

ELECTRONIC MATERIALS

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7.1 FREE ELECTRON THEORY

According to Drude, the metals consists of positive ions cores with the valence electrons moving freely among these cores. The electrons are, therefore bound to move within the metal due to electrostatic attraction between the positive ion cores and the electrons. The potential field of these ion cores, which is responsible for such an interaction, is assumed to be constant throughout the metal and the mutual repulsion among the electrons is neglected. The behaviour of free electrons moving inside the metals is considered to be similar to that of atoms or molecules in perfect gas. These free electrons are, therefore, also referred to as free electron gas and the theory is accordingly named as free electron gas model. The free electron gas, however, differs from an ordinary gas in some respects. Firstly, the free electron gas is negatively charged whereas the molecules of an ordinary gas are mostly neutral. Secondly, the concentration of electrons in an electron gas is quite large as compared to the concentration of molecules in an ordinary gas. The valence electrons are also called the conduction electrons and obey the Pauli's exclusion principle. These electrons are responsible for conduction of electricity through metals. Since the conduction electrons move in a uniform electrostatic field of ion cores, their potential energy remains constant and is normally taken as zero. Thus the total energy of a conduction electron is equal to its kinetic energy. Also since the movement of conduction electrons is restricted to within the crystal only, the potential energy of a stationary electron inside a metal is less than the potential energy of an identical electron just outside it. This energy difference, V_0 , serves as a potential barrier and stops the inner electrons from leaving the surface of the metal. Thus, in free electron gas model, the movement of a free electron gas inside a potential energy box which in one dimensional case is represented by a potential well as shown in Fig. 7.1.

In 1909, H.A. Lorentz postulated that the electrons constituting the electron gas obey Maxwell-Boltzmann statistics under equilibrium conditions. This idea alongwith Drude consideration lead to constitute the Drude-Lorentz theory. This theory is also known as classical theory.

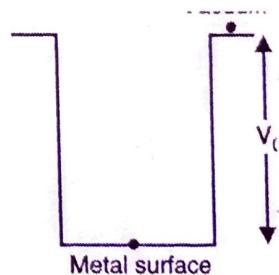


Fig. 7.1 Metallic surface bounded by potential barrier V_0 which represents the difference in potential energy of a stationary electron at the surface of the metal and just outside it.

The free electrons in a metal move isotropically and move in a particular direction on an application of electric field. Because of elastic collisions, the magnitude of steady state current is proportional to the voltage applied provided the temperature of metal remains constant. This lead to Ohms law. Moreover, as the free electrons can move easily, the metals exhibit high electrical and thermal conductivities. The ratio of the electrical conductivity ' σ ' to the thermal conductivity ' K ' should be constant for all metals at a constant temperature *i.e.*, $\frac{\sigma}{K} = \text{constant}$. This is called Weidemann-Franz law, which has been realised even in practice also. This theory also explains the lustre and opaque properties of metals. When an electromagnetic radiation falls on the surface of metal, the free electrons are set into forced oscillation. The electrons return to their normal states by emitting the same amount of energy in all directions, and hence produces metallic lustre.

7.1.1 Electrical Conductivity as per Free Electron Theory

On the basis of free electron theory, the electrons move freely in solid, so it is interesting to see the effect of external electric field on these electrons. Let E be the applied electric field, m be the mass of the electron and e be the charge on the electron. The force F due to applied field will be

$$F = eE$$

Also

$$F = ma, \text{ where } a \text{ is the acceleration.}$$

\therefore

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

Because of collisions of electrons during motion, the electrons will not get accelerated indefinitely. In fact, their velocity will fall to zero. If τ be the *relaxation time* (collision time) then the average electronic velocity known as drift velocity is given by

$$v_d = a\tau = \frac{eE}{m}\tau \quad \dots(1)$$

Let I be the current carried by a conductor on application of electric field E corresponding to drift velocity v_d . In time dt , the electrons will travel a distance $v_d dt$ and the number of electrons crossing any cross-sectional area A in time dt will be contained in volume $Av_d dt$. Thus, if there are n electrons per unit volume of the conductor, the total charge flowing through the section in time dt is

$$dQ = enAv_d dt$$

or

$$I = \frac{dQ}{dt} = en Av_d$$

And current density

$$J = \frac{I}{A} = en v_d \quad \dots(2)$$

Using eqn. (1), we have

$$J = en \left(\frac{eE\tau}{m} \right) = \frac{ne^2 \tau E}{m} \quad \dots(3)$$

For a particular material, the quantity $\frac{ne^2 \tau}{m}$ in (3) is constant at particular temperature and is known as electrical conductivity ' σ ' of the material

$$J = \frac{ne^2\tau E}{m} = \sigma E \quad \dots(4)$$

$$\sigma = \frac{ne^2\tau}{m} \quad \dots(5)$$

We know that the resistance R of a conductor is given by

$$R = \rho \frac{l}{A} \text{ where } \rho \text{ is resistivity of material and } l \text{ is the length of conductor. Also } \rho = \frac{1}{\sigma}, \text{ therefore,}$$

from eqns. (1) and (4), we have

$$I = JA = \sigma EA = \frac{EA}{\rho} = \frac{El}{R}$$

Also

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

$$\therefore I = \frac{Vl}{Rl} = \frac{V}{R}$$

which is nothing but Ohm's law. That is why eqns. (4) and (5) are also known as Ohm's law.

Equation (5) can also be written as

$$\sigma = \frac{ne^2\tau}{m} = ne\mu \quad \dots(6)$$

where $\mu \left(= \frac{e\tau}{m}\right)$ is the mobility acquired by electrons in the presence of electric field. Using eqn. (1), the

mobility of electrons can also be expressed as

$$\mu = \frac{e\tau}{m} = \frac{v_d}{E} \quad \dots(7)$$

Therefore, the mobility of electron in the metal is defined as the steady state drift velocity per unit electric field.

Let λ be the mean free path and V' be the root mean square velocity of electrons, then the relaxation time (commonly known as mean time between collisions) τ is given by

$$\tau = \frac{\lambda}{V'}$$

$$\text{But } V' = \sqrt{\frac{3K_B T}{m}}$$

$$\therefore \tau = \lambda \sqrt{\frac{m}{3K_B T}}$$

Now the electrical conductivity ' σ ' can be expressed as

$$\sigma = \frac{ne^2\tau}{m} = \frac{ne^2\lambda}{m} = \left(\frac{ne^2\lambda}{m}\right) \sqrt{\left(\frac{m}{3K_B T}\right)} \quad \dots(8)$$

or

$$\sigma = \frac{ne^2\lambda}{\sqrt{3m K_B T}} \quad \dots(8)$$

Since electrical resistivity ρ is the reciprocal of electrical conductivity ' σ '.

$$\rho = \frac{\sqrt{3m K_B T}}{ne^2} \quad \dots(9)$$

or

$$\rho \propto \sqrt{T}$$

Above result shows that the resistivity varies as \sqrt{T} whereas actually it is found to vary linearly with temperature. Therefore, it shows that free electron theory must have some limitations.

7.1.2 Limitation of Free Electron Theory

Following limitations have been observed :

- (a) It can not explain why only some crystals are metallic in nature.
- (b) It can not explain why the metals prefer only certain structure e.g., Fe is cubic while Zn is hexagonal.
- (c) It can not explain why the observed specific heat of metals is only 1% of the calculated value
 $\left(i.e., \frac{3}{2} N K_B; N \text{ are number of free electrons per gram atom} \right)$.
- (d) It cannot explain the temperature variation of the electrical conductivity.
- (e) It cannot explain the paramagnetic behaviour of metals.
- (f) It also could not explain the occurrence of long mean free paths at low temperatures.

7.2 QUANTUM THEORY: FERMI GAS

All of the above mentioned limitations of the free electron theory disappear when we treat the electrons by Fermi-Dirac distribution. The Fermi-Dirac distribution allows only a fraction of the total number of free electrons to gain energy and the values of heat capacity and paramagnetic susceptibility thus obtained coincide with the observed ones. Sommerfeld treated the problem quantum mechanically using Fermi-Dirac distribution and considered the corresponding electron gas as Fermi gas (Fermi gas obeys Pauli's exclusion principle). Now we will compare the classical gas with Fermi gas at absolute zero. Classically, all the electrons of a gas at zero temperature have zero kinetic energy i.e., all are at rest. On the other hand, electrons of Fermi gas at zero temperature cannot all have zero kinetic energy because if so they will contradict the Pauli's exclusion principle. Instead, at zero temperature the electrons of Fermi gas will occupy the available states of lowest energy i.e., two electrons with opposite spins in each orbital state.

In the following section, we will describe the possible electronic states of electrons in the potential energy box (one dimensional as well as three dimensional) and their distribution using quantum theory.

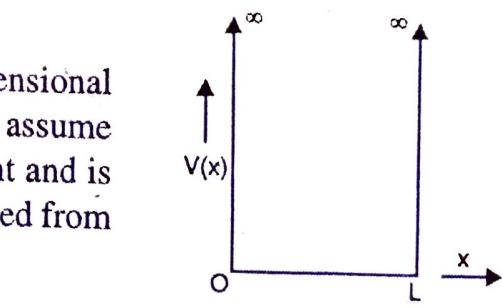
7.2.1 Fermi Gas in One-dimensional Box

Consider an electron of mass m confine to remain within a one dimensional crystal of length L by infinite barriers at the ends of the length. Also assume that the potential energy everywhere within this crystal is constant and is equal to zero. At the two ends of the crystal, the electron is prevented from leaving the crystal by an infinite potential energy barriers.

i.e.,

$$V(x) = 0 ; 0 \leq x \leq L$$

$$= \infty ; x \leq 0, x > L$$



... (10)

Fig. 7.2 I-D potential box bounded by infinite potential energy barriers.

Since the potential energy inside the crystal is zero, the Schrodinger equation is in the form of

$$\frac{d^2\psi_n}{dx^2} + \frac{2m E_n}{\hbar^2} \psi_n = 0 \quad \dots(11)$$

where E_n is the energy of the electron in the state n . As the probability of finding the electron across the wall is zero, so we have the following boundary conditions

$$\psi_n(0) = \psi_n(L) = 0 \quad \dots(12)$$

These boundary conditions are automatically satisfied if the wave function is sinusoidal with an integral number, n , of half wavelengths between 0 and L .

$$\begin{aligned} \psi_n &= A \sin kx \\ &= A \sin \frac{2\pi}{\lambda} x \end{aligned} \quad \dots(13)$$

At $x = L$

$$\psi_n = A \sin \frac{2\pi}{\lambda} L$$

To satisfy eqn. (12), i.e., $\psi_n(L) = 0$

$$\frac{2\pi}{\lambda} L = n\pi$$

or

$$\frac{2\pi}{\lambda} = \frac{n\pi}{L}$$

Hence eqn. (13) becomes

$$\psi_n = A \sin \left(\frac{n\pi}{L} x \right) \quad \dots(14)$$

Now

$$\frac{d\psi_n}{dx} = A \left(\frac{n\pi}{L} \right) \cos \left(\frac{n\pi}{L} x \right)$$

and

$$\frac{d^2\psi_n}{dx^2} = -A \left(\frac{n\pi}{L} \right)^2 \sin \frac{n\pi}{L} x \quad \dots(15)$$

Hence eqn. (11) becomes

$$-A \left(\frac{n\pi}{L} \right)^2 \sin \left(\frac{n\pi}{L} x \right) + \frac{2m E_n}{\hbar^2} A \sin \left(\frac{n\pi}{L} x \right) = 0$$

or

$$\left(\frac{n\pi}{L} \right)^2 = \frac{2m E_n}{\hbar^2}$$

$$\Rightarrow E_n = \frac{\hbar^2}{2m} \left(\frac{n\pi}{L} \right)^2 \quad \dots(16)$$

i.e.,

$$E_n \propto n^2$$

\therefore The energy is a quadratic function of the quantum number as shown in Fig. 7.3. The probability of finding the electron some where on the line is unity.

i.e.,

$$\int_0^L |\psi_n|^2 dx = 1$$

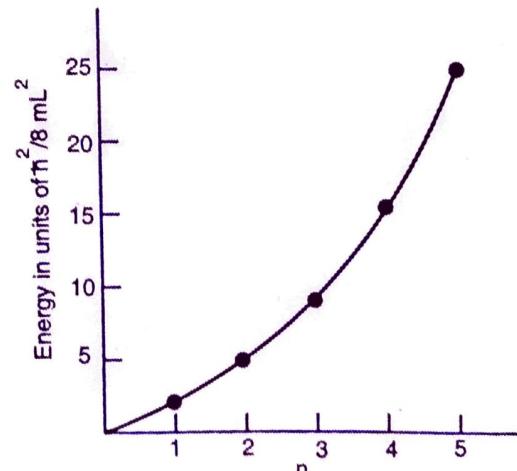


Fig. 7.3 E_n versus n for a 1-D crystal.

or $\int_0^L A^2 \sin^2\left(\frac{n\pi}{L}x\right) dx = 1$

or $A^2 \frac{L}{2} = 1$

$\Rightarrow A = \sqrt{2/L}$

Hence the wave function eqn. (16) becomes

$$\psi_n(x) = \sqrt{2/L} \sin\left(\frac{n\pi}{L}x\right) \quad \dots(17)$$

Let us suppose that we want to accomodate N electrons on the line. According to Pauli exclusion principle, no two electrons can have all their quantum numbers identical, i.e., each quantum state can be occupied by at most one electron. For a given value of n there are two quantum states of the electrons $m_s = \pm \frac{1}{2}$. Each energy level of quantum number n can accomodate two electrons, one with spin up and one with spin down.

