Men always have an urge to know about the basic building blocks of matter. That is why discovering new solid materials are one of the most active areas of research in modern science. Before starting up with the study of macroscopic properties of various engineering materials we should first recall some important fundamental on physics of atom, solids to form a strong base.

In the first chapter, we shall present some matter, which will be useful in the later chapters. We shall accept the idea that materials consist of atoms and that atom consists of nuclei and electron. Such simplified atomic model will play an important role in the discussions in this book.

Keeping it in mind we shall start up with the study of material in general i.e. their constituents, their structure, about interaction between atoms in solids etc. All this will unify our understanding of the properties of various materials and as such prove their scientific and industrial usefulness.

1.1 Atomic Structure

We know that matter consists of atoms. According to Bohr’s theory, the atom consists positively charged nucleus and a number of negatively charged electrons, which revolve round the nucleus in various orbits. The nucleus contains protons and neutrons.

![Atomic model of a hydrogen atom](image)

**Fig. 1.1 Atomic model of a hydrogen atom**

The proton carries a positive charge of magnitude $1.6 \times 10^{-19}$ coulomb while neutrons are electrically neutral. Thus the charge on the nucleus is determined by the number of protons
contained in it. Protons and neutrons are held close together with strong nuclear forces. The electron is a negatively charged ($= -1.6 \times 10^{-19}$ coulomb) particle having a mass $m = 9.1 \times 10^{-31}$ Kg. The mass of a proton or neutron is about $1836 \times m$. Thus practically the entire mass of the atom is concentrated in the nucleus.

Each atom is ordinarily electrically neutral. Hence in the neutral atom, the number of revolving electrons must be equal to the number of protons in the nucleus. The atomic number $Z$ is equal to the number of protons or electrons contained in an atom. Atomic mass number $A$ is the total number of protons or electrons contained in the nucleus of the atom. The atomic weight is the actual weight of an atom and numerically differs slightly from atomic mass number.

### 1.2 Bohr’s Theory of Hydrogen Atom

A hydrogen atom ($Z = 1$) consists of a single proton in the nucleus and an electron moving round the nucleus. Bohr’s theory of hydrogen atom is based on the following assumptions:

(i) The electron moves round the nucleus in circular orbit.

(ii) As shown in Fig. 1.2, the outward centrifugal force is balanced by the net electrostatic attraction towards the nucleus.

$$\frac{mv^2}{r} = \frac{e^2}{4\pi\varepsilon_0 r^2} \quad \text{... (1.1)}$$

![Fig. 1.2](image)

(iii) Only those orbits are possible for which the orbital angular momentum of the electron is equal to an integral multiple of $h/2\pi$, i.e.,

$$mv = n \cdot \frac{h}{2\pi} \quad \text{... (1.2)}$$

where $h$ is Planck’s constant.

(iv) No energy is radiated by the electron so long as it remains in its definite or stationary orbit. Thus the permitted orbits are non-radiating paths of the electron.

(v) Electromagnetic radiations are emitted if an electron jumps from stationary orbit of energy $E_2$ to another stationary orbit of lower energy $E_1$. The frequency of the emitted radiation is related by the equation.

$$E_2 - E_1 = hv \quad \text{... (1.3)}$$

Using Eqs. (1.1) and (1.2), we can calculate the radii of stationary states $r_n$. 
Thus, \( r_n = \ldots \) (1.4)

Equation (1.4) shows that the radii of the permitted orbits vary as the square of \( n \) (called as principal quantum number). For the smallest orbit \( n = 1 \). Substituting the values of \( h, e_0, m \) and \( e \), we have,

Radius of first orbit \( r_1 = 0.529 \times 10^{-10} \) meter = 0.529 Å

This calculation shows that the atom is about 10\(^{-10}\) meter in diameter.

