

# Free Electron Theory of Conduction in Metals

2  
Chapter

## 2.1 Crystalline Structure

A crystalline solid is a solid in which atoms bond with each other in a regular pattern to form a periodic collection or array of atoms. All crystals have periodicity, which leads to long-range order. Local bonding geometry is repeated many times at regular intervals to produce periodic array of atoms that constitute crystal. The location of each atom is well known by virtue of periodicity. Nearly all metals, many ceramics, semiconductors and various polymers are crystalline in solid. The periodic array in which the atoms are located is called the crystal lattice. The arrangement of space positions of the atoms in a crystal is called space lattice or lattice array.

Since a crystal is essentially a periodic repetition of small volume of atoms in three dimensions, it is useful to identify the repeating unit so that the crystal properties can be described through this unit. The most convenient small cell in the crystal structure that carries the properties of the crystal is called unit cell. The repetition of unit cell in three dimensions generates the whole crystal.

There are different types of unit cell geometries of crystals of different materials. In cubic type geometries, there are basically three types of unit cells, namely Simple cubic, Face centered cubic and Body centered cubic. Not all the elements and compounds have cubic structures; there are other unit cell geometries like orthorhombic, monoclinic, hexagonal, tetragonal, etc. In cubic structures, there are diamond cubic structure and zinc blende cubic structure.

### 2.1.1 Simple Cubic Structure

Atoms are placed at the corners of the unit cell geometry and by repeating this in all directions crystal is formed. The length of a side is equal to the distance between two atoms. Each atom touches along the cube edges only. The structure is loosely packed.

Only  $1/8^{\text{th}}$  of each of the atoms belongs to a unit cell. So, each unit cell has  $8 \times 1/8 = 1$  atom. The packing density is defined as the ratio of volume actually occupied by an atom to the volume of the unit cell.

$$\text{Packing Density} = \frac{V_{\text{atom}}}{V_{\text{unit-cell}}}$$

(2.1)

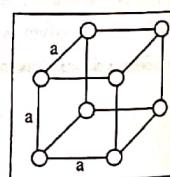


Fig. 2.1 Unit cell of SCC

So, for SCC we have

$$\text{Packing Density} = \frac{\frac{4}{3}\pi R^3}{a^3} = \frac{\frac{4}{3}\pi R^3}{(2R)^3} \approx 0.52$$

### 2.1.2 Face Centered Cubic (FCC) Structure

Here the atoms are placed as in the case of SCC at all the corners of the unit cell and additional atoms are placed at the intersection of face diagonals in all faces. Half of the atom at each of the face diagonals belongs to the unit cell. So the total number of atoms in a unit cell equals to  $(1 + 6 \times 1/2 = 4)$  four. Each FCC unit cell has four atoms in it. The number of neighboring atoms is termed as coordination number. In FCC structure the coordination number is 12.

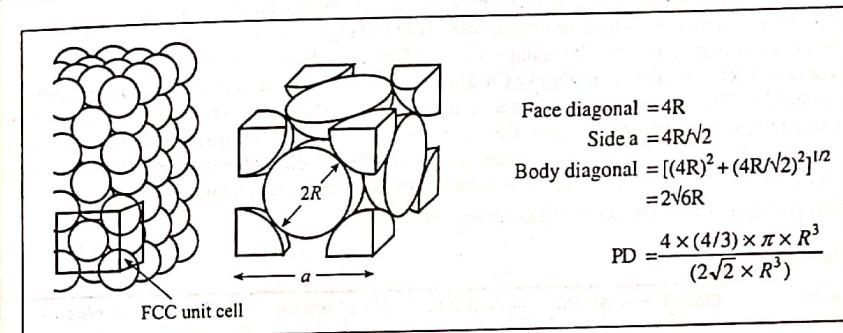


Fig. 2.2 FCC unit cell geometry.

### 2.1.3 Body Centered Cubic (BCC) Structure

In this type of unit cell structure in addition to atoms at the corner of the cell geometry, there is an atom occupying the central place within the unit cell. All the corner atoms are touching the central atom. The coordination number here is 8 and the number of atoms per unit cell =  $1 + 8 = 2$ . Elements with this type of cell geometry have fairly high packing density.

In BCC structure, there is an atom at the center of the unit cell.

$$\text{Body Diagonal} = R + 2R + R$$

$$\text{Face Diagonal} = \frac{\sqrt{2}BD}{\sqrt{3}} = \frac{4\sqrt{2}R}{\sqrt{3}}$$

$$\text{Side } a = \frac{FD}{\sqrt{2}} = \frac{4R}{\sqrt{3}}$$

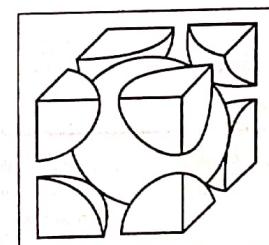


Fig. 2.3 BCC unit cell geometry

$$\text{Packing Density} = \frac{\text{Volume Occupied by atoms}}{\text{Volume of the unit cell}}$$

$$= \frac{2 \times \frac{4\pi R^3}{3}}{\left(\frac{4R}{\sqrt{3}}\right)^3} = \frac{8\pi R^3}{3} \times \frac{3\sqrt{3}}{64R^3}$$

$$= \sqrt{3} \frac{\pi}{8} = 0.68$$

Covalently bonded solids such as Si and Ge have diamond cubic structure. Here the neighboring atoms bond with each other in tetrahedral configuration. In addition to the atoms at the corner and intersections of the face diagonals there are four atoms within the unit cell. So there are altogether 8 atoms/unit cell. In GaAs crystal each atom forms four directional bonds with its neighbors. The unit cell is again a diamond type cubic with Ga and As atoms alternating positions. They are called zinc blende after ZnS, which has this type of unit cell. Atoms of elements like Co, Mg and Zn are formed in a structure known as Hexagonal Close Packed (HCP) structure in which there are 2 atoms per unit cell and the coordination number is 12. In CsCl structure, which is BCC structure, there is visible separation between cation and anion bound together. Each CsCl unit cell consists of 1 cation and 1 anion with coordination number 8. In this case, since there are different atoms, the cell geometry can not be expressed in term of atomic geometry.

Some properties of important crystals are presented below.

Table 2.1

Crystal Structure	Side $a$ and atomic radius $r$	Coordination Number	No of atoms/unit cell	Packing Density	Examples
Simple cubic	$a = 2R$	6	1	0.52	None
BCC	$a = 4R/\sqrt{3}$	8	2	0.68	Cr, Mo, W, $\alpha$ -Fe
FCC	$a = 4R/\sqrt{2}$	12	4	0.74	Ag, Au, Cu, Pt
HCP	$a = 2R$	12	2	0.74	Co, Mg, Ti, Zn
Diamond	$a = 8R/\sqrt{3}$	4	8	0.34	Diamond, Si, Ge
CsCl		8	1 cation		Ionic solids CsCl, CsBr, CsI
Zinc blende		4	1 anion		ZnS, GaAs, GaSb, InAs, InSb
			8	0.34	

**Bravais Lattices** There can be number of possibilities for choosing a unit cell for a given crystal structure. As a convention the geometry of a unit cell is represented by a parallelepiped with sides  $a$ ,  $b$  and  $c$  and angles  $\alpha$ ,  $\beta$ , and  $\gamma$  as shown in figure. The sides  $a$ ,  $b$ ,  $c$  and angles  $\alpha$ ,  $\beta$ , and  $\gamma$  are referred to as lattice parameters. Based on different lattice parameters there are only seven possible distinct unit-cell geometries called crystal systems. These seven crystal system only categorize the unit cell based on geometry but do not mention where the atoms are placed within the cell. Depending upon the lattice arrays where the atoms are placed we can distinguish between similar crystal systems as in case of SC, FCC and BCC which all