If there are five electrons, e.g., Boron, then the ground state ($n = 1$) of the system has 2, next state $n = 2$ has two and third state $n = 3$ has only one electron and the higher states are empty (Fig. 7.4).

Let the top most filled energy level be represented by n_f . If N , i.e., the total number of electrons to be accomodated is even, then

$$2n_f = N \quad \dots(18)$$

determines the value of n_f .

The Fermi energy E_f is defined as the energy corresponding to the top most filled energy level in the ground state of the N electron system. From eqn. (16)

$$E_f = \frac{\hbar^2}{2m} \left(\frac{n_f \pi}{L} \right)^2 = \frac{\hbar^2}{8\pi^2 m} \left(\frac{n_f \pi}{L} \right)^2$$

or

$$E_f = \frac{\hbar^2}{2m} \left(\frac{n_f}{L} \right)^2$$

But

$$n_f = \frac{N}{2}$$

$$\therefore E_f = \frac{\hbar^2}{2m} \left(\frac{N}{4L} \right)^2 \quad \dots(19)$$

The total energy E_0 of N electrons in the lowest energy state of the entire system can be obtained by adding the individual energies E_n between $n = 1$ to $n_f = \frac{N}{2}$

Thus

$$E_0 = 2 \sum_{n=1}^{N/2} E_n \quad \dots(20)$$

The factor 2 is due to fact that we are taking account of two electrons in each level. Substituting, the value of E_N from eqn. (19) in eqn. (20), we have

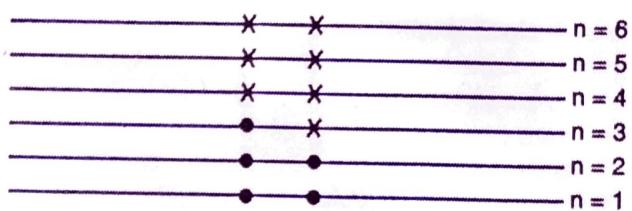


Fig. 7.4 Dots and cross representing filled and empty states respectively.

$$\begin{aligned}
 E_0 &= 2 \sum_{n=1}^{N/L} \frac{\hbar^2}{2m} \left(\frac{n\pi}{L} \right)^2 = 2 \frac{\hbar^2}{8m} \left(\frac{1}{L} \right)^2 \sum_{n=1}^{N/L} n^2 \\
 &= 2 \cdot \frac{\hbar^2}{2m} \left(\frac{1}{2L} \right)^2 \sum_{n=1}^{N/L} n^2
 \end{aligned} \quad \dots(21)$$

Now $\sum_{n=1}^s n^2 = \frac{1}{6} s(2s^2 + 3s + 1) \approx \frac{1}{3} s^3$ for $s \geq 1$

Here

$$s = \left(\frac{N}{2} \right)$$

$$\therefore \sum_{n=1}^{N/2} n^2 \approx \frac{1}{3} \left(\frac{N}{2} \right)^3$$

Hence eqn. (21) becomes,

$$\begin{aligned}
 E_0 &\approx 2 \frac{\hbar^2}{2m} \left(\frac{1}{2L} \right)^2 \times \frac{1}{3} \left(\frac{N}{2} \right)^3 = \frac{1}{3} \frac{\hbar^2}{m} \left(\frac{1}{2L} \right)^2 \left(\frac{N}{2} \right)^2 \\
 &= \frac{1}{3} N \frac{\hbar^2}{2m} \left(\frac{N}{4L} \right)^2
 \end{aligned}$$

Using eqn. (19), we have

$$E_0 = \frac{1}{3} N E_f \quad \dots(22)$$

Thus, the average kinetic energy in the ground state is one third of the Fermi energy. From eqn. (16), we have

$$\begin{aligned}
 \frac{dE_n}{dn} &= \frac{\hbar^2}{2m} \left(\frac{\pi}{L} \right)^2 2n = \frac{\hbar^2}{8m} \left(\frac{1}{L} \right)^2 \times 2n \\
 &= \frac{\hbar^2}{m} \left(\frac{n}{2L} \right) \frac{1}{2L}
 \end{aligned}$$

or

$$\frac{dn}{dE_n} = \frac{4L^2 m}{\hbar^2 n} \quad \dots(23)$$

which gives the number of energy levels.

7.2.2 Density of States in One-dimension

As there are two quantum states for each energy levels (Pauli exclusion principle), therefore, the density of states (number of electronic states per unit energy range) of a free electron gas in one dimension is

$$\begin{aligned}
 D(E) &= 2 \frac{dn}{dE_n} = 2 \cdot \frac{4L^2 m}{\hbar^2 n} \\
 &= \frac{8L^2 m}{\hbar^2} \frac{1}{n}
 \end{aligned} \quad \dots(24)$$

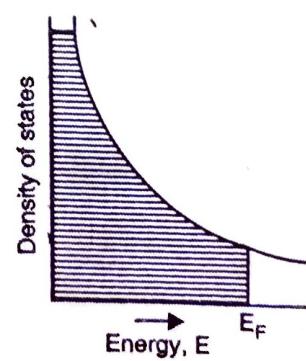


Fig. 7.5 Variation of DOS with energy for a 1-D metallic crystal. At 0K all the states upto Fermi level are filled.

From eqn. (16), the above equation reduces to

$$\begin{aligned} D(E) &= \frac{8L^2 m}{\hbar^2} \frac{h}{2L} \left(\frac{1}{2m E} \right)^{1/2} \\ &= \frac{4L}{\hbar} \sqrt{m/(2E)} \end{aligned} \quad \dots(25)$$

The variation of density of states $D(E)$ with energy E is shown in Fig. 7.5.

It shows that the levels are filled from 0 to E_f beyond which all the states are empty.

7.2.3 Density of States in Three-dimension

In three dimensional case, the Schrodinger wave equation for a free particle is

$$\nabla^2 \psi_n + \frac{2mE}{\hbar^2} \psi_n = 0 \quad \dots(I)$$

where

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Let

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

\therefore

$$E = \frac{\hbar^2 k^2}{2m} \quad \text{(2)}$$

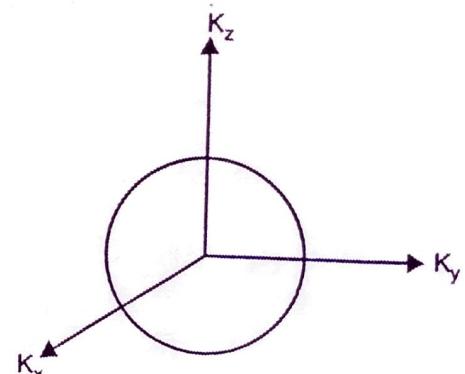


Fig. 7.6 Fermi sphere.

In the present case, let us consider a parallelopiped of volume V . The shape of fermi surface in momentum space (k -space) for the free electron gas model is perfectly spherical (see Fig. 7.6), whose Fermi radius is k_f when $E = E_f$ i.e., $E_f = \frac{\hbar^2 k_f^2}{2m}$.

The eqn. (I) has solution similar to the plane wave of the type

$$\psi_n(r) = A e^{ikr} = A e^{i(k_x x + k_y y + k_z z)} \quad \text{(3)}$$

which must satisfy the periodic boundary conditions as discussed in Kronig-Penny model. These boundary conditions will give the value of k_x , k_y and k_z each equal to $\frac{2\pi}{L}$.

\therefore In k -space, the volume occupied by solid is $\frac{2\pi}{L} \times \frac{2\pi}{L} \times \frac{2\pi}{L} \left(= \frac{8\pi^3}{L^3} \right)$.

Therefore, the number of energy states inside the Fermi sphere are

$$\begin{aligned} n_f &= \frac{\text{Volume of Fermi sphere}}{\text{Volume of solid in } k\text{-sphere}} = \frac{\frac{4}{3}\pi k_f^3}{\frac{8\pi^3}{V}} \quad (\because L^3 = V) \\ &= \frac{V k_f^3}{6\pi^2} \quad \text{(4)} \end{aligned}$$

As described earlier, the total number of electrons to be accommodated are even i.e., $N = 2n_f$

$$\frac{N}{2} = \frac{V k_f^3}{6\pi^2}$$

$$k_f = \left(\frac{3\pi^2 N}{V} \right)^{1/3}$$

or

Thus, Fermi energy E_f is given by

$$E_f = \frac{\hbar^2 k_f^2}{2m} = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3}$$

— (5)

The Fermi energy E_f is corresponding to Fermi velocity v_f and is given by

$$\frac{1}{2} m v_f^2 = E_f$$

$$v_f = \frac{\hbar}{m} \left(\frac{3\pi^2 N}{V} \right)^{1/3}$$

— (6)

Moreover, the Fermi temperature is given by

$$E_f = K_B T_f$$

$$T_f = \frac{\hbar^2}{2m K_B} \cdot \left(\frac{3\pi^2 N}{V} \right)^{2/3}$$

or

The density of states $D(E)$ can be obtained by the fact that, in the ground state of the system, all the energy states below E_f are occupied and the total number of states is equal to the total number of electrons i.e.,

$$\int_0^{E_f} D(E) dE = N$$

$$\text{or } \int_0^{E_f} D(E) dE = \frac{2V K_f^3}{6\pi^2} = \frac{V}{3\pi^2} \left(\frac{2m E_f}{\hbar^2} \right)^{3/2}$$

If we express the above relation in an indefinite form, we get

$$\int D(E) dE = \frac{V}{3\pi^2} \left(\frac{2m E}{\hbar^2} \right)^{3/2} = \int \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{1/2} dE$$

$$\text{or } D(E) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{1/2} = \frac{V 8\sqrt{2}\pi m^{3/2} E^{1/2}}{h^3}$$

Therefore, the electron density $C(E)$ is given by

$$C(E) = \frac{D(E)}{V} = \frac{8\sqrt{2}\pi m^{3/2} E^{1/2}}{h^3}$$

7.2.4 Effect of Temperature on Fermi Energy

The kinetic energy of the electron gas increases as the temperature is increased: some energy levels are occupied which were vacant at 0 K and some levels are vacant which were occupied at absolute zero.

Since the electron density (number of electrons per unit volume) is very large and motion of the electron is random, the energy levels occupied by electrons at a given temperature can be determined statistically. As the electrons obey Pauli exclusion principle, therefore, according to Fermi-Dirac statistics, the number of electrons occupying energy states between E and $E + dE$ in a unit volume is given by

$$N(E) dE = C(E) F(E) dE \quad \dots(26)$$

where

$$C(E) = \frac{8\sqrt{2} \pi m^{3/2} E^{1/2}}{h^3}$$

and

$$F(E) = \frac{1}{e^{(E - E_f)/K_B T} + 1}$$

$F(E)$ gives the probability of a state corresponding to energy E (Fig. 7.7) occupied by an electron at temperature T . $K_B = (8.62 \times 10^{-5} \text{ eV/K} = 1.38 \times 10^{-23} \text{ J/K})$ is the Boltzmann constant and E_f is the Fermi energy. $F(E)$ is also known as Fermi function.

The total number of electrons per unit volume n in the free electron gas is determined by integrating the eqn. (26) i.e.,

$$n = \int_0^\infty N(E) dE = \int_0^\infty C(E) F(E) dE$$

At $T = 0 \text{ K}$,

1. If $E > E_f$, then $F(E) = 0$, i.e., energy state is empty.
2. If $E < E_f$, $F(E) = 1$, i.e., energy state is occupied by an electron.

Therefore, we get

$$\begin{aligned} n &= \int_0^{E_f} C(E) \cdot (1) dE + \int_{E_f}^\infty C(E) \cdot (0) dE = \int_0^{E_f} C(E) dE \\ &= \int_0^{E_f} \frac{8\sqrt{2} \pi m^{3/2} E^{1/2}}{h^3} dE = \frac{8\sqrt{2} \pi m^{3/2}}{h^3} \cdot \frac{2}{3} \left| E^{3/2} \right|_0^{E_f} \\ &= \frac{8\sqrt{2} \pi m^{3/2}}{h^3} \cdot \frac{2}{3} E_f^{3/2} \end{aligned}$$

or

$$E_f = \frac{h^2}{8m} \left(\frac{3n}{\pi} \right)^{2/3}$$

Thus, the Fermi energy may be calculated simply by knowing the electron concentration n . The calculated values for a number of metals are given as

Na	K	Cu	Ag	Ba	Al	Li
3.12 eV	2.14 eV	7.04 eV	5.51 eV	3.8 eV	11.7 eV	4.72 eV

At $T > 0 \text{ K}$ and $E = E_f$, $F(E) = \frac{1}{2}$ i.e., energy state is half filled.

