\frac{\alpha a}{2}\right)\cos\left(\frac{\alpha a}{2}\right)$$

Hence $$\frac{P}{\alpha a} = \frac{2\sin^2\left(\frac{\alpha a}{2}\right)}{2\sin\left(\frac{\alpha a}{2}\right)\cos\left(\frac{\alpha a}{2}\right)}$$

$\therefore$ $$\frac{P}{\alpha a} = \tan\left(\frac{\alpha a}{2}\right) \quad \text{... (iii)}$$

Since $P << 1$, hence $\frac{P}{\alpha a} = \tan\left(\frac{P}{\alpha a}\right)$ ... (iv)

From (ii) and (iv), we get

$$\tan\left(\frac{\alpha a}{2}\right) = \tan\left(\frac{P}{\alpha a}\right)$$

$\therefore$ $$\frac{\alpha a}{2} = \frac{P}{\alpha a}$$

$\therefore$ $$\alpha^2 = \frac{2P}{a^2}$$

From (ii), $$\alpha^2 = \frac{2mE}{\hbar^2}$$

Hence $$\frac{2P}{a^2} = \frac{2mE}{\hbar^2}$$

$\therefore$ $$E = \frac{P\hbar^2}{ma^2}$$

Example 2 : *An insulator has an optical absorption which occurs for all wave length shorter than 1800Å. Find the width of the forbidden energy band for this insulator* ***[Luck. U. 1994]***

Solution : Since the insulator can absorb only wavelength which is shorter than 1800Å, hence the minimum energy which is required to move the electron from valence band to conduction band across the forbidden gap of the insulator is equal to the energy corresponds to wave length 1800Å.

Hence $\lambda = 1800\text{Å} = 1800 \times 10^{-10}$ m

Thus the frequency, $\nu = \frac{c}{\lambda} = \frac{3 \times 10^8}{1800 \times 10^{-10}}$

$\therefore$ $$\nu = \frac{10^{16}}{6}$$

Hence width of the forbidden band

$$E_g = h\nu$$

$$= \frac{6.626 \times 10^{-34} \times 10^{16}}{6} \text{ Joules}$$

$$\therefore \quad E_g = \frac{6.626 \times 10^{-34} \times 10^{16}}{6 \times 1.6 \times 10^{-19}} \text{ eV}$$

$$\therefore \quad E_g = \mathbf{6.9\ eV}$$

Example 3 : *Consider a two-dimensional square lattice having side 0.3 nm. At what electron momentum values do the side of the first Brillouin zone come? What is the energy of the free electron with this momentum?* ***[B.N.M.U. 2003]***

Solution : Here $a = 0.3\,\text{nm} = 0.3 \times 10^{-9}$ m

Mass of electron $m = 9.1 \times 10^{-31}$ kg

Planck's const. $h = 6.626 \times 10^{-34}$ Js

At the first Brillouin zone, $k = \pm \frac{\pi}{a}$

Hence the momentum of electron,

$$p = \frac{kh}{2\pi} = \left(\frac{h}{2\pi}\right) \times \left(\frac{\pi}{a}\right) = \frac{h}{2a}$$

Energy of the electron is given by

$$E = \frac{p^2}{2m}$$

Hence $$E = \frac{1}{2m}\left(\frac{h}{2a}\right)^2$$

$$\therefore \quad p = \frac{h}{2a} = \frac{6.626 \times 10^{-34}}{2 \times 0.3 \times 10^{-9}} = 1.1 \times 10^{-24} \text{ kg ms}^{-1}$$

$$E = \frac{p^2}{2m} = \frac{(1.1 \times 10^{-24})^2}{2 \times 9.1 \times 10^{-31}} = 6.63 \times 10^{-19} \text{ Joule}$$

$$= \frac{6.63 \times 10^{-19}}{1.6 \times 10^{-19}} \text{ eV}$$

$$= \mathbf{4.1.\ eV}$$

Example 4 : *Show that for a two dimensional square lattice, the kinetic energy of a free electron at the corner of the first zone is greater than that of an electron at mid point of a side face of zone by a factor of 2.* ***[B.N.M.U. 2005]***

Solution :

The kinetic energy of the electron is given by

$$K.E. = \frac{p^2}{2m}$$

We know that $$\lambda = \frac{h}{p} \quad \therefore \quad \frac{1}{\lambda} = \frac{p}{h}$$

$$\because \quad K = \frac{2\pi}{\lambda} \quad \therefore \quad K = \frac{2\pi p}{h}$$

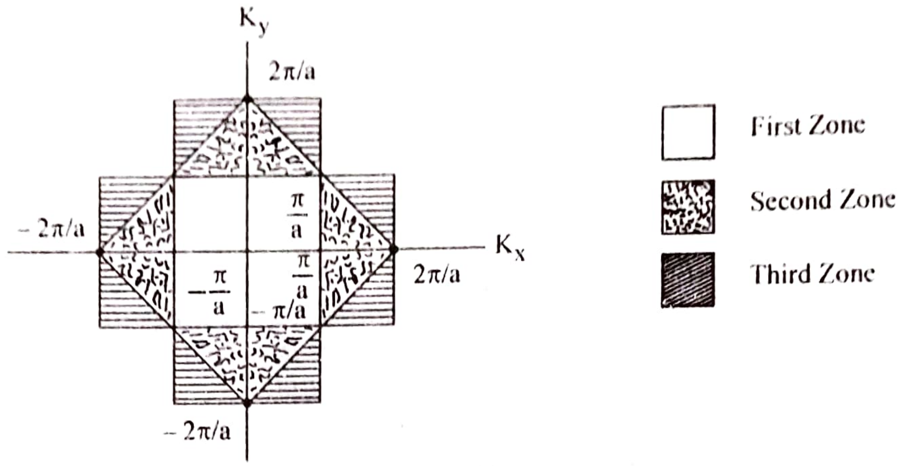


Fig. 6.15.

$$\therefore \quad p = \frac{Kh}{2\pi} = K\hbar$$

Hence $$K.E. = \frac{K^2\hbar^2}{2m}$$

At the mid point of a side,

$$K = \frac{\pi}{a}$$

Hence $$K.E. = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2 = E_1 \text{ (say)} \quad \text{... (i)}$$

At the corner of the first Brillouin zone,

$$K = \left(\frac{\pi^2}{a^2} + \frac{\pi^2}{a^2}\right)^{1/2}$$

$$\therefore \quad K^2 = \frac{2\pi^2}{a^2}$$

Hence the K.E. in this case,

$$E_2 = \frac{\hbar^2 K^2}{2m} = \frac{\hbar^2}{2m} \times \frac{2\pi^2}{a^2}$$

$$\therefore \quad E_2 = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2 \times 2 \quad \text{... (ii)}$$

(ii) and (i) give $$\frac{E_2}{E_1} = \frac{2}{1}$$

$$\therefore \quad E_2 = 2E_1$$ **Proved.**

EXERCISE

1. What is an energy band? What is the basic reason that energy bands, rather than specific energy levels, exist in solids? ***[Patna 1991, 89]***
2. What is Bloch Theorem? Deduce Bloch Thoerem and discuss its results. ***[Luck. 1996, 2001; H.P. 2000; Patna U. 1992, Ranchi U. 1991]***
3. What is Kronig-Penney Model? Apply it to a periodic potential and discuss it to a periodic potential and discuss its conclusions. ***[Patna 1992, 1997, Lucknow 1993]***