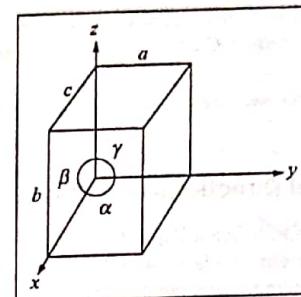


Fig. 2.4 Unit cell geometry

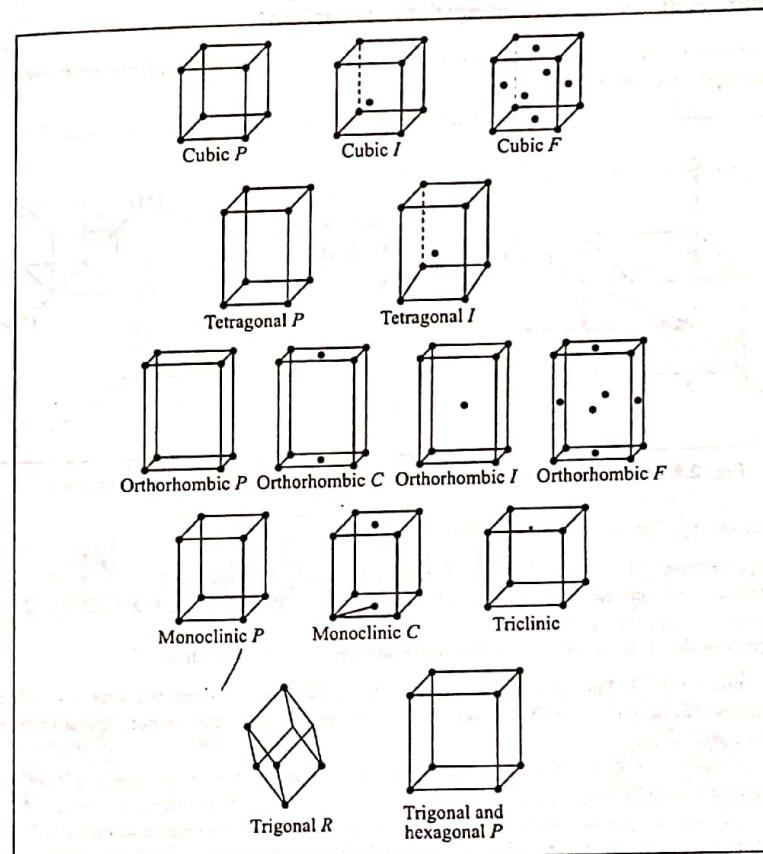


Fig. 2.5 Seven crystal systems and 14 Bravais lattices

have cubic crystal system. There are only 14 different distinct lattices that exist in three dimensions. These 14 distinct lattices are called *Bravais Lattice*. Cu has FCC Bravais lattice whereas Cr has BCC Bravais lattice.

For Cu and Fe, the unit cell geometry has  $a = b = c$ ,  $\alpha = \beta = \gamma = 90^\circ$  and so cubic symmetry. For  $Zn$   $a \neq c$ , and  $\alpha = \beta = 90^\circ$  and  $\gamma = 120^\circ$ .

## 2.2 Miller Indices: Crystal Directions and Planes

In explaining crystal properties, we must frequently specify a direction and a plane of atoms in the crystal. Many properties such as modulus of elasticity, electrical resistivity, magnetic susceptibility are directional within a crystal. Here we use convention for labeling them crystal direction and plane.

### 2.2.1 Miller Indices for Crystallographic Direction

All parallel vectors have same indices. Therefore the directions to be labeled can be moved to pass through the origin of the unit cell.

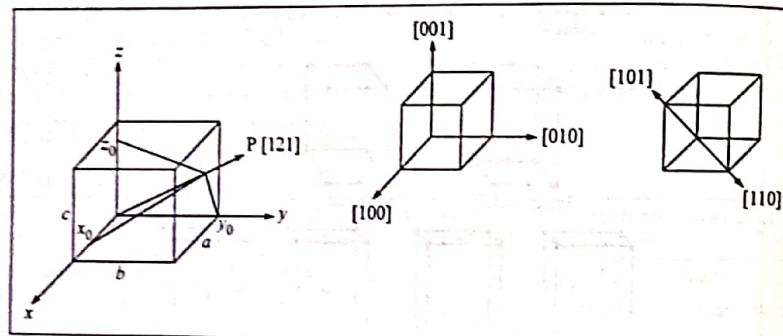


Fig. 2.6 (a) Identification of crystal direction (b) Various directions in crystals

Steps in finding Miller indices for directions:

- Find projections on the respective axes from point  $P(x_0, y_0, z_0)$  in Fig 2.6.b)
- Express these coordinates in terms of lattice parameters  $a, b$  and  $c$ .  $x_0, y_0, z_0$  are  $a/2, b, c/2$
- $P$  is at  $x_1, y_1, z_1$  i.e.  $\frac{1}{2}, 1, \frac{1}{2}$
- Multiply or divide these numbers till we have smallest integers including 0.

Here we will get 2,1,2. Putting these numbers without commas in square brackets, we will express required indices for direction as [212]. To indicate negative crystal direction we put a bar atop the number representing the index.

Directions [100], [010], [001], [010] and [100] are different because of our assigning them respective axes. Otherwise their directional natures from each other are identical. All these six indices for crystal direction consisting two zeroes and a unity can be represented by  $\langle 100 \rangle$  known as family of directions [100], [010], [001], etc. Similarly, all the directions with [111] as Miller indices can also be represented in the manner expressed above.

### 2.2.2 Miller Indices for Crystallographic Planes

The indices used to represent a crystallographic plane are called Miller indices for crystallographic planes. Here also the intercepts of the plane are expressed in terms of lattice parameters.

Steps in finding Miller indices for crystal planes:

- Find the intercepts of the plane on respective axes ( $x_0, y_0, z_0$ )
- Express these intercepts in terms of lattice parameters to obtain  $x_1, y_1, z_1$
- Invert these numbers  $1/x_1, 1/y_1, 1/z_1$
- Unlike in crystal directions, clear the fractions without reducing to lowest integers
- Put them in parentheses without commas.

For example, for the plane shown in figure 2.7.a,  $x_0, y_0, z_0$  are  $(1/2)a, 1b$  and  $\infty c$ . Intercepts  $x_1, y_1, z_1$  are  $\frac{1}{2}, 1$  and  $\infty$ . Their reciprocals are 2,1 and 0. There are no fractions, so (210) are the required Miller indices for crystallographic plane. In case there are negative numbers, bars atop these numbers are placed to distinguish them from positive indices. If a plane passes through origin we can shift it by a lattice parameter since planes shifted by a lattice parameter have same Miller indices. The planes represented by (100), (010), (001), (010), (010) and (100) are different due to our assigning them different axes. Otherwise their properties are exactly identical to each other. They are represented as family of planes  $\langle 100 \rangle$ . Similar principle applies to planes with (111)s.

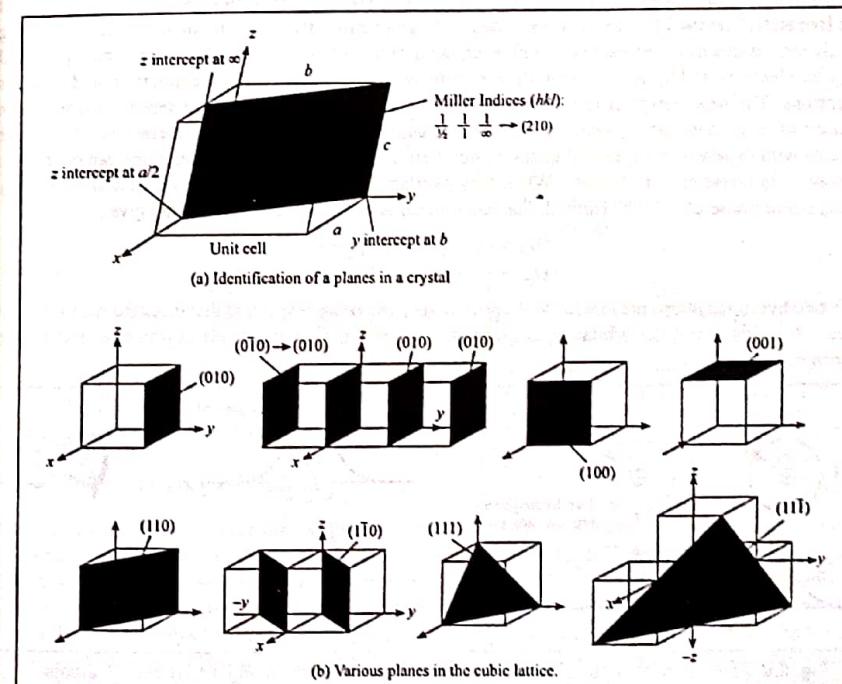


Fig. 2.7 Labeling of crystal planes and typical examples in cubic lattice.