The orbital energy of an electron revolving in \( n \)th orbit is given by

\[
E_n = -\frac{m e^4}{8 e_0^2 \hbar^2} \cdot \frac{1}{n^2},
\]

or

\[
E_n = -\frac{21.7 \times 10^{-19}}{n^2} \text{ Joules} = -\ldots \text{ eV}
\]

\[
= -\ldots \text{ eV} \quad (\because 1 \text{ eV} = 1.6 \times 10^{-19} \text{ Joule})
\]

The significance of negative sign in Eq. (1.5) is that the electron is bound to the nucleus by attractive forces and to separate the electron from the nucleus, energy must be supplied to it. Giving different values to \( n \), we can calculate the orbital energy or binding energy of the electron in different orbits. Thus we have,

\[
E_1 = -13.6 \text{ eV} \quad \text{when } n = 1 \quad (\text{K-shell})
\]

\[
E_2 = -3.4 \text{ eV} \quad \text{when } n = 2 \quad (\text{L-shell})
\]

\[
E_3 = -1.51 \text{ eV} \quad \text{when } n = 3 \quad (\text{M-shell})
\]

\[
E_n = 0 \text{ eV} \quad \text{when } n = \infty \quad (\text{Limiting case})
\]

**Energy level in an isolated hydrogen atom.** Here we shall consider a single isolated atom of hydrogen i.e. an atom that has been removed from other atoms and is not affected at all by their electric fields. The orbital energies have already been calculated. Here we shall consider the energy level diagram (Fig. (1.3)).

The lowest energy level \( n = 1 \) corresponds to normal unexcited state of hydrogen. This state is also called as ground state. In energy level diagram the lower energies (more negative) at bottom while higher energies (less negative) are at the top. So it is easier to remove an electron from higher orbit than lower one. So when the electron jumps between the allowed orbits, the greater is the difference in their energies, higher is the frequency of emitted radiation.
1.3 EXCITATION AND IONIZATION OF ATOMS

**Excitation:** The process of raising or transferring the electron from lower energy state to higher energy state is called *excitation*. When the atom is in a state of high energy it is said to be *excited*. However, the atom does not remain in the excited state for long and returns to the normal state or ground state in $10^{-8}$ second. In doing so, it gives out the energy in the form of radiations.

**Ionization:** When by the process of excitation, the electron is completely removed from the nucleus, the atom is said to be *ionized*. Now the atom has left with a positive charge. Thus the process of raising the atom from the normal state to the ionized state is called *ionization*.

The process of excitation and ionization both are absorption phenomenon.

1.4 DUAL NATURE OF LIGHT

Consider an electron in the excited state. As discussed the mean lifetime of the electron in the excited state lies in the range $10^{-7}$ to $10^{-10}$ sec. Thus when the excited electron return to its normal state, the difference of energy between the two states is lost which appears in the form of electro-magnetic radiation or waves.

The radiant energy is emitted not continuously but discontinuously in the form of small packets of light energy called *photon*. Each wave packet or quantum is associated with a definite amount of energy. Thus the energy possessed by the radiations is quantized and the quantum of electromagnetic radiation is called as Photon.

Energy of each photon is given as

$$E = h\nu$$

... (1.6)
Also according to Einstein's equation
$$E = mc^2$$
...(1.7)
where \(m\) is the mass of photon.

From Eqs. (1.6) and (1.7)
$$h \nu = mc^2$$
$$m = \frac{h \cdot c}{\lambda^2}$$

or
$$m = \frac{h c}{\lambda}$$
...(1.8)

From Eq. (1.8) mass of the photon can be calculated.

This concept of quantized nature of radiation was first introduced by Planck in 1901.

Thus photon are treated as particles. On the other hand, radiations exhibit phenomenon of interference and diffraction, which indicate that they possess wave nature. So it is concluded that radiation possess dual nature i.e. particle as well as wave nature.