Hence, we conclude that at absolute zero, all the states above Fermi level E_f are empty and when the temperature is raised above absolute zero, then there is greater probability of electrons being found above Fermi level, with equal probability of finding holes (deficiency of electrons) below the Fermi level.

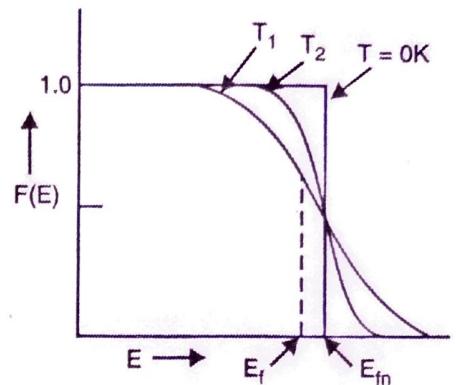


Fig. 7.7 Schematic representation of the Fermi distribution function for three different temperatures.

7.2.5 Density of States for Two-dimensional Objects (Quantum Well)

In last section, we derived DOS for free electrons when they were free to move in all the directions. Now, we will see how DOS of electrons behaves when their motion is restricted one direction and they are free to move in two directions. Consider a slab of material that has macroscopic dimensions in the x - and y -directions while the thickness is small (in the nanometer range). Periodic boundary conditions in the x - and y -directions lead to

$$k_x = \frac{n2\pi}{L_x}, \quad k_y = \frac{l2\pi}{L_y}, \quad n, l = 1, 2, 3, \dots$$

The area per k -point in k -space is then

$$S_k = \frac{4\pi^2}{L_x L_y} = \frac{4\pi^2}{L^2} \quad (\text{If } L_x = L_y = L)$$

The number of states within a circle with radius k is then

$$N(k) = 2 \frac{\pi k^2}{4\pi^2/L^2} = \frac{k^2 L^2}{2\pi^2}$$

where factor 2 is due to spins of electrons.

Therefore, DOS (2D) is

$$\frac{dN}{dE} = \frac{dN}{dK} \cdot \frac{dK}{dE}$$

Also,

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

$$\therefore \frac{dk}{dE} = \frac{1}{2\hbar} \sqrt{\frac{2m}{E}}$$

and

$$\frac{dN}{dk} = \frac{kL^2}{\pi}$$

Therefore, density of states $D(E)$ is

$$D(E) = \frac{dN}{dE} = \frac{mL^2}{\pi\hbar^2}$$

which is independent of the energy. However, $D(E)$ depends upon the number of levels and thus a sum of contributions from the discrete levels. Therefore, we have

$$D(E) = \frac{mL^2}{\pi\hbar^2} \sum H(E - E_{cn})$$

where $H(E - E_{cn})$ is the Heaviside step function and E_{cn} denotes the conduction band minima of the discrete levels.

Semiconductor Quantum Well

The semiconductor quantum well (QW) is a region of lower energy where it can trap electrons and holes. Here, properties of the semiconductors are governed by the quantum mechanical laws that allows

only specific energies and band gaps. *QW* structures are very thin and can be realized in real world considering epitaxial growth of a sequence of ultrathin layers consisting of semiconducting materials of varying composition. In *QW* structure, the electrons are confined in their motion in one direction while they move as in the corresponding bulk material in the other two directions. These effects are widely used in semiconductor lasers where the band structure of quantum wells are tuned to give the desired emission wavelengths. One such example of a semiconductor quantum well is the GaAs – $\text{Ga}_{1-x}\text{Al}_x\text{As}$ as multilayer system. By changing the composition of the GaAlAs layer, the depth of the well can be adjusted.

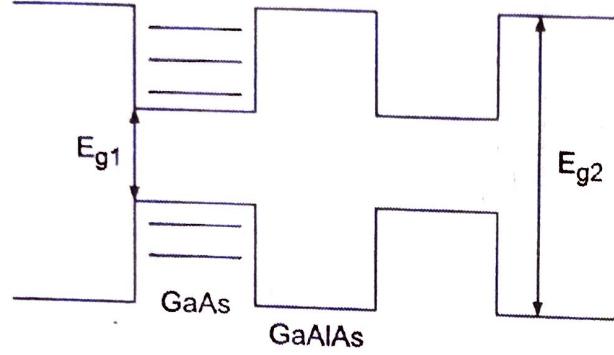


Fig. 7.8(a) Quantum well structure formed in GaAs layers which are sandwiched between GaAlAs layers. The energy band gap E_{g2} (GaAlAs) is more than E_{g1} (GaAs).

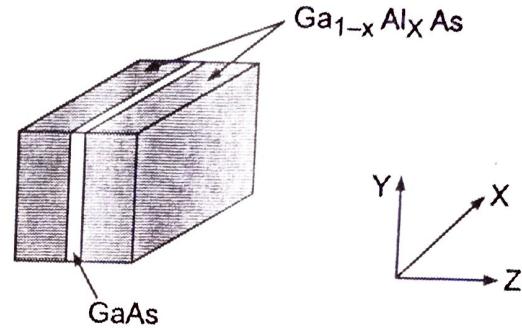


Fig. 7.8(b) The layered structure of quantum well.

7.2.6 Density of States for One-dimensional Objects (Quantum Wire)

If we allow electrons to move freely in one direction and confine its motion in the other two directions (in nanometer range), then a system so called quantum wire is formed. A large number of different structures have been grown and a wide range of interesting applications have been suggested for these types of system, including electronic components, sensors, and light emitting components. Now, the number of electronic states present on single level in k -space are

$$N = \frac{2k}{2\pi/L} = \frac{kL}{\pi}$$

Therefore, the DOS (1D) is

$$D(E) = \frac{dN}{dE} = \frac{dN}{dk} \cdot \frac{dk}{dE} = \frac{L}{\pi} \cdot \frac{1}{2\hbar} \sqrt{\frac{2m}{E}} = \frac{L}{\pi\hbar} \sqrt{\frac{m}{2E}}$$

For discrete energy levels, we have

$$D(E) = \frac{L}{\pi\hbar} \sqrt{\frac{m}{2(E - E_i)}}$$

In this simple model $D(E) \rightarrow \infty$ for $E = E_i$.

Quantum Wire

A quantum well layer can be etched in such a way to give the structure of the type shown in Fig. 7.8(c), known as quantum wire. Here, the charge carriers are confined along an additional direction in comparison to the quantum well i.e., motion of charge carriers is confined in x and y direction whereas they are free to move along z -direction. The following Fig. 7.8(c) shows a view of single quantum wire.

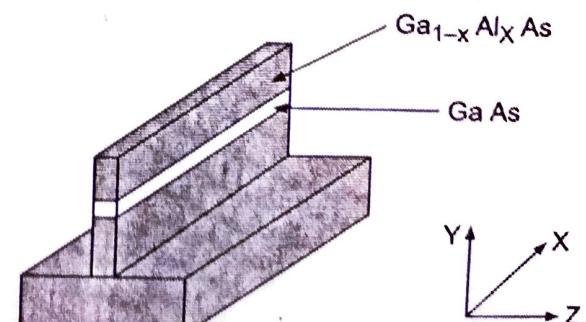


Fig. 7.8(c) Structure of Quantum wire

7.2.7 Density of States for Zero-dimensional Objects (Quantum Dot)

Following the line of the earlier sections on two-dimensional and one-dimensional objects, we will now move down to zero dimensional systems where the electrons are confined in their motion in all the three directions. Here in this case, the system appears as an artificial atom because energy of the confined electrons is quantized and is represented by discrete energy levels. Therefore, the density of states can be written directly as

$$D(E) = 2\sum \delta(E - E_i)$$

The density of states DOS for bulk, quantum well, quantum wire and quantum dot are shown in Fig. 7.8(d) as a function of energy.

Quantum Dot

If we further each the quantum wire, then we obtain structure of the type of shown in Fig. 7.8(d), known as quantum dot. In this structure, a charge carrier is confined in all the three dimensions.

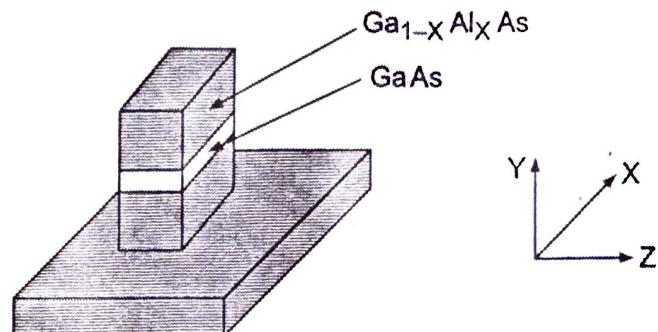


Fig. 7.8(d) Structure of quantum dot

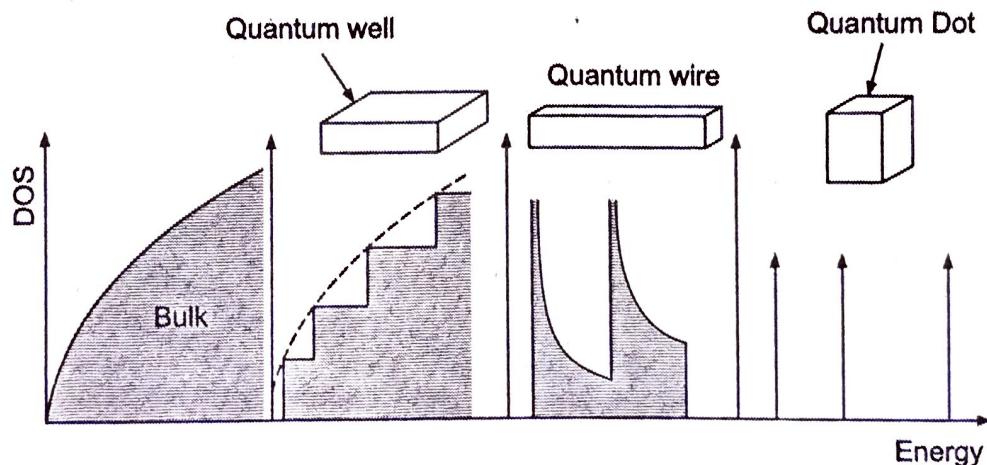


Fig. 7.8(e) Normalized densities of states for bulk material (3D object with no confinement), quantum well (2D object with confinement in one dimension), quantum wire (1D object with confinement in 2 dimensions) and quantum dot (confinement in all three dimensions).

7.2.8 Density of States for Photons and Phonons

1. Photons

Consider electromagnetic radiation in a cavity (e.g., black body radiation) for which the quanta are called photons. Here, the dispersion relation for energy is linear:

i.e.,

$$E = \hbar\omega = \hbar ck$$

Also, the total number of states are given by

$$N = \frac{\text{Volume of Fermi sphere}}{\text{Allowed volume for each state}} = \frac{\frac{4}{3}\pi k^3}{\left(\frac{2\pi}{L}\right)^3} = \frac{V}{6\pi^2}k^3$$

where $L^3 = V$ is the volume. Therefore, the density of states can be calculated as

$$\text{DOS}(E) = 2 \frac{dN}{dE} = 2 \frac{dN}{dk} \cdot \frac{dk}{dE}$$

The above relation is multiplied by 2 because there are two (transverse) polarization states of the photon. Therefore, we have

$$\text{DOS}(E) = \frac{V}{\pi^2} k^2 \cdot \frac{1}{\hbar c}$$

Also, $E = \hbar ck$, therefore, we have

$$\text{DOS}(E) = \frac{V}{\pi^2} \cdot \frac{E^2}{(\hbar c)^3}$$

Hence, the density of states for photons is proportional to E^2 .

2. Phonons

Just as light waves are quantized into photons, the sound waves (or lattice vibrations) are also quantized and the quantum of energy is known as "phonon". The dispersion relation gives energy as

$$E = \hbar\omega = \hbar\nu k$$

where ν is the speed of sound. Unlike light, sound waves can be polarized longitudinally (1 direction) as well as transversely (2 directions), so there are 3 different polarizations (photons have only 2 polarization directions). Therefore, the density of states is given by

$$\text{DOS}(E) = 3 \frac{dN}{dE} = 3 \frac{dN}{dk} \cdot \frac{dk}{dE}$$

$$\text{DOS}(E) = \frac{3}{2} \cdot \frac{V}{\pi^2} \cdot \frac{E^2}{(\hbar\nu)^3}$$

where ν is the velocity of the sound waves.