## 2.3 Band Theory of Solids

### 2.3.1 General Introduction

The free electron theory described in previous chapter can successfully explain the various properties of metal such as electrical and thermal conductivity, specific heat capacity, etc. However, the theory could not explain why certain solids behave as good conductors while certain others behave like insulators. It also could not explain why in certain solid, resistivity decreases with the increase in temperature.

The failure of the theory is due to the assumption of:

- constant or zero potential due to ion cores;
- the ion cores are free to move about in a crystal.

In fact, the potential due to ion cores is not constant rather it is periodic and the ion cores is at rest. These two reasonable considerations form the basis of the band theory of solids which results in the existence of band gap.

### 2.3.2 Molecular Orbital Bonding Theory

When two hydrogen atoms are very far apart so that they can not influence each other's energy, each has its own energy levels, labeled as 1s, 2s, 2p, etc. The electron energy in each atom is -13.6eV with respect to the free state. The total energy of two isolated hydrogen atom is twice that of single atom. If we bring them closer, the electrons interact both with each other and with other nuclei. By finding new potential energy for electrons and by solving Schrödinger's equation, we can find new wave functions and energies of electrons. The new energy is lower than the total energy of electrons when at separate state, so the formation of H<sub>2</sub> is energetically favourable. When the ψ<sub>1s</sub> orbital of both the atoms interact, two new wave functions with different energies and quantum numbers are formed. Two wave functions can overlap in two ways – in phase or out of phase. When they overlap in phase, ψ<sub>σ</sub> will be formed and when they overlap out of phase ψ<sub>σ\*</sub> will be formed. The two molecular orbitals in H-H system are given by

$$\begin{aligned}\psi_{\sigma} &= \psi_{1s}(r_A) + \psi_{1s}(r_B) \\ \psi_{\sigma^*} &= \psi_{1s}(r_A) - \psi_{1s}(r_B)\end{aligned}\quad (22)$$

where two hydrogen atoms are labeled as A and B, and r<sub>A</sub> and r<sub>B</sub> are respective distances from their parent nucleus. The first molecular orbital ψ<sub>σ</sub> is symmetric whereas the second ψ<sub>σ\*</sub> is asymmetric and a node between nuclei.

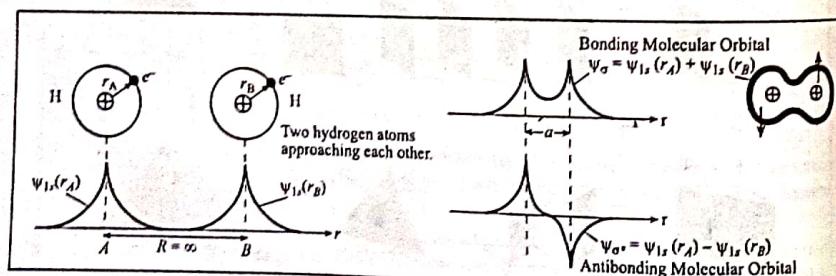


Fig. 2.8 Formation of molecular orbitals, bonding and antibonding when two H atoms approach each other

The wave functions of electrons in H<sub>2</sub> system must be determined by solving Schrodinger's equation, but we can guess that they must look like ψ<sub>σ</sub> and ψ<sub>σ\*</sub>. The two energies E<sub>σ</sub> and E<sub>σ\*</sub> are widely different with E<sub>σ</sub> below E<sub>1s</sub> and E<sub>σ\*</sub> above E<sub>1s</sub>. The electrons are most likely to favour ψ<sub>σ</sub> orbital as that would be the most stable outcome. The system would have lowest energy at R = a, where a is the separation between atoms. R-the atomic radius. The difference between energy of two isolated H atoms and minimum energy of H-H system is called bonding energy.

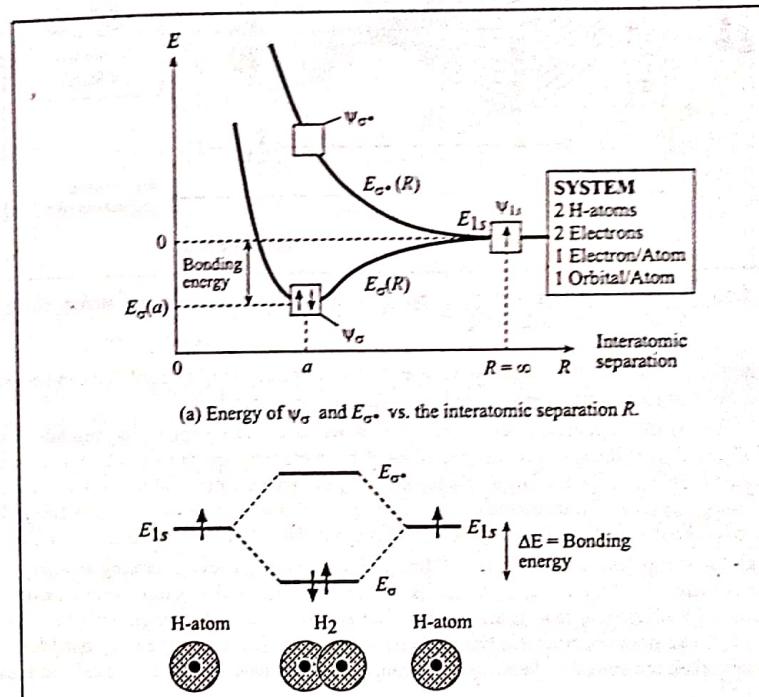


Fig. 2.9 Schematic diagram showing changes in electron energy as two isolated H atoms come together to form hydrogen molecule.

### 2.3.3 Band Theory of Solids

Alike in hydrogen atom, there are number of orbitals in atoms of different elements which at normal temperature give rise to a solid when they come together in large number. The identical orbitals of different atoms, with or without electrons within them interact (overlap) with each other and the outcome will be as shown in figure 2.10. Some of the orbitals will have electrons occupying the state available where as some would have electrons occupying only the part of states available and others with no states occupied by electrons. When identical orbitals, for example ψ<sub>1s</sub> or ψ<sub>2s</sub> of different atoms overlap with respective orbitals, although the energy levels formed by overlapping of identical orbitals are finely separated from each other,

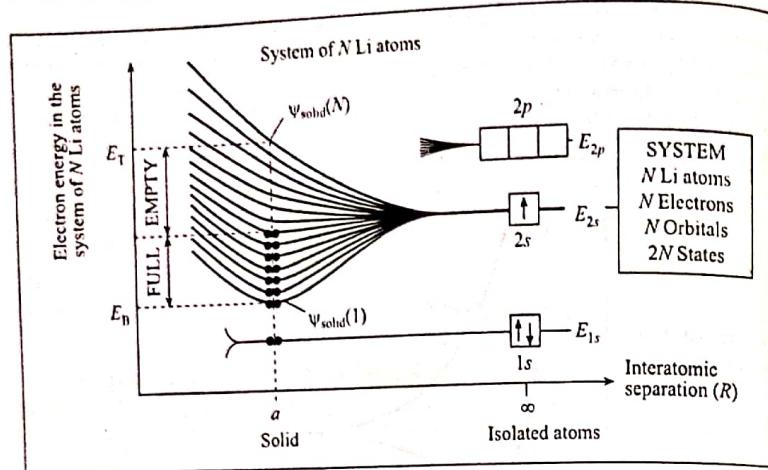


Fig. 2.10 Formation of 2s energy band from 2s orbitals when  $N$  Li atoms come together to form Li solid.

the separation is so small that for very large number of atoms required to form a solid, it can be assumed continuous. So, that continuous energy level is regarded as energy band.