1.5 Dual Nature of Matter

Lewis de Broglie proposed that just like electromagnetic radiation material particle also have dual nature. He also gave a relation for calculating the wavelength of the wave associated with a particle of mass \(m\) moving with velocity \(v\).

$$\lambda = \frac{h}{mv}$$
...(1.9)

Where \(p\) is the momentum of the particle.
On the basis of de Broglie’s hypothesis and Heisenberg’s uncertainly principle a new model of atom was developed during 1920’s. The model is known as quantum mechanical model. In this model behavior of the electron in an atom is described by an equation known as the Schrodinger wave equation:

\[
\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{\hbar^2} (E - V) \psi = 0 \quad \ldots \quad (1.10)
\]

where \(x, y, z\) are the three co-ordinates,
\(m\) is mass of the electron,
\(h\) is the Planck’s constant,
\(E\) is the total energy and \(V\) is the potential energy of the electron.

\(\psi\) (Greek letter psi) is amplitude of electron wave and is called wave function, and \(\frac{\partial^2 \psi}{\partial x^2}\) refers to the second derivative of \(\psi\) with respect to \(x\) only and so on.

The solutions of Schrodinger wave equation are known as wave functions. When Schrodinger wave equation is solved for hydrogen atom, several solutions are obtained. Out of these only certain solutions are permissible. These permitted solutions of wave equation are known as eigen functions. Each permitted solution or wave function corresponds to a definite energy state and is called orbital. Each orbital can be considered as quantum mechanical analog of the electron orbits as proposed by Bohr. The electron orbital in an atom are called atomic orbital while those in a molecule are called molecular orbital. Since in an atom (or a molecule) only specific or definite energy states are permitted, it implies that an electron in an atom (or a molecule) can have only certain specific values of energy. In other words, energy of electron in an atom is quantised.

**Significance of \(\psi\)**

\(\psi\) refers to the amplitude of electron wave. It has got no physical significance. However, the square of \(\psi\) i.e. \(\psi^2\) has a physical significance. Just like light radiations where square of amplitude gives the intensity of light, similarly in electron wave, \(\psi^2\) gives the intensity of electron at any point. In other words, the knowledge of \(\psi^2\) is helpful in assessing the probability of electron in a particular region. Thus \(\psi^2\) is called probability density and \(\psi\) is referred to as amplitude.

**1.7 QUANTUM NUMBERS**

In an atom large number of electron orbital are permissible. These orbital are designated by a set of numbers known as quantum numbers. These numbers follows directly from the solutions of Schrodinger wave equation.

(i) **Principle Quantum Number \((n)\)**

This is the most important quantum number as it determines to a large extent the energy of an electron. It also determines the energy shell or level in which the electron is present.
Thus, the site of the orbital is determined by this quantum number. It is denoted by ‘n’. It can have any whole number value such as \( n = 1, 2, 3, \ldots \). The energy level or shell corresponding to these numbers are designated as K, L, M, N, etc.

Energy of the electron in hydrogen atom is given by

\[
E_n = -\frac{1}{3}\frac{1}{n^2} \text{eV}
\]

As the value of \( n \) increases, the electron gets farther away from the nucleus and its energy increases (becomes less negative).

**(ii) Azimuthal Quantum Number \((l)\)**

This quantum number determines the orbital angular momentum of the electron. This is denoted by ‘\( l \)’. In fact, the orbital angular momentum of electron is given by,

\[
\text{Orbital angular momentum} = \hbar l \frac{1}{2} \hat{p} + b g
\]

The value of \( l \) gives the sub-shell or sub-level in which the electron is located. And the number of sub-shells within a shell is determined by the value of \( n \) for each energy level. Thus, \( l \) may have all possible whole number values from 0 to \( n - 1 \).

The sub-shell corresponding to \( l = 0, 1, 2, 3 \) etc. are designated as s, p, d, f

1. When \( n = 1, l = 0 \), i.e. there is only one possible sub-shell (1s)
2. When \( n = 2, l = 0, 1 \), there are two possible sub-shells (2s and 2p)
3. When \( n = 3, l = 0, 1, 2 \), there are three possible sub-shells (3s, 3p, 3d)
4. When \( n = 4, l = 0, 1, 2, 3 \), there are four possible sub-shells (4s, 4p, 4d, 4f) and so on.