7.3 PERIODIC POTENTIAL IN CRYSTALLINE SOLID

In solids one deals with a large number of interacting particles and hence the problem of determining the electron wave functions and the energy levels is extremely complicated. A simple quantum mechanical picture of an electron in a crystal can, however, be obtained by assuming that the atomic nuclei are at rest in the crystalline state and that the electron is in a periodic potential which has periodicity of the lattice. The periodic potential may be considered to be caused by the fixed nuclei plus some average potential due to all other electrons. The solution of Schrodinger equation for this potential gives a set of state or levels which may be occupied by the electrons according to Pauli's exclusive principle.

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

$$V = -\frac{ze^2}{4\pi\epsilon_0 r} \quad \dots(27)$$

To form a crystal, a number of such nuclei are brought close to each other. Therefore, the potential energy of an electron is the sum of potential energies due to the individual nuclei. Hence, the variation of potential energy with distance for a one-dimensional crystal is as shown in the Fig. 7.8(f).

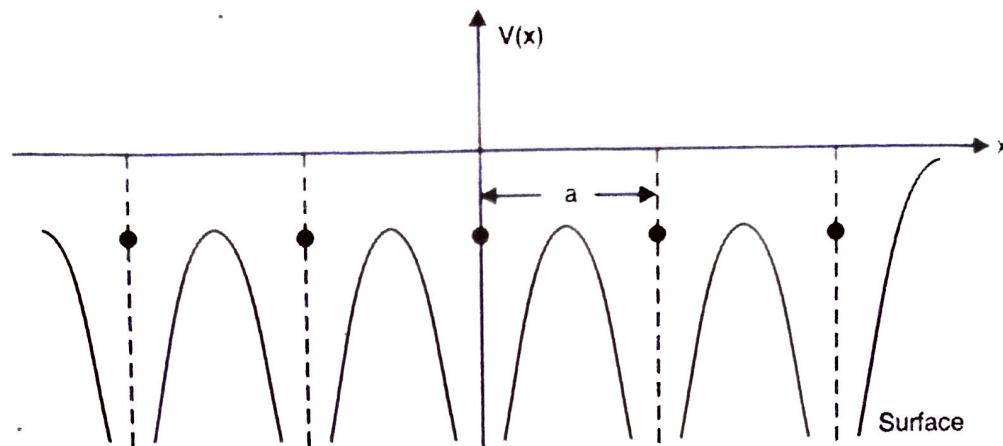


Fig. 7.8(f) 1-D representation of potential experienced by an electron in a perfectly preiodic crystal lattice with lattice parameter a .

7.4 BLOCH THEOREM

In the free electron theory, an electron moves in a constant potential V_0 and the Schrodinger equation for a one dimensional case is

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

The solution of this equation is plane waves of the type

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

where k represents the momentum of the e^- divided by \hbar . From above equation, we get the kinetic energy of the electron

$$E_{kin} = E - V_0 = \frac{\hbar^2 k^2}{2m} = \frac{p^2}{2m}$$

The complete solution for the wave function containing the time is obtained by multiplying $\psi(x)$ by e^{-iwt}

where $w = \frac{E}{\hbar}$

Now, consider the Schrodinger equation for an electron moving in a one dimension periodic potential. In this case, the potential energy of an electron satisfies the equation

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

where a is the period.

In this case, the Schrodinger equation is

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

With reference to the solutions of this equation, there is an important theorem which states that there exist solutions of the form

$$\psi(x) = e^{\pm ikx} u_k(x) \quad \dots(28)$$

where

$$u_k(x) = u_k(x + a)$$

Thus, the solutions are plane waves modulated by the function $u_k(x)$, which has the same periodicity as the lattice. This theorem is known as the Bloch Theorem or Floquet's Theorem. The functions defined

by above equation are known as Bloch functions and can be decomposed into sum of travelling waves. These functions can be assembled into localized wave packets to represent electrons that propagate freely through the potential fields of the ion cores.

7.5 ENERGY GAPS

Every solid contains electrons. The important question for electrical conductivity is how the electrons respond to an applied electric field. We shall see that electrons in crystals are arranged in energy bands separated by regions in energy for which no wavelike electron orbitals exist. Such forbidden regions are called energy gap or energy bands and result from the interaction of the conduction electron waves with the ion cores of the crystal.

The energy band calculations is very difficult task and is learned by experience. Several approaches (Tight Binding Approximation, Kronig-Penny model etc.) which partly compete and partly complement, have been used for the measurements of energy band calculations.

7.6 TIGHT BINDING APPROXIMATION: FORMATION OF ENERGY BONDS

Consider an isolated hydrogen atom. We know that the wave function of an electron in the atom in the ground state is

$$\psi(r) = \left(\frac{\pi}{a_0^3} \right)^{1/2} e^{-r/a_0} \quad \dots(29)$$

where a_0 is Bohr's radius corresponding to first orbital.

Now bring two such atoms closer and watch the changes in the atomic energy levels as the charge distributions of adjacent atoms overlap when the atoms are brought together to form a crystal. Here, we are considering two hydrogen atoms, each with an electron in the ground state. Let ψ_1 and ψ_2 be the electronic wave functions of the two atoms respectively, when these are infinite distance apart. As the atoms are brought together, the wavefunctions ψ_1 and ψ_2 overlap and the resultant wave function is either $\psi_1 + \psi_2$ or $\psi_1 - \psi_2$ [Fig. 7.9 (a)]. Each combination shows an electron with the two protons, but an electron in the state $\psi_1 + \psi_2$ will have a somewhat lower energy than in the state $\psi_1 - \psi_2$.

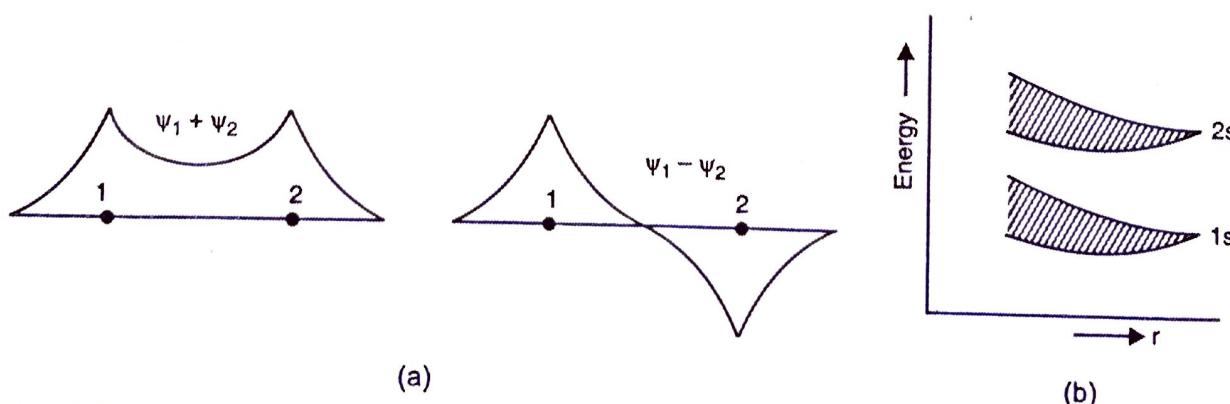


Fig. 7.9 (a) Resulting wavefunction of the electrons on two atoms at closer atoms : $\psi_1 + \psi_2$ representing ground state and $\psi_1 - \psi_2$ the excited state. (b) The band formation for 1s and 2s states.

In $\psi_1 + \psi_2$ combination, the electron spends part of the time in the region midway between the two protons and hence has finite probability. In this region, the binding energy increases because the electron experiences the force of both the nuclei. On the other hand, for the wave functions $\psi_1 - \psi_2$ the probability of finding an electron midway between two nuclei is zero. Thus the extra contribution of energy disappears.

Therefore, there is a difference in energy between the states $\psi_1 + \psi_2$ and $\psi_1 - \psi_2$. It means that when two isolated atoms are brought together, each energy state splits into the distinct energy states.

Now if N atoms are brought close to each other, each energy states will split into N number of energy states. If N is very large, then the separation between these energy states is very small and appears as a band [Fig. 7.9 (b)]. Thus, we conclude that energy state is considered to split into a band of energy levels. The width of a band depends on the strength of interaction between neighbouring atoms.

7.7 KRONIG-PENNY MODEL

In this model, it is assumed that the potential energy of an electron in a linear array of positive nuclei has the form of a periodic array of square wells (Fig. 7.10). Let the period of the periodic potential be $(x + b)$. For $-b < x < 0$ the potential energy is V_0 while for $0 < x < a$ the potential energy is zero. The Schrodinger equations for two cases are

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E\psi = 0 \text{ for } 0 < x < a \quad \dots(30)$$

and $\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} (E - V_0)\psi = 0 \text{ for } -b < x < 0 \quad \dots(31)$



If $V_0 > E$ and α, β are real quantities then eqns. (30) and (31) will become

$$\frac{d^2\psi}{dx^2} + \alpha^2\psi = 0 \text{ for } 0 < x < a \quad \dots(32)$$

and $\frac{d^2\psi}{dx^2} + \beta^2\psi = 0 \text{ for } -b < x < 0 \quad \dots(33)$

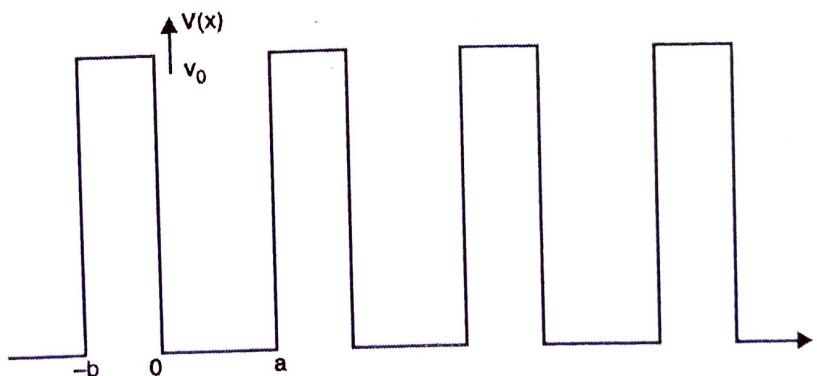
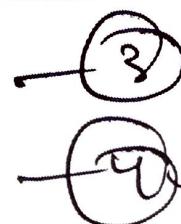


Fig. 7.10 1-D periodic potential for Kronig and Penny model.

where

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

The potential is periodic i.e.,

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

According to Bloch, the Solutions of the Schrodinger equations are of the form

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

where $u_k(x)$ is a periodic function with the periodicity of lattice i.e.,

$$u_k(x) = u_k(x + a + b)$$

Therefore, eqns. (30) and (31) can be written as

$$\frac{d^2 u}{dx^2} + 2ik \frac{du}{dx} + (\alpha^2 - k^2)u = 0, \quad -0 < x < 0 \quad \text{--- (5)}$$

and $\frac{d^2 u}{dx^2} + 2ik \frac{du}{dx} - (\beta^2 - k^2)u = 0, \quad -b < x < 0 \quad \text{--- (6)}$

The solutions of these equations are

$$u_1 = A e^{i(\alpha-k)x} + B e^{-i(\alpha+k)x}, \quad 0 < x < a \quad \dots(32) \quad \text{--- (7)}$$

and

$$u_2 = C e^{i(\beta-k)x} + D e^{-i(\beta+k)x}, \quad -b < x < 0 \quad \dots(33) \quad \text{--- (8)}$$

where A, B, C and D are constants.