When  $N$  Li atoms are brought together to form Li solid, we have  $N$  electrons in  $N\psi_{2s}$  orbitals. Since 1 orbital is full and close to nucleus it is not affected much by interatomic interaction. The energy band  $E_1$  will be formed from  $N\psi_{2s}$  orbitals. The atoms separated by distance greater than  $R = a$  will cause lesser amount of energy splitting. The interatomic interactions between  $N\psi_{2s}$  orbitals spread the  $N$  energy levels from bottom level  $E_B$  to top  $E_T$  respectively which is determined by closest interatomic distance  $a$ .

The single  $2s$  energy levels  $E_{2s}$  splits into  $N$  finely separated energy levels forming an energy band. Consequently there are  $N$  separate energy levels each of which can take two electrons with opposite spins. The  $N$  electrons fill all levels up to level at  $N/2$ . Therefore the band is half filled means half of the available states are filled. This does not mean that half the spread of the band is filled. The energy band formed by atomic energy levels are termed as their respective bands such as 2s band, 2p band, 3d band, etc as shown in figure 2.11.

As atoms approach each other's to form solids, at first, outermost energy levels are affected, and then only gradually, the inner or lower energy levels are affected. These close atoms' molecular orbitals interact resulting in new orbital of which only where the energy of the system is lower will be occupied by electrons. The splitting of energy level in very large finely separated energies that can be regarded continuous gives rise to what is called energy band. Not all the states available are filled, so with the energy bands also.

The splitting of single energy level of an isolated atom into an energy band in the crystal lattice is responsible for various physical properties such as electrical, magnetic and optical.

In different solids, valence band is either completely or partially full. This is the highest occupied energy band with valence electrons. Valence band is the highest filled band. The next higher energy band is called conduction band, which can be completely or partially empty. Conduction band is the lowest unfilled band. The energy gap between valence band and conduction band is called forbidden gap where no states are available and so no electrons.

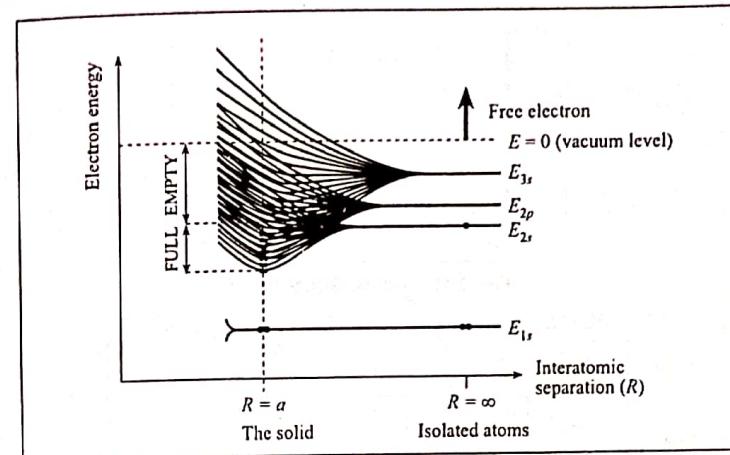


Fig. 2.11 Formation of different energy bands in Li solid due to large number of Li atoms brought close together.

The covalent forces of a crystal lattice are due to the valence band. If a valence electron absorbs enough energy, it can jump the energy gap and become a conduction electron after which it can freely move entirely through the material.

All the materials are classified on the basis of energy band gap. According to which there basically conductors, semiconductors and insulators. In conductors, there is virtually no energy gap between valence band and conduction band. They overlap with each other. The valence electrons can be readily assumed as conduction electron. In insulators, the energy band gap between valence band and conduction band is of the order of 10 eV. At absolute zero, all the states in valence band are completely filled and in conduction band completely empty. Even at room temperature there are very few electrons present in conduction band of an insulator. In semiconductors the energy band gap between valence band and conduction band is in average 1eV. Here also at absolute zero all the states in valence band are occupied and all the states in conduction band are empty. But at room temperature the number of electrons per unit volume in semiconductor is fairly higher than that of in insulators as less energy is required to excite valence electrons to conduction band in semiconductors compared with insulators.

### 2.3.4 Kronig-Penny Model

The free electron model implies that potential inside the solid is uniform in metals. A more accurate model allows for variation in potential energy due to the fixed positively charged lattice ions. In figure 2.12 a 1-dimensional lattice with ions separated by lattice parameter  $a$ , is presented.

The highest potential is half way between the atom and goes to  $-\infty$  as position of the ion is approached. This potential distribution is quite complicated and for mathematical solution of Schrodinger's equation a simpler model known as "Kronig-Penny model" is used. The Kronig-Penny model still displays the following essential features where the function:

- has the same period as lattice
- potential is higher between ions and lower near the lattice ion

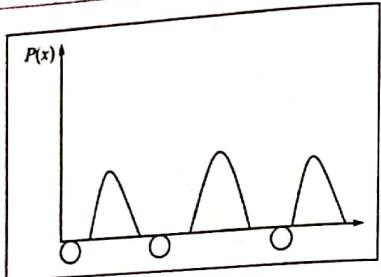


Fig. 2.12 1-dimensional lattice

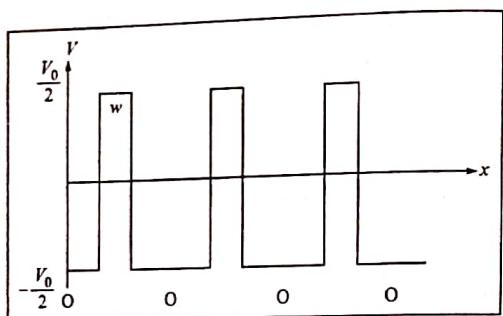


Fig. 2.13 Geometrical arrangement for Kronig-Penny model

The ions are located at  $x = 0, a, 2a, 3a, \dots$ . The potential wells are separated from each other by potential barrier of height  $V_0$  and width  $w$ . The Schrödinger's equation should be solved for potential distribution separately for  $V = +V_0/2$  and  $V = -V_0/2$  and compare the solutions at the boundary conditions.

The assumed wave function has the form

$$\psi(x) = U_k(x)e^{ikx} \quad (2)$$

where  $U_k(x)$  is a periodic function with the same period as the lattice.

The solution for the above equation exists if  $k$  is related to energy  $E$  by the following equation assuming that as  $w \rightarrow 0$ ,  $V \rightarrow \infty$ ,  $wV = \text{const}$

$$\cos ka = \frac{P \sin \alpha a}{\alpha a} + \cos \alpha a \quad (2)$$

where

$$P = \frac{4\pi^2 ma}{h^2} V_0 w \quad (2)$$

$$\alpha = \frac{2\pi}{h} (2mE)^{1/2} \quad (2)$$

Here the relationship between  $E$  and  $k$  is not as easy as that of free electron. To find the exact  $E-k$  curve we must first of all plot the right hand side of equation (2.4) as a function of  $\alpha a$  and then by plotting the left hand side and using the fact that this always must be between +1 to -1, a solution will be found for the values of  $E$  for which right side is within these limits.

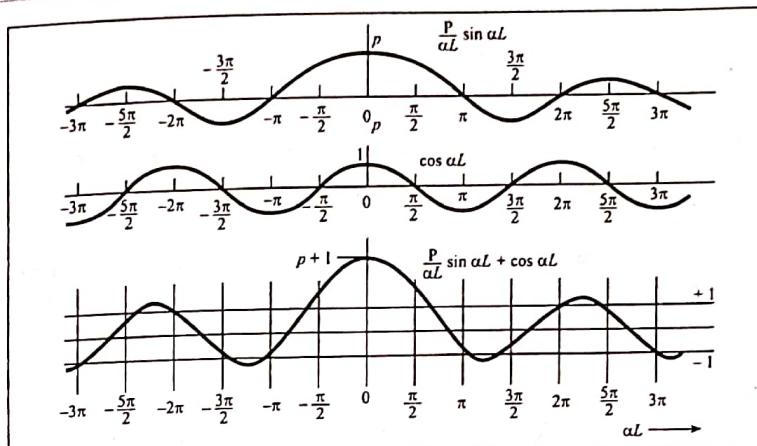


Fig. 2.14 Solution for Kronig-Penny model

The solution is defined only in the shaded region, i.e. only certain values are allowed. This implies that there are only certain allowed energy bands in crystal solids.

For the solution of Kronig-Penny model mentioned above, if the value of  $P$  is large i.e.  $V_0 w$  is large, the function given by right hand side of equation 2.4 crosses at a steep slope. This means that the allowed bands are narrower and forbidden bands are wider. Let us observe some specific conditions.

1. As  $P \rightarrow \infty$ , the band reduces to a single energy level, i.e. discrete energy spectrum for isolated atoms which is the actual case. So  $P$  is proportional to the potential barrier of the given system.

$$\frac{\sin \alpha a}{\alpha a} = 0$$

$$\sin \alpha a = 0$$

$$\alpha a = n\pi$$

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

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

which is exactly same as the equation for an electron in an infinite potential well of width  $a$ . So, all the electrons are independent of each other and confined to infinite potential barrier.

2. When  $P \rightarrow 0$ ,

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

$$\frac{2\pi a}{h} \sqrt{2mE} = ka$$

$$E = \frac{h^2 k^2}{8\pi^2 m} = \frac{h^2 k^2}{2m} \quad (2.6)$$

Equation (2.6) is exactly same as that of equation for a free electron. So the variation in the value of  $P$  from zero to infinity accounts for the whole range of conditions in the crystalline solid.

3. At the boundary conditions of the allowed band, i.e.  $\cos ka = \pm 1$

$$\cos ka = \cos n\pi$$

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

Below  $E$  vs.  $k^2$  curve is plotted for 1-dimensional lattice structure from Kronig-Penny model. At the boundaries, we can see discontinuities in energy levels as the value of  $n$  changes. By transferring the curves by an appropriate multiple of  $\pi/a$  to the axis  $E$  we can see the separation between energy levels very clearly. Each of these energy levels is termed as *Brillouin zone*.

From the figure 2.15, we can say that in the middle of the Brillouin zones the  $E$ - $k$  curve is identical to the free electron. But at the boundaries of the zones i.e. at  $k = n\pi/a$ , their behavior is totally different.

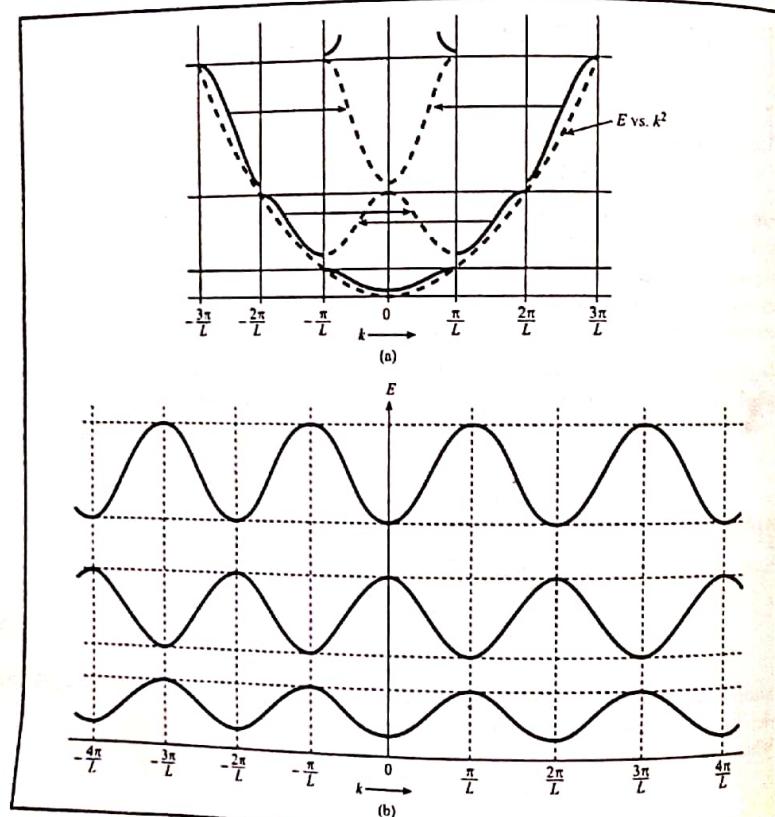


Fig. 2.15 E-k curve for 1-dimensional lattice structure from Kronig-Penny model for the normal and reduced zone cases. Also shown in the figure is the E-k curve for free electron. (b) plot of the extended zone curves for the same lattice structure.

Electrons that occupy Brillouin zone can move freely inside a crystal. All the information for the BZs are contained in the first BZ if we use the reduced zone plot. So, the BZs are the allowed energy regions in  $k$ -space, which corresponds to the allowed bands.

### 2.3.5 Effective Mass of an Electron

For a free particle the relationship between energy and momentum and correspondingly the wave number is

$$E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \quad (2.7)$$

For a particle in the crystal, energy in terms of  $k$  applies. Differentiating equation (2.7) with respect to  $k$  we will have

$$\frac{dE}{dk} = \frac{\hbar^2 k}{m} \quad (2.8)$$

$$\text{But the velocity, } v = \frac{p}{m} = \frac{\hbar k}{m}$$

And, comparing this with equation (2.8), we will get

$$\frac{1}{\hbar} \frac{dE}{dk} = v \quad (2.9)$$

In equation (2.9)  $v$  is the velocity of particle in the crystal. Now acceleration is given by

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

$$\frac{d}{dt} = \frac{dk}{dt} \frac{d}{dk}$$

$$a = \frac{\hbar}{m} \frac{dk}{dt}$$

So

$$\frac{\hbar}{m} \frac{dk}{dt} = \frac{1}{\hbar} \frac{dk}{dt} \frac{d^2 E}{dk^2}$$

or,

$$m = \frac{\hbar^2}{(d^2 E / dk^2)} \quad (2.10)$$

Thus, mass is associated with curvature of energy in  $k$ -space. For a free particle this curvature  $d^2 E / dk^2$  is

constant, so the  $E$ - $k$  diagram is parabolic. But in the crystal solids this is not the case. The curvature  $d^2 E / dk^2$  is not always constant for bands representing  $E$ - $k$  diagram for electrons within the solids.

For solids we can write

$$m^* = \frac{h^2}{(d^2 E / dk^2)}$$

Where  $m^*$  represents the effective mass of the electron in crystal structure.

As the value of  $k$  goes from  $-\pi/a$  to 0, electron velocity changes from negative to zero. Similarly when  $k$  changes from zero to  $+\pi/a$ , velocity goes also changes from zero to positive values. The effective mass of the particle is positive for the curvature of  $\frac{d^2 E}{dk^2} > 0$

i.e. the curvature is concave upward and the effective mass is negative when the curvature is concave downward for  $\frac{d^2 E}{dk^2} < 0$ . For certain values of  $k$  the curvature is zero pointing toward the infinite mass.  $F_x$

$\frac{d^2 E}{dk^2} > 0$ , mass is positive and electron is accelerated in the direction of the applied external force (due to

external electric field) which matches with our perception of mass. In crystals, sometimes the electrons decelerated due to the external applied field. As external forces try to impel into a region dominated by repulsive potential whose magnitude increases as the particle penetrates farther into the region, the result is what would be expected if the mass of the particle were negative. For certain cases, the electron cannot be accelerated whatever be the magnitude of the applied external force. The internal forces in the crystal cancel out the effect of external force. When electrons are accelerated indicating their positive mass they can be accelerated beyond the zone boundary. When reaching the zone boundary, no further acceleration is possible whatever the applied force be. This can only be possible if the mass of the electron were infinite. This concept of velocity and mass of an electron in crystal is based upon perfect crystal structure, which is not the general case. There are always some crystal imperfections present in the structure.