These constants can be determined in such a way that the wave function ψ and its derivative $\frac{d\psi}{dx}$ are single valued and continuous.

i.e.,

$$u_1(0) = u_2(0), \quad u_1(a) = u_2(-b)$$

$$\left. \frac{du_1}{dx} \right|_{x=0} = \left. \frac{du_2}{dx} \right|_{x=0}$$

$$\left. \frac{du_1}{dx} \right|_{x=a} = \left. \frac{du_2}{dx} \right|_{x=-b}$$

Using these boundary conditions in eqns. (32) and (33) we get

$$A + B = C + D \quad \dots(34) \quad \text{--- (9)}$$

$$Ai(\alpha - k) - Bi(\alpha + k) = C(b - ik) - D(\beta + ik) \quad \dots(35) \quad \text{--- (10)}$$

$$Ae^{i(\alpha-k)a} + Be^{-i(\alpha+k)a} = Ce^{-(\beta-ik)\beta} + De^{(\beta+ik)\beta} \quad \dots(36) \quad \text{--- (11)}$$

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

$$= C(\beta - ik)e^{-(\beta-ik)b} - D(\beta + ik)e^{(\beta+ik)b} \quad \dots(37) \quad \text{--- (12)}$$

These equations have non-zero solutions if the determinant of the coefficients A, B, C and D vanishes. That is

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

On expanding this determinant and after simplification, we get

$$\frac{\beta^2 - \alpha^2}{2\alpha\beta} - \sinh \beta b \sin \alpha a + \cosh \beta b \cos \alpha a = \cos k(a+b) \quad \dots(38) \quad \text{--- (13)}$$

In order to express the relation in a more simplified form, Kronig and Penny suggested delta functions such that $V_0 \rightarrow \infty$ and $b \rightarrow 0$ but the product $V_0 b$ or $\beta_2 b$ remains finite. Within such limit, eqn. (38) reduces to

$$\frac{\beta^2 b}{2\alpha} \sin \alpha a + \cos \alpha a = \cos ka \quad \dots(39) \quad \text{--- (M)}$$

Because when $b \rightarrow 0$, $\sinh \beta b - \beta b$ and $\cosh \beta b \rightarrow 1$

Equation (39) can be written as

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

~~15~~

... (40)

Where the quantity P is defined as

$$P = \frac{\beta^2 ab}{2} = \frac{2mv_0 ab}{2h^2} = \frac{mv_0 ab}{h^2}$$

~~16~~

... (41)

Since $V_0 \rightarrow \infty$ i.e., P is a measure of the quantity $V_0 b$ which is the area of the potential barrier. When P is increased, the area of the potential barrier is increased and the given electron is bound more strongly to a particular potential well. When $P \rightarrow 0$, the potential barrier becomes very weak which means that electrons are free electrons. In this case, from eqn. (40), we get

$$\alpha a = ak$$

\Rightarrow

$$\alpha = k$$

Now

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

Hence

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

~~17~~

... (41)

If we plot a graph between $\cos ka$ and αa for $P = \frac{3\pi}{2}$, we get the curve as shown in Fig. 7.11. Since $\alpha = \sqrt{2m E / h^2}$, the abscissa αa is a measure of energy and by finding the value of αa at any point, the energy represented by the function at that point is calculated. The values of αa satisfying equation (40) are obtained by drawing a line parallel to αa -axis at a distance $\cos ka$ from it. If we change ka continuously from 0 to π i.e., $\cos ka = \pm 1$, we obtain all possible values of αa and hence that of energy. From Fig. 7.11 following conclusions are drawn:

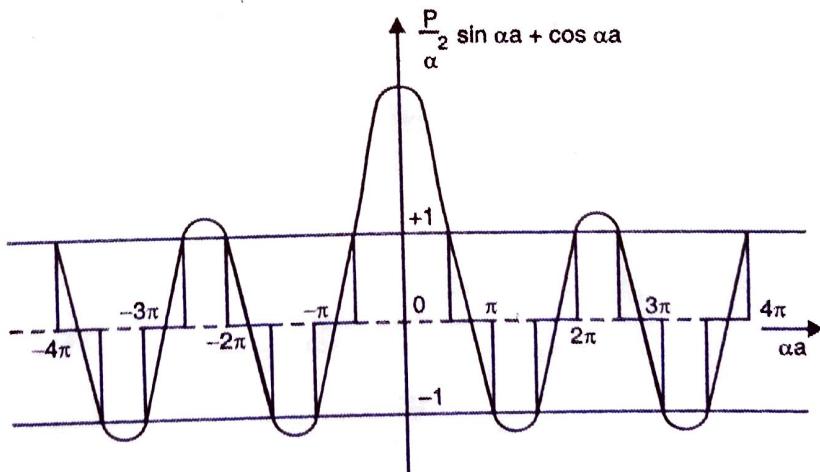


Fig. 7.11 Plot of $(P/\alpha a) \sin \alpha a + \cos \alpha a$ as a function of αa using $P = (3\pi/2)$. The solid and broken lines on the abscissa correspond to allowed and forbidden energy regions respectively.

1. The energy spectrum consists of an infinite number of allowed energy bands separated by intervals in which there are no energy levels. These are known as forbidden regions.
The boundaries of the allowed energy levels corresponding to the values of $\cos ka = \pm 1$

or

$$ka = n\pi$$

or

$$k = \frac{n\pi}{a}$$

2. As αa increases, the first term on L.H.S. of eqn. (40) decreases, so the width of allowed energy bands increases and hence forbidden regions become narrower.
3. The width of allowed band decreases with increasing value of P (i.e., with increasing the binding energy of electrons). When $P \rightarrow \infty$, the allowed energy bands are infinitely narrow and are independent of k .

We find eqn. (40) has solutions in this case only if

$$\sin \alpha a = 0$$

 \Rightarrow

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

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

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

$$E = \frac{n^2 \pi^2 h^2}{2ma^2} \quad \dots(42)$$

i.e., E is independent of k .

From eqn. (41) it is also possible to find the energy E as a function of wave number k . The graph between E and k is shown in Fig. 7.12.

The discontinuities in E vs k occur at

$$k = \frac{n\pi}{a}$$

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

The k values define boundaries of 1st, 2nd, ... Brillouin zones

From $k = \frac{\pi}{a}$ to $-\frac{\pi}{a}$, there exists the first Brillouin zone. The second zone consists of two parts, one from $+\frac{\pi}{a}$ to $+\frac{2\pi}{a}$ and second from $-\frac{\pi}{a}$ to $\frac{2\pi}{a}$. These zoned boundaries represent the maximum energies that the electron can have without any discontinuity.

A further boundaries conclusion may be drawn from equation (40). Within a given energy band, the energy is a periodic function of k . For example, if we replace k by $k + \frac{2\pi n}{a}$, where n is an integer, the R.H.S. of equation (40) remains the same. In other words,

k is not uniquely determined. Therefore, it is convenient to introduce the reduced wave vector which limits to the region

$$-\frac{\pi}{a} \leq k \leq \frac{\pi}{a}$$

The energy versus reduced wave vector is represented in Fig. 7.13.

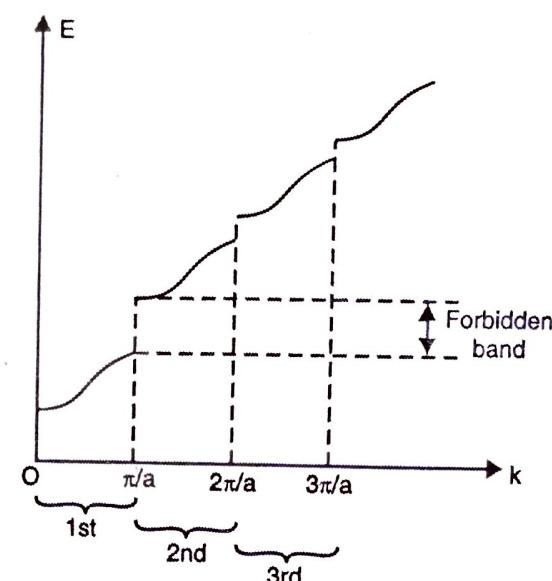


Fig. 7.12 Energy as a function of wavelength for extended zone scheme.

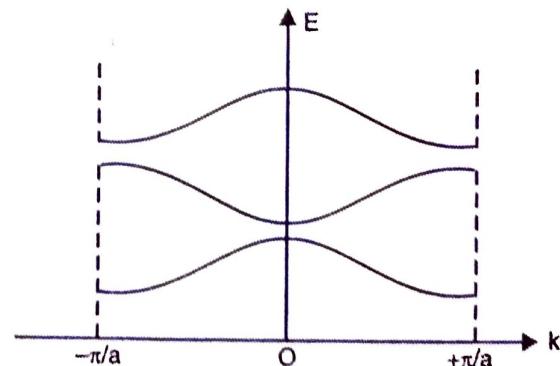


Fig. 7.13 E-k curve for reduced zone-scheme.

So far, we have assumed the crystal to be infinite, but now it will be necessary to investigate the consequences of imposing boundary condition. For a linear crystal of length L , the boundary condition may be taken as

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

Making use of Bloch functions

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

Because of the periodicity of u_k , we have $u_k(x+L) = u_k(x)$. The boundary conditions, thus require

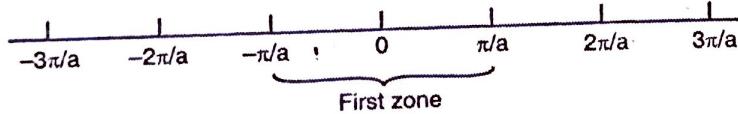
$$k = \frac{2\pi x}{L} \quad \dots(43)$$

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

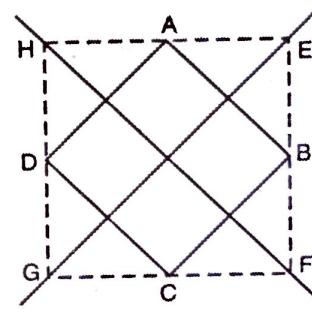
The number of possible wavefunctions (k -values) in the ring dk is therefore

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

Since $k = \frac{n\pi}{a}$, it follows that the maximum value of n in eqn. (43) is $\frac{L}{2a} = \frac{N}{2}$, where N is the number of unit cells. Hence we conclude that the total number of possible wave functions in any energy band is equal to the number of unit cells N .



(a)



(b)

Fig. 7.14 (a) The line segments representing 1-D Brillouin zones (b) Illustrating 2-D Brillouin zone.

7.7.1 Brillouin Zone

We have concluded in the Kronig-Penny model that the energy discontinuities in a monatomic one-dimensional lattice occur when $k = (n\pi/a)$, where n is any positive or negative integer. In one-dimensional monatomic lattice, a line representing the value of k is divided up by energy discontinuities into segments of length π/a as shown in Fig. 7.14(a). These line segments are known as Brillouin zones. The segment $-\pi/a \leq k \leq +\pi/a$ is the first Brillouin zone. The segments $-\frac{2\pi}{a} \leq k \leq -\frac{\pi}{a}$ and $\frac{\pi}{a} \leq k \leq \frac{2\pi}{a}$ form the

second Brillouin zone. Each crystal structure gives rise to its own characteristics Brillouin zones. The first zone for two dimensional square lattice will be a square ABCD, the boundaries of which will be given by the relations.

$$k_x = \pm \pi/a ; k_y = \pm \pi/a$$

The boundaries of the zone are given by

$$\pm k_x = \pm k_y = 2\pi/a$$

This zone is represented by $EFGH$ as shown in Fig. 7.14(b). Note that the right half of the second Brillouin zone is similar to the left region of the first zone. Similarly, the regions of third and higher zones match with those of the first zone.

7.8 MOTION OF ELECTRONS

According to de-Broglie, the motion of an electron with a velocity v is equivalent to the motion of a wave packet with group velocity v_g .

Thus

$$v = v_g = \frac{dw}{dk}$$

Now

$$E = h\nu = 2\pi\hbar \cdot \frac{v}{2\pi} = \hbar\omega \quad (\because \omega = 2\pi\nu)$$

or

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

\therefore

$$v = \frac{1}{\hbar} \frac{dE}{dk} \quad \dots(44)$$

But

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

or

$$\frac{dE}{dk} = \frac{\hbar^2 k}{m}$$

\therefore

$$v = \frac{1}{\hbar} \frac{\hbar^2 k}{m} = \frac{\hbar k}{m} = \frac{p}{m} \quad \dots(45)$$

The velocity of free electrons is proportional to k .

Now on the basis of band theory, the variation of E with k is shown in Fig. 7.15(a). Since the curve is symmetrical having points of inflexion at M and N , the value of slope $\frac{dE}{dk}$ is different for different portions of the curve. As the curve is horizontal at A , O and B , therefore, for these regions $\frac{dE}{dk} = 0$. The variation of v with k is shown in Fig. 7.15 (b). The absolute value of velocity becomes maximum at $k = k_0$, where k_0 corresponds to the point of inflection in the $E-k$ diagram. Beyond this point, the velocity decreases with the increasing energy which is different in behaviour from that of free electrons.

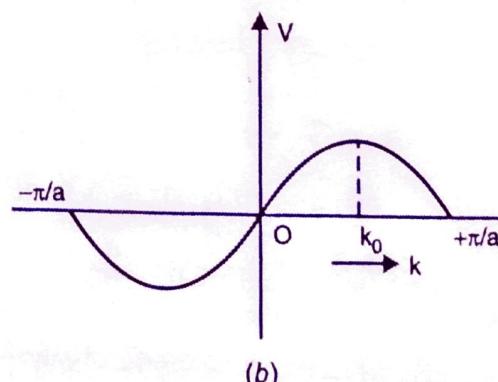
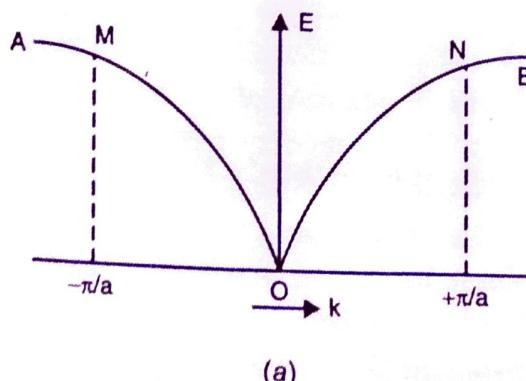


Fig. 7.15 Variation of energy, velocity with wave vector k . The dashed lines correspond to inflection points in the E - k curve.