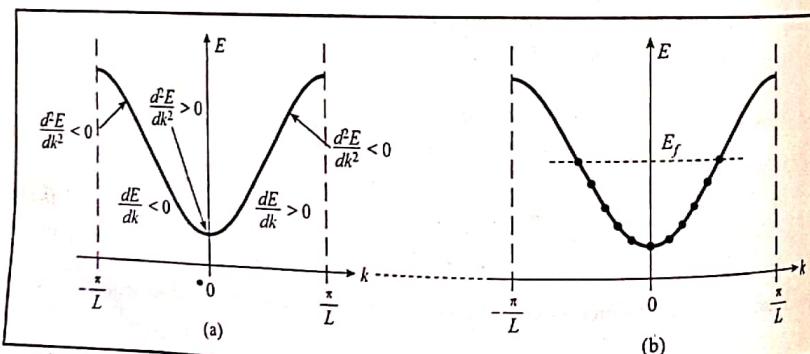


Fig. 2.16 Electron motion in the conduction band of a conductor for a simplified 1-dimensional structure (a) empty band; (b) at the equilibrium.

## 2.4 Thermal Velocity of Electron at Equilibrium

Applying kinetic molecular theory of gases for gas molecules contained in a container we can write the final theoretical derivation in the form

$$PV = \frac{Nm v^2}{3} \quad (2.12)$$

where  $P$  = Pressure of gas inside the container

$V$  = Volume of the container

$N$  = Number of gas molecules in container

$m$  = Mass of the gas molecule

$v^2$  = mean square velocity of molecules

The experimental observation is

$$PV = \frac{N}{N_A} RT = nRT \quad (2.13)$$

where  $N_A$  = Avogadro's number

$R$  = Universal gas constant

$T$  = Temperature

$n = N/N_A$  = Number of moles of gas

For  $N$  molecule gas, every molecule will have its random velocity. The change in momentum of the molecule following collision with the wall of the container is  $\Delta p_x = 2mv_x$  where  $m$  is the molecular mass. Time interval between collision will be  $\Delta t = 2a/v_x$  where  $a$  is the side of container. Force exerted by this

molecule on the face  $A$  of the container is  $F_x = \frac{\Delta P}{\Delta t} = \frac{mv_x^2}{a}$ .

And the total pressure exerted by  $N$  molecules on face  $A$  due to total force is

$$P = \frac{\text{Total Force}}{\text{Area}} = \frac{mv_{x1}^2 + mv_{x2}^2 + \dots + mv_{xN}^2}{a^3} = \frac{m}{a^3} (v_{x1}^2 + v_{x2}^2 + \dots + v_{xN}^2)$$

$$P = \frac{mN}{V} v_x^2$$

where  $Nv_x^2 = v_{x1}^2 + v_{x2}^2 + \dots + v_{xN}^2$

Since the molecules are in random motion and collide randomly with each other, mean square velocity in  $x$  direction will be equal to that in  $y$  and  $z$  directions.

So,

$$v_x^2 = v_y^2 = v_z^2$$

The velocity of any molecule is given by

$$v^2 = v_x^2 + v_y^2 + v_z^2 = 3v_x^2$$

$v^2$  = mean square velocity of the molecule.

We will find that average kinetic energy per degree of freedom is (can be derived)  $kT/2$ . So for three degrees of freedom this is  $3kT/2$ . Average kinetic energy per mole is  $mv^2/2$ .

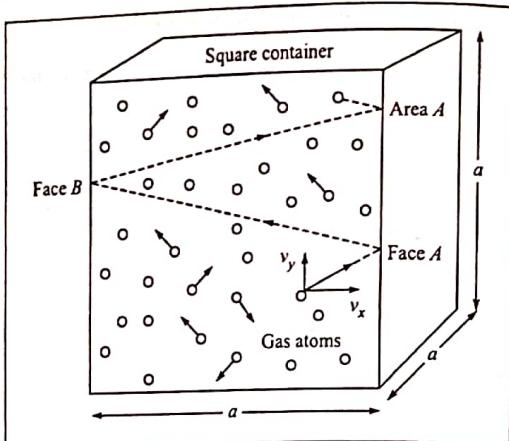


Fig. 2.17 The gas molecules in the container

So,

$$KE = \frac{mv^2}{2} = \frac{3}{2} kT$$

$$v_{th} = (3kT/m)^{1/2}$$
(2.14)

where  $v_{th}$  is the mean thermal velocity of electrons.

The equilibrium is maintained through the interaction with the lattice. Lattice vibrations called **phonons** are the result. Thermal energy possessed by lattice atoms causes vibrations about the equilibrium positions of regular periodic array. These distortions are called phonons. The energy exchange between electron and lattice crystal is called scattering.

## 2.5 Electron Mobility, Conductivity and Resistivity

Although the electrons are in thermal random motion, no net flow of electron in a particular direction persists in the absence of external electric field. So to maintain the flow of electron we need to apply an external electric field.  $V$  is the applied potential across the length  $L$  of the conductor. Then the electric field will be given by

$$E = \frac{V}{L}$$
(2.15)

This electric field is present at every point of the solid. The application of this field will result in acceleration of the electron given by

$$F = ma$$

$$F = -eE$$

So,

$$a = \frac{(-e)}{m} E$$
(2.16)

Thus in addition to random velocity, electron acquires a velocity in the direction of applied field. This directed velocity is lost after each collision with the lattice atoms because of the fact that electron is very

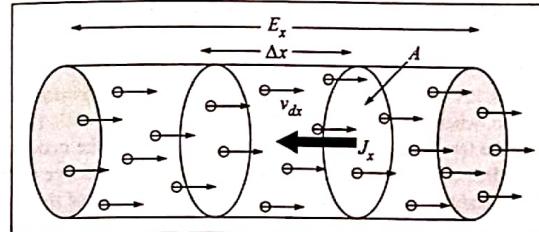


Fig. 2.18 Drift of electrons in a conductor in the presence of an applied electric field

light compared to the atom. Therefore, only the part of the velocity that is picked up between collisions actually counts. The average time between two collisions is termed as **collision time** or **mean free time** or **relaxation time**.

It is denoted by Greek alphabet tau ( $\tau$ ). If  $\tau$  is the average time between collision, then the final velocity of electron will be  $a\tau$ . So the average velocity is

$$v_{av} = a\tau/2$$
(2.17)

A more careful technique for averaging the velocities results in the replacement of the factor 2 from the denominator of equation (2.17) with unity.

So

$$v_{av} = a\tau$$
(2.18)

 $v_{av}$  is called drift velocity of electron.

From equations (2.16) and (2.18) and neglecting the negative sign in (2.16), we have

$$v_D = (e\tau/m)E$$
(2.19)

$$v_D = \mu_D E$$
(2.20)

where  $v_D$  = drift velocity of electron in crystalline solid $\mu_D$  = drift mobility of electron

Drift mobility is related to mean free time and mass of electron as

$$\mu_D = \frac{e}{m} \tau \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$$
(2.21)

Assuming that all the electrons drift with  $v_D$ , the number of electrons crossing a plane of unit area per second can be obtained by multiplying the drift velocity by the free electron density  $N_e$ .

$$\text{Electron Flow} = N_e v_D \text{ s}^{-1} \text{m}^{-2}$$

$$\text{Current Density} = \text{Charg ex Flow}$$

$$J = N_e v_D e$$

But

$$v_D = \mu_D E = \frac{e}{m} \tau E$$

So,

$$J = eN_e \frac{e}{m} \tau E = \frac{e^2 N_e \tau}{m} E$$
(2.22)

$$J = \sigma E$$
(2.23)

where

 $\sigma$  = Electrical conductivity

$$\sigma = \frac{e\tau}{m} eN_e = \mu_D eN_e \text{ Sm.m}^{-1}$$
(read: Siemens per meter)
(2.24)

So, it is clear from equation (2.24) that conductivity of any metal is the product of charge density (electron density) and drift mobility of electron. Although metals have very low mobilities approximately 1/100<sup>th</sup> of that of semiconductors, their high conductivity is by the courtesy of very high free electron densities. In semiconductors, low free charge density implies that conductivity is low despite high mobility compared to the metals. So, when comparing between conductivities of metals (which are called good conductors or simply conductors) and semiconductors, we can say that the conductivity difference is mainly associated with the free or mobile charge density rather than that of charge mobility although both are directly related to the conductivity. In metals free charge densities are of the order of  $10^{28}$  per m<sup>3</sup>, whereas in semiconductors it is around  $10^{16} - 10^{22}$  per m<sup>3</sup>. As mentioned above, the variation in drift mobility is not as high as that of free charge density so as to compensate the latter's effect.

The reciprocal of the conductivity is termed as Resistivity of the material.

$$\rho = \frac{1}{\sigma}, \Omega \cdot \text{m} \text{ (read: ohm meter)} \quad (2.25)$$

Resistance of a conductor with cross-sectional area  $A$  and length  $L$  is calculated as

$$R = \rho \frac{L}{A} \quad (2.26)$$

When calculating resistance, there should be no confusion between the usual meaning of length and the length of current path. In usual meaning, the longest dimension is referred as length whereas for electrical resistance calculation, the length of the path along which current flows is taken as length. In the similar manner, the cross-sectional area of the current path is calculated.

## 2.6 Physical Properties of Some Common Metals

Table 2.2 Resistivity, thermal coefficient of Resistivity at 273° K for various metals.  $n$  is the index in  $\rho \propto T^n$ .

Metal	$\rho_0, 10^{-8} \Omega \cdot \text{m}$	$\alpha_0, \text{K}^{-1}$	$n$	Comments
Aluminum	25	1/233		
Copper	15.7	1/232	1.15	
Gold	22.8	1/251		
Antimony	38	1/196		
Platinum	98	1/255	0.94	
Silver	14.6	1/244	1.11	
Tantalum (Ta)	117	1/294	0.93	
Tungsten	50	1/202	1.2	
Tin	110	1/217	1.11	
Iron	84	1/152	1.8	Magnetic 273K < T < 1043K
Nickel	59	1/125	1.72	Magnetic 273K < T < 627K

## 2.7 Solved Numerical Examples

1. Calculate the root mean square velocity of nitrogen molecule in atmospheric air at 27°C. Also calculate the rms velocity in one direction.

*Solution:*

We have

$$\frac{mv^2_{rms}}{2} = \frac{3kT}{2}$$

$$v_{rms} = \left[ \frac{3kT}{m} \right]^{1/2}$$

where  $m$  is the mass of nitrogen molecule  $N_2$ ,  $k$  = Boltzmann's universal constant.

$k = 1.38 \times 10^{-23} \text{ J/K}$  and the atomic mass of  $N$  is  $M_{at} = 14 \text{ g/mol}$

Avogadro's Number,  $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

Mass of the molecule is related to atomic mass and  $N_A$  as

$$m = \frac{2M_{at}}{N_A} = \frac{2 \times 14 \times 10^{-3} \text{ kg/mol}}{6.022 \times 10^{23} / \text{mol}}$$

And the required rms velocity is

$$v_{rms} = \left[ \frac{3 \times (1.38 \times 10^{-23} \text{ J/K})(300\text{K})}{(28 \times 10^{-26} / 6.022\text{kg})} \right]^{1/2}$$

$$v_{rms} = 517 \text{ (J/kg)}^{1/2} = 517[\text{kg (m/s)}^2/\text{kg}]^{1/2} \\ = 517 \text{ ms}^{-1}$$

Now, velocity in one direction (for example x-direction) can be found as

$$v^2_{rmsx} = v^2_{rmsx} + v^2_{rmsy} + v^2_{rmsz}$$

The average velocities in all three directions are supposed to be equal to each other in magnitude. So,

$$v_{rmsx} = \sqrt{\frac{v^2_{rms}}{3}} = \frac{v_{rms}}{\sqrt{3}} = 298 \text{ m/s}$$

2. Calculate the density of copper with  $a = .362 \text{ nm}$ ,  $M_{at} = 63.5 \text{ g/mol}$ ,  $N_A = 6.022 \times 10^{23} / \text{mol}$ .

*Solution:*

Copper has FCC structure and 4 atoms per unit cell.

$$\text{Density } \rho = \frac{m_{\text{unitcell}}}{V_{\text{unitcell}}} = \frac{4 \times (63.5 \times 10^{-3} \text{ kg/mol}) / (6.022 \times 10^{23} / \text{mol})}{(0.362 \times 10^{-9} \text{ m})^3} \\ = 8890 \text{ kg/m}^3$$

3. Calculate the drift mobility of electrons in copper at room temperature. Conductivity, mass and density of copper are  $5.9 \times 10^5 \text{ Sm/cm}$ ,  $63.5 \text{ g/mol}$  and  $8.93 \text{ g/cm}^3$  respectively.

*Solution:*

Drift mobility is given by  $\mu_d = \sigma/en$  where  $n$  is the electron concentration in the material. From Avogadro's number, we know that one mole of copper has  $6.022 \times 10^{23}$  atoms and each Cu atom contributes one

electron to the conduction band. The mass of one mole of copper is 63.5g. So, from this concentration of electrons in copper can be found as

$$n = \frac{\rho N_A}{M_{at}} = \frac{(8.93 \text{ g/cm}^3)(6.022 \times 10^{23} / \text{mol})}{(63.5 \text{ g/mol})} = 8.5 \times 10^{22} / \text{cm}^3$$

Now, the drift mobility is  $\frac{(8.93 \text{ g/cm}^3)(6.022 \times 10^{23} / \text{mol})}{(63.5 \text{ g/mol})}$

$$\mu_d = \frac{\sigma}{en} = \frac{(5.9 \times 10^5 \text{ Sm/cm})}{(1.6 \times 10^{-19} \text{ C})(5.5 \times 10^{22} / \text{cm}^3)} \\ \mu_d = 43.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$$

which is more than experimental value of  $32 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  (Hall effect) and due to the fact that more than one electron is contributed to the conduction band by each atom.

4. What applied electric field can impose a drift velocity equal to 10% of mean speed  $\sim 1.2 \times 10^6 \text{ ms}^{-1}$  of the conduction electrons in copper? Use the experimental value of drift mobility.

*Solution:*

Applied electric field is related to drift velocity and drift mobility as

$$E = \frac{v_d}{\mu_d} = \frac{1.2 \times 10^6 \times 0.1 \text{ ms}^{-1}}{32 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}} = 3.8 \times 10^5 \text{ V cm}^{-1} \\ = 3.8 \times 10^7 \text{ V m}^{-1} = 3.8 \text{ MV m}^{-1}$$

So, for even the highest working voltages, the drift velocity is much smaller than the mean speed of the electrons. Consequently, when an electric field is applied to a conductor, mean speed is unaffected for all practical purpose.

5. The width of energy band is typically  $\sim 10 \text{ eV}$ .

*Calculate:*

- (i) The density of states at the center of the band;
- (ii) ii. The number of states per unit volume within a small energy range  $kT$  about the center;
- (iii) iii. The density of states  $kT$  above the center;
- (iv) iv. The number of states per unit volume within a small energy range of  $kT$  to  $2kT$  from the bottom of the band.