7.8.1 Effective Mass

Let us now consider the motion of an electron in a crystal in the presence of an external applied field. According to quantum theory, the velocity of the electron v is equal to the group velocity of the wave packet representing the electron.

Let ϵ = external applied electric field, then the gain in the energy of the electron in time dt is

$$dE = -e\epsilon v dt \quad \dots(46)$$

where e is the charge on the electron.

Using eqns. (44) and (46) can be written as

$$dE = -\frac{e\epsilon}{\hbar} \frac{dE}{dk} dt$$

Now

$$dE = \frac{dE}{dk} \cdot dk$$

\therefore

$$\frac{dE}{dk} \cdot dk = -\frac{e\epsilon}{\hbar} \frac{dE}{dk} dt$$

\Rightarrow

$$\frac{dk}{dt} = -\frac{e\epsilon}{\hbar}$$

or

$$\hbar \frac{dk}{dt} = -e\epsilon$$

or

$$\frac{d(\hbar k)}{dt} = -e\epsilon \quad \dots(47)$$

Equation (47) shows that time rate of change of crystal momentum is equal to the impressed force $-e\epsilon$. The acceleration of the electron is

$$\begin{aligned} a &= \frac{dv}{dt} = \frac{d}{dt} \left(\frac{1}{\hbar} \frac{dE}{dt} \right) \\ &= \frac{1}{\hbar} \frac{d^2 E}{dk^2} \frac{dk}{dt} \end{aligned} \quad \dots(48)$$

Substituting the value of $\frac{dk}{dt}$ from eqn. (47), we get

$$a = -\frac{e\epsilon}{\hbar} \frac{1}{\hbar} \frac{d^2 E}{dk^2} = -\frac{e\epsilon}{\hbar} \frac{d^2 E}{dk^2} \quad \dots(49)$$

For free electron, we have

$$a = -\frac{e\epsilon}{m} \quad \dots(50)$$

Equations (49) and (50) suggest that on the basis of band theory, the electron behaves as if it had an effective mass m^* equal to $\hbar^2 / d^2 E / dk^2$.

Thus, effective mass of an electron is

$$m^* = \hbar^2 / \frac{d^2 E}{dk^2} \quad \dots(51)$$

Equation (51) shows that effective mass is determined by $\frac{d^2E}{dk^2}$. Since for the lower positions of $E-k$ curve, $\frac{d^2E}{dk^2}$ is +ve, so m^* is +ve and for upper position $\frac{d^2E}{dk^2}$ is -ve, so m^* is -ve. At the points of inflexion, $\frac{d^2E}{dk^2} = 0$, so at these points m^* becomes infinite. Physically speaking an electron behaves as a particle with +ve charge in the upper half of the band. The variation of m^* with k is shown in Fig. 7.15(c).

Sometimes, it is convenient to introduce a factor

$$f_k = \frac{m}{m^*} = \frac{m}{\hbar^2} \frac{d^2E}{dk^2} \quad \dots(52)$$

which determines the extent upto which the electron in a k -state is a free electron. If f_k is small, i.e., m^* is large, the particle behaves as a heavy particle or we can say that the wavefunctions centred on neighbouring atoms overlap very little, then the overlap integral will be small and as a result the width of the band will be narrow. Here the overlap integral determines the rate of quantum tunneling of an electron from one ion to another and in case of large effective mass, the electron tunnels very slowly from one ion to an adjacent ion in the lattice, e.g., 4f electrons of the rare-earth metals.

7.9 DISTINCTION BETWEEN METALS, INSULATORS AND SEMICONDUCTORS ON THE BASIS OF BAND THEORY

We will make the distinction between metals, insulator and semiconductor on the basis of band theory. For this, let us consider an energy band which is supposed to be filled with electrons upto a certain value k , as shown in Fig. 7.16. As far as the influence of an external electric field is concerned, we would like to know that with how many free electrons the N electrons in the band are equivalent? By knowing the answer to this question, it would be possible to draw conclusions regarding conductivity associated with this band. The effective number of free electrons in the band is given by

$$N_{eff} = \sum f_k \quad \dots(53)$$

where the summation extends over all occupied states in the band.

The number of states in the range dk for a one-dimensional lattice of length L is given by

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

Since two electrons occupy each of the state, therefore, the effective number of free electrons in the shaded region of Fig. 7.16 is given by

$$N_{eff} = 2 \int_{-k_1}^{+k_1} f_k \left(\frac{L}{2\pi} \right) dk = \frac{2L}{2\pi} \int_{-k_1}^{+k_1} f_k dk \quad \dots(54)$$

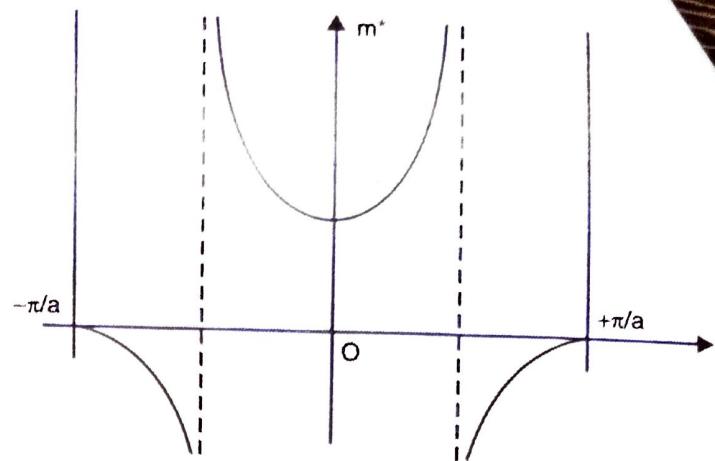


Fig. 7.15 (c) Variation of effective mass with wave vector k .

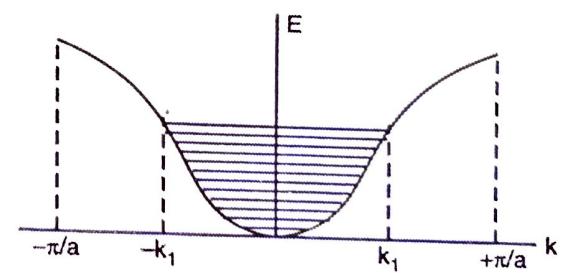


Fig. 7.16 Energy band filled up to the state k_1 .

Using the value of f_k from eqn. (52), we have

$$\begin{aligned} N_{\text{eff}} &= 2 \frac{2L}{2\pi} \int_0^{k_1} \frac{m}{\hbar^2} \frac{d^2E}{dk^2} dk = \left(\frac{2Lm}{\pi\hbar^2} \right) \int_0^{k_1} \left(\frac{d^2E}{dk^2} \right) dk \\ &= \frac{2Lm}{\pi\hbar^2} \left| \frac{dE}{dk} \right|_{k=k_1} \end{aligned} \quad \dots(55)$$

From above equation we conclude that:

- (i) The effective number of free electrons N_{eff} in a completely filled band vanishes, because $(dE/dk) = 0$ at the top of the band.
- (ii) The effective number of electrons reaches to a maximum value corresponding to the point of inflexion, where dE/dk is maximum.

From above two points, it follows that a solid for which a certain number of energy bands are completely filled, the other bands are completely empty, is an insulator. On the other hand, a solid having an energy band which is incompletely filled has metallic character. The clear picture only exists at absolute zero, when the crystal is in the lowest energy state. At temperature higher than zero, some electrons from the upper filled band will be excited into next empty band and the conduction becomes possible. If the forbidden energy gap is of the order of several electron volts, then the solid remains an insulator. For example, for diamond energy gap = 7 eV, so is insulator. For a small energy gap, say 1 eV, the number of thermally excited electrons are appreciable and the solid having such gap is called intrinsic semiconductor e.g., Ge, Si. In fact, all intrinsic semiconductors are insulators at $T=0$, whereas all insulators may be considered semiconductor at $T > 0$. It may be noted that the conductivity of the semiconductor increases with temperature, while that of the metal decreases with increase in temperature (e.g., Hg).

7.10 CLASSICAL PICTURE OF ENERGY BANDS IN SOLIDS

For the transition of an electron from the inner orbit to the outer orbit of the atom, some energy is required. Thus, the different orbits have the different levels of potential energy. In an atom, the electrons try to occupy the inner orbit (having minimum energy) but according to Pauli's exclusion principle not more than two electron can exist in the one energy state. The electrons start occupying the energy states having low energy. Therefore, in normal atom, the lower energy levels are completely filled, while the higher energy levels remain unoccupied.

When two similar atoms are brought close together, then there is an interaction between the orbits of their electrons. This interaction causes a splitting of each individual energy levels into two slightly different levels. The atoms in almost every crystalline solids are so close together that the energy levels produced after splitting due to interaction between the various orbits of different electrons will be very large and so close together as to form a band. If the energy band contains the number of electrons equal to the number of electrons allowed by Pauli exclusion principle, then the band is said to

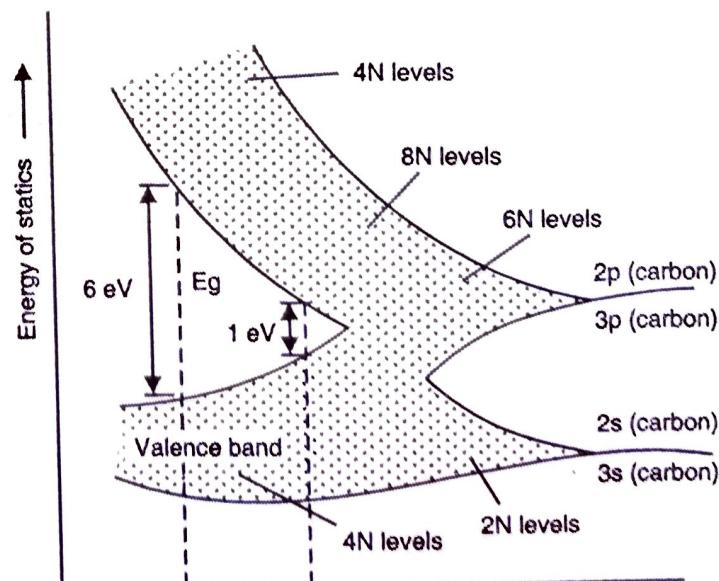


Fig. 7.17 Energy band as a function of interatomic spacing for diamond. The 2s and 2p levels of carbon atoms spread into bands that first overlap with decreasing atomic separation and then split into diverging bands. The lower band is occupied by valence electrons and the upper conduction band is empty.

be completely filled. In a completely filled band, there is no free electron for the conduction of current. On the other hand, the conduction is possible in a partially filled band. The energy band as a function of inter-atomic spacing is shown in Fig. 7.17.

In a solid, many atoms are brought together, so that the split energy levels form essentially continuous bands of energies. As an example, Fig. 7.17 illustrates the imaginary formation of a diamond crystal from isolated carbon atoms. Each isolated carbon atom has an electronic structure $1s^2 2s^2 2p^2$ in the ground state. Each atom has available two $1s$ states, two $2s$ states, six $2p$ states and higher states. If we consider, N atoms, there will be $2N$, $2N$ and $6N$ states of type $1s$, $2s$ and $2p$ respectively. As the interatomic spacing decreases, their energy level split into bands, beginning with the outer shell, i.e., $n = 2$. As the $2s$ and $2p$ bands grow, they merge into a single band composed of a mixture of energy levels. This band of $2s-2p$ levels contains $8N$ available states. As the distance between atoms approaches the equilibrium interatomic spacing of the diamond, this band splits into two bands separated by an energy gap E_g . The upper band (conduction band) contains $4N$ states, as does the lower band (valence band). Thus, apart from the low lying and tightly bound $1s$ levels, the diamond crystal has two bands of available energy levels separated by an energy gap E_g wide which contains no allowed energy levels for electrons to occupy.

The lower $1s$ band is filled with the $2N$ electrons which originally resided in the collective $1s$ states of the isolated atoms. However, there were $4N$ electrons in the original isolated ($n = 2$) shell ($2N$ in $2s$ and $2N$ in $2p$ states). These $4N$ electrons must occupy states in the valence band or the conduction band in the crystal. At 0 K the electrons will occupy the lowest energy states available to them. In the case of diamond crystal, there are exactly $4N$ states in the valence band available to the $4N$ electrons. Thus at 0 K , every state in the valence band will be filled, while the conduction band will be completely empty of electrons.

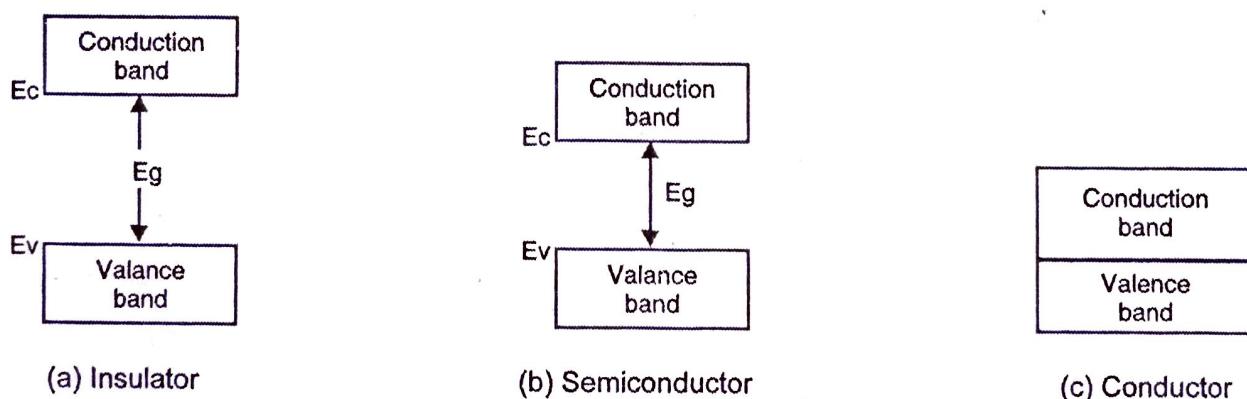


Fig. 7.18 Energy band diagram for insulator, semiconductor and conductor.

In an insulator and pure semiconductor, lower band is completely filled and the upper band is completely empty. The energy of the forbidden gap is denoted by E_g . The conduction takes place only when the electron in valence band jumps to the conduction band. In other words, the electron in valence band requires energy equal to E_g to jump to the conduction band. When the electron jumps from the valence band to the conduction band, then a vacancy electron called a hole is created in the valence band. Since hole is a deficiency of an electron and hence is positively charged.

The forbidden energy gap in an insulator is of the order of 5 to 10 eV. The amount of energy cannot be imparted to the electrons in the valence band and hence the electron cannot jump from the valence to conduction band. Therefore, conduction is not possible in the insulators.

The forbidden energy gap in case of semiconductor is usually, of the order of 0.75 to 1 eV. This amount of energy can be easily imparted to the electrons in the valence band by thermal agitation of the crystal lattice. Thus, with the increase in temperature, many electrons from the valence band acquire the required amount of energy to jump to the conduction band and this results in the increase of electron

hole pairs. The forbidden energy gap E_g is the energy required to break the covalent bands so as to make the electron free for conduction.

7.11 DIRECT AND INDIRECT BAND GAP

In a typical energy band calculations, a single electron is assumed to travel through a perfectly periodic lattice as pointed out earlier. The wave function of the electron is assumed to be in the form of a plane wave, e.g., moving in the x -direction with propagation constant K , so called a wave vector. The space-dependent wave function for the electron is

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

where the function $V_k(x)$ modulates the wave function according to the periodicity of the lattice. In such calculation, allowed values of energy can be plotted versus the propagation constant K . Since the periodicity of most lattices is different in various directions, the $E-K$ diagram must be plotted for the various crystal directions, and the full relationship between E and K is a complex surface which should be visualized in three-dimensions.

The band structure of GaAs has a minimum in the conduction band and a maximum in the valance band for the same K value ($K = 0$). On the other hand, Si has its valence band maximum at a different value of K than its conduction band minimum. Thus an electron making a smallest energy transition from the conduction band to the valence band in GaAs can do so without a change in K value; on the other hand, a transition from the minimum point in the Si conduction band to the maximum point of the valence band requires some change in K . Thus there are two classes of semiconductor energy bands; direct and indirect (Fig. 7.19). In case of an n indirect transition, a change in K requires a change in momentum for the electron. In a direct semiconductor, an electron in the conduction band can fall to an empty state in the valence band, giving off the energy difference E_g as a photon of light. On the other hand, an electron in the conduction band minimum of an indirect semiconductor cannot fall directly to the valence band minimum but must undergo a momentum change as well as change in its energy. For example, it may go through some defect state

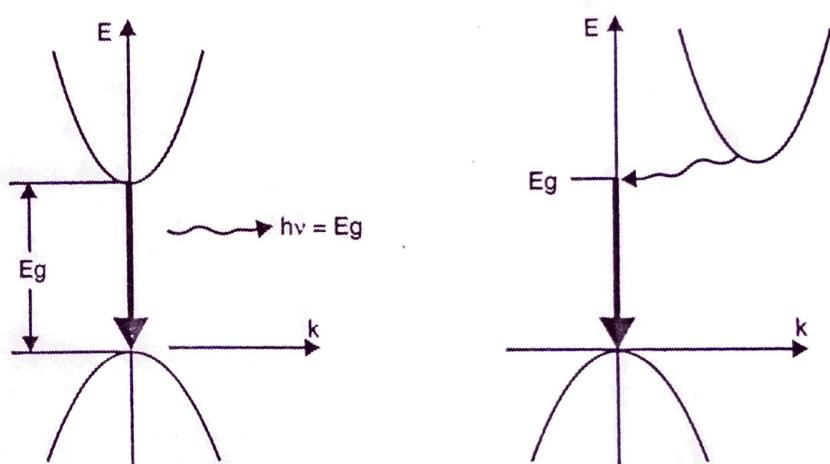


Fig. 7.19 (a) Direct band gap accompanying photon emission.

In case of an n indirect transition, a change in K requires a change in momentum for the electron. In a direct semiconductor, an electron in the conduction band can fall to an empty state in the valence band, giving off the energy difference E_g as a photon of light. On the other hand, an electron in the conduction band minimum of an indirect semiconductor cannot fall directly to the valence band minimum but must undergo a momentum change as well as change in its energy. For example, it may go through some defect state

Table 7.1 Direct and Indirect Semiconductor at 300 K

Semiconductor	Type	E_g (eV)	Applications
Si	Indirect	1.11	Diodes, transistors, ICs etc.
Ge	Indirect	0.67	Diodes, transistors
GaAs	Direct	1.43	High frequency transistor, Lasers
InAs	Direct	0.36	Optical devices, LED
ZnSe	Direct	2.7	Optical devices, LED
PbTe	Indirect	0.29	Infrared detectors

E_f within the band gap. In an indirect transition which involves a change in K , the energy is generally given up as heat to the lattice rather than as an emitted photon. This difference between direct and indirect band structures is very important for deciding which semiconductors can be used in devices requiring light output, e.g., semiconductor light emitters and laser generally must be made of materials capable of direct band-to-band transition or of indirect materials with vertical transitions between defect states.

7.12 THERMAL CONDUCTIVITY OF METALS

We know that in a solid, atoms vibrate about their equilibrium position at ordinary temperature and the amplitude of vibration decreases to a minimum at absolute zero of temperature. These vibrations of atoms bring about elastic distortion in the lattice and therefore the waves associated with the vibrations are the elastic waves of varying frequencies. The waves superimpose to form a wave packet that moves through the solid. The quantum of elastic energy is known as phonon, whose energy is given by $E = h\nu$; ν being frequency of vibration. The increasing number of vibration of atoms with temperature are represented by increasing number of phonon passing through the crystal. It is the phonons together with valence electrons which are responsible for the transfer of thermal energy from high temperature region to low temperature region. The property that characterizes the ability of a material to transfer thermal energy (or hence the heat) is known as thermal conductivity. The thermal conductivity of a solid is proportional to its specific heat and to the mean free path of phonons and electrons. The mean free path of electrons is very large in comparison to the mean free path of phonons (10 to 100 Å), as a result, the electrons undergo less number of collisions. Since in metals the free electrons are sufficiently mobile, metals have shown high thermal conductivity due to the mobility of electrons and phonons as well. On the other hand, in insulators, phonons are the only particles to conduct heat, as the valence electrons are not present (ionic solids or covalent solids). In case of alloys, electrons remain scattered due to the presence of impurity elements, the thermal conductivity of alloys is reduced.

Conclusions. It has been observed that:

- (i) The thermal conductivity of metals decreases at higher temperatures.
- (ii) The thermal conductivity of polycrystalline metals is lower than that of single crystal due to scattering of electrons and phonons along grain boundaries.
- (iii) The thermal conductivity of metals is lower than their alloys due to scattering of electrons and phonons with the atoms of alloying element.
- (iv) The thermal conductivity of semiconducting materials increases with increasing temperature due to flow of excited electrons.
- (v) The thermal conductivity of metals, alloys, semiconductors and dielectrics are in the descending order.

7.12.1 Wiedemann Franz Lorentz Relation

Suppose a homogeneous isotropic material is subjected to a temperature gradient $\frac{dT}{dx}$. The flow of heat will result in the direction opposite to the temperature gradient through the conducting medium. The heat flux Q (heat flow per unit time per unit area) will be proportional to the temperature gradient i.e., $Q \propto \frac{dT}{dx}$

or

$$Q = -K \frac{dT}{dx}$$

where K is the proportionality constant and is known as coefficient of thermal conductivity. If Q is expressed in W/m^2 and $\frac{dT}{dx}$ in $^\circ\text{K/m}$, the units of K will be W/mK .

As discussed earlier, the transformation of heat in solids is due to phonons and free electrons. Hence, the coefficient of thermal conductivity K can be written as

$$K = K_{\text{phonon}} + K_{\text{electron}}$$

In order to derive the expression for K , let us consider the heat flow from high temperature to low temperature in a metal slab having temperature gradient $\frac{dT}{dx}$.

Let C_v be the heat capacity, the heat transfer per unit area per second will be

$$Q = \frac{mnv}{3} C_v \frac{\lambda dT}{dx}$$

where v is the velocity of electrons and λ being mean free path of collisions.

$$\text{Also, heat flux } Q = K \frac{dT}{dx}$$

$$\therefore K \frac{dT}{dx} = \frac{mnv}{3} C_v \lambda \frac{dT}{dx}$$

$$\Rightarrow K = \frac{mnv}{3} C_v \lambda$$

The energy of free electron is given by

$$mC_v T = \frac{3}{2} K_B T,$$

K_B is Boltzmann constant

$$\therefore \text{Thermal conductivity } K = \frac{3}{2} K_B \cdot \frac{nv}{3} \cdot \lambda$$

$$\text{or } K = K_B \left(\frac{nv\lambda}{2} \right)$$

Specific heat at constant volume for an ideal gas is

$$C_v = \frac{3}{2} n K_B$$

$$\therefore K = \frac{1}{3} C_v \lambda v$$

Above expression implies that the thermal conductivity of solids depends upon (i) specific heat, (ii) mean free path of collisions (iii) velocity of electrons.

Now consider the electrical conductivity σ .

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

and relaxation time (collision time) τ

$$\tau = \frac{\lambda}{v_d}$$

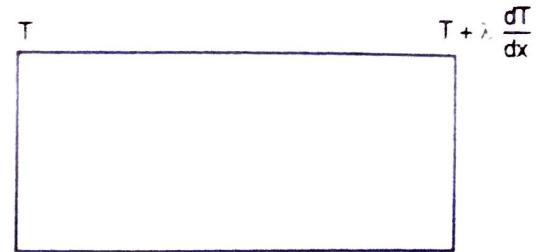


Fig. 7.20.

Also

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

$$\sigma = \frac{ne^2\lambda}{mv_d} = \frac{ne^2\lambda v_d}{3K_B T}$$

Therefore, the ratio of thermal conductivity K to electrical conductivity σ is

$$\frac{K}{\sigma} = \frac{K_B n v \lambda}{2} \times \frac{3K_B T}{ne^2 \lambda v_d}$$

$$= \frac{3}{2} \frac{K_B^2}{e^2} \cdot T,$$

if we assume $v = v_d$

or

$$\begin{aligned}\frac{K}{\sigma T} &= 5.838 \times 10^{-9} \Omega \text{ cal}/{}^\circ\text{K-sec} \\ &= 2.44 \times 10^{-8} \Omega \text{ W}/{}^\circ\text{K}^2\end{aligned}$$

which indicates that the ratio $\frac{K}{\sigma}$ is some for all metals and is a function of temperature only. This empirical law is known as Weidemann-Franz Lorentz relation. Hence, we can say that best electrical conductor will be a best thermal conductor.

SOLVED NUMERICAL PROBLEMS

PROBLEM 1. The Fermi energy for lithium is 4.72 eV at $T = 0$ K. Calculate the number of conduction electrons per unit volume in lithium. Given mass of electron 9.11×10^{-31} kg and Planck's constant $= 6.63 \times 10^{-34}$ JS.

Solution: We know that the Fermi energy is given by

$$E_f = \frac{h^2}{8m} \left(\frac{3n}{\pi} \right)^{2/3}$$

where m is mass of electrons, n is the number of electrons per unit volume.