*Solution:*

The density of states or the number of states per unit energy range per unit volume considering Pauli's exclusion principle is

$$Z(E) = 8\pi\sqrt{2} \frac{m_e^{3/2}}{h^3} E^{1/2} \\ = 8\pi\sqrt{2} \frac{(9.1 \times 10^{-31} \text{ kg})^{3/2}}{(6.624 \times 10^{-34} \text{ Js})^3} (5 \times 1.6 \times 10^{-19} \text{ J})^{1/2} = 9.5 \times 10^{46} \text{ m}^{-3} \text{ J}^{-1}$$

In per  $\text{cm}^3$  per eV,

$$Z(E) = (9.5 \times 10^{46} \text{ m}^{-3} \text{ J}^{-1})(10^{-6} \text{ m}^3 \text{ cm}^{-3})(1.6 \times 10^{-19} \text{ eV}^{-1}) \\ = 1.52 \times 10^{22} \text{ cm}^{-3} \text{ eV}^{-1}$$

To find the number of states per unit volume within  $kT$  about the center of the band we will multiply the density of states at the center by  $E = kT = 0.0259 \text{ eV}$  at 300K.

$$N(E) = Z(E) E = 1.52 \times 10^{22} \text{ cm}^{-3} \text{ eV}^{-1} \times 0.0259 \text{ eV} = 3.9 \times 10^{20} \text{ cm}^{-3}$$

$$Z(E)kT = 8\pi\sqrt{2} \frac{(9.1 \times 10^{-31} \text{ kg})^{3/2}}{(6.624 \times 10^{-34} \text{ Js})^3} (0.0259 \times 1.6 \times 10^{-19} \text{ J})^{1/2} = 6.84 \times 10^{45} \text{ m}^{-3} \text{ J}^{-1} \\ = 1.1 \times 10^{21} \text{ cm}^{-3} \text{ eV}^{-1}$$

Within the  $kT$  the number of states is

$$N(E) = 1.1 \times 10^{21} \text{ cm}^{-3} \text{ eV}^{-1} \times 0.0259 \text{ eV} = 2.8 \times 10^{19} \text{ cm}^{-3}$$

So, even at the bottom of the band, the concentration is fairly high.

6. For silver with  $E_{F0} = 5.5 \text{ eV}$  and  $\Phi = 4.5 \text{ eV}$ , calculate the total number of states per unit volume and compare this with atomic concentration of silver. Density and atomic mass of silver are  $10.5 \text{ g/cm}^3$  and  $107.9 \text{ g/mol}$  respectively.

*Solution:*

For silver with Fermi energy at absolute zero =  $5.5 \text{ eV}$  and work function =  $4.5 \text{ eV}$ , the width of the energy band  $E = 5.5 + 4.5 = 10 \text{ eV}$ . The density of states function reaches maximum at the center of the band. From integrating from bottom of the band to center of the band, we will find number of states per unit volume up to the center of the band which is half the total number of states.

$$\frac{1}{2} N(E) = \int_0^5 Z(E) dE = \int_0^5 8\pi\sqrt{2} \frac{m_e^{3/2}}{h^3} E^{1/2} dE$$

$$\frac{1}{2} N(E) = \frac{16\sqrt{2}\pi n_e^{3/2}}{3h^3} (5 - 0)^{3/2} = 5.08 \times 10^{28} \text{ m}^{-3}$$

So,

$$N(E) = 10.16 \times 10^{28} \text{ states/m}^3$$

Now,

$$\text{Density } \rho = \frac{n M_{at}}{N_A}$$

$$n = \frac{\rho N_A}{M_{at}} = \frac{(105 \times 10^{-3} \text{ kg} / 10^{-6} \text{ m}^3)(6.022 \times 10^{23} / \text{mol})}{107.9 \times 10^{-3} \text{ kg/mol}}$$

$$n = 5.85 \times 10^{28} \text{ atoms/m}^3$$

So, even with a crude approximation, as expected, the number of states is double the atomic concentration.

7. Calculate the Fermi energy at 0K for copper. Given its density is  $8.96 \text{ g/cm}^3$  and atomic mass  $63.5 \text{ g/mol}$ .  $N_A = 6.022 \times 10^{23} / \text{mol}$ .

*Solution:*

Assuming each atom contributes one electron to the conduction band, the electron concentration of copper is

$$n = \frac{\rho N_A}{M_{at}} = \frac{(8.96 \text{ g/cm}^3)(6.022 \times 10^{23} / \text{mol})}{(63.5 \text{ g/mol})} = 8.5 \times 10^{22} \text{ cm}^{-3}$$

The Fermi energy at 0K is given by

$$E_{F0} = (h^2/8m_e) (3n/2\pi)^{2/3}$$

$$E_{F0} = \frac{(6.624 \times 10^{-34} \text{ Js})^2}{8 \times 9.1 \times 10^{-31} \text{ kg}} \left( \frac{3 \times 8.5 \times 10^{22} \text{ cm}^{-3}}{2\pi} \right)^{2/3} = 1.1 \times 10^{-18} \text{ J} = 7 \text{ eV}$$

8. Drift mobility of conduction electron is  $43 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and mean speed is  $1.2 \times 10^6 \text{ ms}^{-1}$ . Calculate the mean free path of electrons between collisions.

Solution:

The mean free path between collisions is given by

$$L_e = v_e \tau$$

where  $v_e$  is the electron velocity,

$\tau$  - is the mean free time between collisions.

But,

$$\mu_d = \frac{e\tau}{m_e} \quad \tau = \frac{\mu_d m_e}{e}$$

So,

$$L_e = v_e \frac{\mu_d m_e}{e} = 1.2 \times 10^6 \text{ ms}^{-1} \frac{(43 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})(9.11 \times 10^{-31} \text{ kg})}{1.6 \times 10^{-19} \text{ C}}$$

$$L_e = 2.99 \times 10^{-8} \text{ m} = 29.9 \text{ nm}$$

## Exercise

- Calculate the rms velocity of oxygen molecules at  $127^\circ\text{C}$  at a pressure of  $2 \times 10^5 \text{ Nm}^{-2}$ . [558ms<sup>-1</sup>]
- Calculate the number of electrons per unit volume of copper. Molar mass of copper = 63.5 and Avogadro's number =  $6.022 \times 10^{23}/\text{mol}$ . [8.45  $\times 10^{28} \text{ m}^{-3}$ ]
- Calculate the Fermi kinetic energy at absolute zero temperature for valence electrons in Na and Li. Why does the Fermi energy not depend on the size of the piece of a given metal? Assume  $m^* = m$ . [3.11 eV and 4.72 eV]
- Calculate the number of atoms per unit cell of a metal having lattice parameters of  $2.9 \text{ \AA}$  and density of  $7.87 \text{ g/cc}$ . Atomic weight of the metal is 55.85 and  $N_A = 6.023 \times 10^{23}/\text{mol}$ . [2]
- If the electrical conductivity of potassium is  $1.39 \times 10^5 \text{ Sm/cm}$ , calculate the drift mobility of electrons at room temperature. Molar mass and density of potassium are 39.95 and  $0.91 \text{ g/cc}$ . [61.96  $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ]
- Show that for cubic lattice, the lattice constant  $a$  is given by  $a = \left[ \frac{NM}{N_A \rho} \right]^{1/3}$  where  $N$  is the number of atoms per unit cell,  $M$  is atomic weight,  $N_A$  is Avogadro's number, and  $\rho$  is density of the crystal material.

7. Show that for any cubic lattice, the separation of the planes corresponding to the Miller indices  $(hkl)$  is given by  $d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$

8. Platinum having molar mass 195.1 crystallizes in the FCC structure and has a density of  $21.4 \times 10^3 \text{ Kg.m}^{-3}$ . Calculate the length of the edge of the unit cell. [0.392nm]

9. Using the Kronig – Penny model, show that the energy of the lowest energy band is  $E = \frac{h^2 P}{ma^2}$  where  $p \ll 1$ .

10. Zinc has the crystal structure HCP. At room temperature, its unit cell parameters are  $c = 4.947 \text{ \AA}$  and  $a = 2.665 \text{ \AA}$ . The bulk density of zinc is  $7134 \text{ Kg.m}^{-3}$ . Determine the atomic weight of zinc. [65.38]

11. A copper wire of cross-sectional area of  $5 \text{ mm}^2$  carries a steady current of 50A. Calculate (a) density of free electrons and (b) average drift velocity of electrons. (Hints: Assume one free electron per atom) [(a)  $8.37 \times 10^{28} \text{ m}^{-3}$  (b)  $7.47 \times 10^{-4} \text{ m.s}^{-1}$ ]

12. Prove that the conductivity of a metal is inversely proportional to its absolute temperature.

13. The valence band of the simple cubic metal has the form  $E = AK^2 + B$ , where  $A = 10^{-3} \text{ J.m}^2$  and  $B = -12 \text{ eV}$ . The band is a p-band states up to  $K_a = (2\pi)^{1/3}$