Above relation can also be written as

$$\begin{aligned}n &= \frac{\pi}{3} \left(\frac{8m E_f}{h^2} \right)^{3/2} = \frac{\pi}{3} \left(\frac{8 \times 9.1 \times 10^{-31} \times 4.72 \times 1.6 \times 10^{-19}}{(6.63 \times 10^{-34})^2} \right)^{3/2} \\ &= 2.5 \times 10^{28} \text{ electrons/m}^3.\end{aligned}$$

PROBLEM 2. Calculate the temperature at which there is 1% probability that a state, with an energy 2 eV is occupied. Given Fermi energy $E_f = 1.5$ eV.

Solution: We know that the probability of a state corresponding to energy E occupied by an electron at temperature TK is

$$F(E) = \frac{1}{e^{(E - E_f)/K_B T} + 1}$$

Given

$$E = 2 \text{ eV}, E_f = 1.5 \text{ eV} \text{ and } F(E) = 1\% = \frac{1}{100}$$

$$\therefore \frac{1}{100} = \frac{1}{e^{0.5/K_B T} + 1} = \frac{1}{e^y + 1} \text{ where } y = \frac{0.5}{K_B T}$$

$$\Rightarrow e^y = \frac{0.99}{0.01} = 99$$

Taking log on both sides

$$y = 2.303 \log 99$$

$$\text{or } \frac{0.5}{K_B T} = 2.303 \log 99$$

$$\text{or } T = \frac{0.5 \times 1.6 \times 10^{-19}}{2.303 \log 99 \times 1.38 \times 10^{-23}} = 1264 \text{ K}$$

PROBLEM 3. There are about 5.9×10^{28} conduction electrons/m³ in silver. Calculate the Fermi energy.

Solution: We know that the Fermi energy E_f is given by

$$E_f = \frac{h^2}{8m} \left(\frac{3n}{\pi} \right)^{2/3}$$

Given

$$n = 5.9 \times 10^{28}$$

Also

$$h = 6.63 \times 10^{-34} \text{ J.sec}, m = 9.1 \times 10^{-31} \text{ kg}$$

$$\begin{aligned} \therefore E_f &= \frac{(6.63 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31}} \left(\frac{3 \times 5.9 \times 10^{28}}{\pi} \right)^{2/3} \\ &= 8.8 \times 10^{-19} \text{ J} = \frac{8.8 \times 10^{-19}}{1.6 \times 10^{-19}} \text{ eV} = 5.4 \text{ V.} \end{aligned}$$

PROBLEM 4. Calculate the Fermi velocity of electrons in potassium if its Fermi energy is 2.1 eV. Also calculate number of electrons per unit volume.

Solution: We know that

$$E_f = \frac{h^2}{8m} \left(\frac{3n}{\pi} \right)^{2/3} = 3.65 \times 10^{-19} n^{2/3} \text{ eV}$$

or

$$n^{2/3} = \frac{E_f}{3.65 \times 10^{-19}}$$

Given

$$E_f = 2.1 \text{ eV}$$

$$\therefore n^{2/3} = \frac{2.1}{3.65 \times 10^{-19}}$$

or

$$n = 1.38 \times 10^{28}/\text{m}^3$$

Also

$$\frac{1}{2} m V_f^2 = E_f$$

or

$$V_f = \sqrt{\frac{2E_f}{m}}$$

$$V_f = \sqrt{\frac{2 \times 2.1 \times 1.6 \times 10^{-19}}{9.1 \times 10^{-31}}}$$

$$(\because 1 \text{ eV} = 1.6 \times 10^{-19} \text{ J})$$

PROBLEM 5. At what temperature we can expect a 10% probability the electrons in silver have an energy which is 1% above the Fermi energy. Given Fermi energy = 5.5 eV.

Solution: According to the given problem

$$E = E_f + 1\% E_f$$

or

$$E - E_f = 1\% E_f = \frac{5.5}{100} = 0.055 \text{ eV}$$

Also

$$F(E) = \frac{1}{e^{(E-E_f)/K_B T} + 1} = \frac{1}{e^x + 1} \quad \left(\because x = \frac{E - E_f}{K_B T} \right)$$

Also given $F(E) = 10\%$

$$\therefore \frac{10}{100} = \frac{1}{e^x + 1}$$

or

$$x = 2.197$$

or

$$\frac{E - E_f}{K_B T} = 2.197$$

or

$$T = \frac{E - E_f}{2.197 \times K_B} = \frac{0.055 \times 1.6 \times 10^{-19}}{2.197 \times 1.38 \times 10^{-23}} = 290 \text{ K}$$

PROBLEM 6. What is the occupation number at room temperature of an electron state lying (a) 0.1 eV above the Fermi level and (b) 0.1 eV below the Fermi level ?

Solution: At room temperature of 300 K, $K_B T = 0.025 \text{ eV}$.

We know that the occupation number is given by

$$F(E) = \frac{1}{e^{(E-E_f)/K_B T} + 1}$$

(a) Given

$$E = (E_f + 0.1) \text{ eV} \text{ or } E - E_f = 0.1 \text{ eV}$$

$$\therefore F(E) = \frac{1}{e^{0.1/0.025} + 1} = 0.018$$

(b) Given

$$E = (E_f - 0.1) \text{ eV} \text{ or } E - E_f = -0.1 \text{ eV}$$

$$\therefore F(E) = \frac{1}{e^{-0.1/0.025} + 1} = 0.98.$$

PROBLEM 7. The carrier concentration in a material of conductivity $0.018/\text{ohm m}$ is 10^{19} electrons/m³. A voltage of 0.16 volts is applied across the 0.29 mm thick material. Determine the drift velocity of the carriers. Take standard values of mass of electron and electronic charge.

Solution: The given data and the standard values for electron are

$$\begin{aligned} n &= 10^{19} \text{ electrons/m}^3, & e &= 1.602 \times 10^{-19} \text{ C}, \\ \sigma &= 0.018/\text{ohm m}, & m &= 9.1 \times 10^{-31} \text{ kg}, \\ V &= 0.16 \text{ volt, and} & t &= 0.29 \text{ mm} \end{aligned}$$

where V is voltage and t is thickness of the material. As the electric field gradient τ is equal to voltage per unit thickness, therefore

$$\tau = \frac{V}{t} = \frac{0.16}{0.29 \times 10^{-3}} = 551.72 \text{ V/m}$$

We know that

$$\frac{v_d}{E} = \frac{e\tau}{m}$$

Also

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

∴

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

Therefore,

$$v_d = 6.19 \text{ m/sec.}$$

PROBLEM 8. The Fermi energy of sodium is 3 eV. Calculate the difference in energy between the neighbouring levels at the highest energy state in a cubical box of side 1 cm.

Solution: We know that

$$E = E_F = \left(\frac{h^2}{8ma^2} \right) (n_x^2 + n_y^2 + n_z^2)$$

If we assume $n_x = n_y = n_z$, then

$$E_F = \left(\frac{h^2}{8ma^2} \right) 3n_x^2$$

Given

$$E_F = 3 \text{ eV} = 3 \times 1.6 \times 10^{-19} \text{ J}, a = 10^{-2} \text{ m}$$

$$\therefore 3 \times 1.6 \times 10^{-19} = \left[\frac{(6.62 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31} \times (10^{-2})^2} \right] 3n_x^2$$

$$\Rightarrow n_x = 1.63 \times 10^7$$

Now the energy level just below this level is obtained using the quantum numbers $(n_x - 1)$, n_x and n_x . Let this energy is E_1 .

$$\therefore E_1 = \frac{h^2}{8ma^2} [(n_x - 1)^2 + n_x^2 + n_x^2] = \frac{h^2}{8ma^2} [3n_x^2 - 2n_x + 1]$$

or

$$E_1 = \frac{h^2}{8ma^2} [3n_x^2 - 2n_x] \text{ if } n_x \gg 1$$

Now

$$E - E_1 = \frac{h^2}{8ma^2} [3n_x^2 - (3n_x^2 - 2n_x)] = \frac{h^2}{8ma^2} [2n_x]$$

$$\begin{aligned}
 &= \frac{(6.62 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31} \times (10^{-2})^2} [2 \times 1.63 \times 10^7] \\
 &= 1.962 \times 10^{-26} \text{ J} = 1.2 \times 10^{-7} \text{ eV}
 \end{aligned}$$

PROBLEM 9. Calculations of Fermi energy for some monovalent elements yield of following results :

Metals	Cu	Li	Rb	Cs	Ag	K
EF (eV)	7.04	4.72	1.82	1.53	5.51	2.12

If the Fermi velocity of the electron in one of the metals of the above series is $0.73 \times 10^6 \text{ m/sec}$, identify the metal. Also compute the Fermi temperature.

Solution:

$$\text{K.E.} = \frac{1}{2}mV_F^2 = E_F$$

i.e.,

$$\begin{aligned}
 E_F &= \frac{1}{2}mV_F^2 = \frac{1}{2} \times (9.1 \times 10^{-31}) (0.73 \times 10^6)^2 \\
 &= 2.42 \times 10^{-19} \text{ Joules} \\
 &= \frac{2.42 \times 10^{-19}}{1.6 \times 10^{-19}} = 1.51 \text{ eV}
 \end{aligned}$$

The element is *Caesium*.

Fermi temperature is calculated as:

$$K_B T_F = E_F$$

$$T_F = \frac{E_F}{K_B} = \frac{2.42 \times 10^{-19}}{1.38 \times 10^{-23}}$$

$$T_F = 1.75 \times 10^4 \text{ K.}$$

PROBLEM 10. Calculate the thermal conductivity for a metal assuming

$$\tau = 3.0 \times 10^{-14} \text{ sec.}, T = 300 \text{ K and}$$

$$n = 2.5 \times 10^{22} \text{ electrons per cm}^3$$

Solution:

$$\begin{aligned}
 \sigma &= \frac{ne^2\tau}{m} \\
 &= \frac{2.5 \times 10^{22} \times (1.6 \times 10^{-19})^2 \times 3.0 \times 10^{-14}}{9.1 \times 10^{-31}} \\
 &= 21.09 \times 10^6 \quad [1 \text{ cm}^3 = 10^{-6} \text{ m}^3]
 \end{aligned}$$

$$\frac{K}{\sigma T} = 2.44 \times 10^{-8} \Omega \cdot \text{W/K}^2$$

$$\begin{aligned}
 K &= \sigma T \times 2.44 \times 10^{-8} \Omega \cdot \text{W/K}^2 \\
 &= 21.09 \times 300 \times 2.44 \times 10^{-8} \times 10^6 \text{ W/m-K} \\
 &= 154.37 \text{ W/m-K.}
 \end{aligned}$$

CONCEPTUAL QUESTIONS AND ANSWERS

Q.1. What is free electron theory?

Ans. The first reasonable approach to an explanation of electrical conduction in solids was proposed by Drude. Drude imagined conductive metal in the form of a gas of free electrons. An applied electric field accelerates the electrons along the field, because the ions they encounter in the crystal lattice deflect them and they interpose resistance, the electrons settle into a constant drift velocity that is proportional to the strength of the applied electric field. Drude assumed that the mean free path i.e., average distance travelled between two collisions with the ions in the lattice, is of the order of interatomic distance.

Q.2. How does free electron gas in metal differ from ordinary gas in some respects?

Ans. Firstly the free electron gas is charged while the ordinary gas molecules are generally neutral. Secondly the concentration of electrons in metals is larger than that in the ordinary gas.

Q.3. What do you mean by the drift velocity and mobility of a free electron?

Ans. The average velocity of a free electron is known as drift velocity whereas mobility of an electron is defined as the drift velocity per unit electric field.

Q.4. What are the factors which affect the value of conductivity of material?

Ans. The factors affecting the conductivity of a material are: (i) Temperature (ii) Alloying (iii) Mechanical stressing (iv) Age hardening.

QUESTIONS AND NUMERICAL PROBLEMS

1. Distinguish between metals, insulators and semiconductors on the basis of band theory.
2. Define the term effective mass of an electron. Is it different from the free electron mass ?
3. What are the main conclusions of the Kronig-Penny mode ?
4. What is the concept of effective mass ? What information does one obtain about the effective mass of electron in a periodic potential ?
5. Explain how the atomic energy levels split into bands when a number of atoms are brought together to form a crystal.
6. Discuss Kronig-Penny model for the energy band structure of solis. Show that each band can accomodate $2N$ electrons, where N is the total number of atoms in the crystal.
7. What is the origin of energy gap or band gap ?
8. What is mant by Fermi-energy? Calculate its value for the free electron gas at 0 K and mention its significance.
9. Derive expressions for th ewave function and the energy vlaues for electrons confined to a line of length L . Also derive expressions for the Fermi-energy and density of this system.
10. What is the significance of Fermi energy at 0 K?
11. Using the Kronig-Penny model, show that for $P \ll 1$, the energy of the lowest energy band is

$$E = \frac{h^2 P}{ma^2}.$$
12. The atomic radius of Na is 1.88 Å. Calculate the Fermi energy of Na at 0 K.
13. What is Fermi Level ? How does it change with temperature and concentration of electrons ?