Order of energies of various sub-levels is \( s < p < d < f \)

**(iii) Magnetic Quantum Number \((m_l)\)**

This quantum number is denoted by ‘\( m_l \)’ and refers to the different orientations of electron cloud in a particular subshell.

The possible values of \( m_l \) are all integral values from \(+l\) through \(0\) to \(-l\), thus, making a total of \((2l + 1)\) values.

- For \( l = 0 \) (i.e., s subshell) \( m_l \) can have only one value \( m_l = 0 \)
- For \( l = 1 \) (i.e., p subshell) \( m_l = +1, 0, -1 \)
- For \( l = 2 \) (i.e., d subshell) \( m_l = +2, +1, 0, -1, -2 \)
- For \( l = 3 \) (i.e., f subshell) \( m_l = +3, +2, +1, 0, -1, -2, -3 \)

**(iv) The Spin Quantum Number(s)**

This quantum number which is denoted by ‘\( s \)’, does not follow from the wave mechanical treatment but arises from the spectral evidence that electron in its motion about the nucleus also rotates or spins about its own axis. The spin quantum number, describes the spin orientation of the electron.
The electron spin can be either clockwise or anticlockwise. The spin quantum number can have only two values which are $+\frac{1}{2}$ and $-\frac{1}{2}$. The ($+\frac{1}{2}$) value indicates clockwise spin (denoted by $\uparrow$) and ($-\frac{1}{2}$) value indicates anticlockwise spin (denoted by $\downarrow$).

**1.8 PAULI’S EXCLUSION PRINCIPLE**

According to Pauli’s exclusion principle:

*No two electrons in an atom can have same values of all four quantum numbers.*

Direct implication of this principle is that it is not possible to accommodate more than two electrons in an orbital. This can be easily understood as follows:

All the electrons in particular orbital have same values of principle quantum number ($n$), azimuthal quantum number ($l$) and magnetic quantum number ($m_l$). Therefore, in order to have a unique set of quantum number they must have different values of spin quantum number ($s$). But $s$ can have only two values $+\frac{1}{2}$ and $-\frac{1}{2}$. Hence, in an orbital only two electrons can be accommodated, one spinning clockwise ($s = +\frac{1}{2}$) and the other spinning anticlockwise ($s = -\frac{1}{2}$).

Thus, we can derive the number of electrons in different subshells.

<table>
<thead>
<tr>
<th>Type of subshell</th>
<th>No. of orbitals</th>
<th>No. of electron</th>
</tr>
</thead>
<tbody>
<tr>
<td>s-subshell</td>
<td>1</td>
<td>$7 \times 2 = 14$</td>
</tr>
<tr>
<td>p-subshell</td>
<td>3</td>
<td>$3 \times 2 = 6$</td>
</tr>
<tr>
<td>d-subshell</td>
<td>5</td>
<td>$5 \times 2 = 10$</td>
</tr>
<tr>
<td>f-subshell</td>
<td>7</td>
<td>$7 \times 2 = 14$</td>
</tr>
</tbody>
</table>

**1.9 THE SOLID STATE**

As we know that gases and liquids belong to fluid state. The fluidity of liquids and gases is determined by the relative motion of their molecules. In solids, on the contrary, molecules/atoms/ions are not free to move but can oscillate around their fixed positions due to strong intermolecular/interatomic/interionic forces. Majority of commonly used materials are in solid state.

Solids are broadly classified as crystalline and non-crystalline (or amorphous) solids. Based on the structure the crystalline solids are further classified as single crystal and polycrystalline solid.

The most important property of crystals is *periodicity*.

![Classification of solids](image)

*Fig. 1.5 Classification of solids*
A *single crystal* is a solid in which the regular periodic arrangement of atoms, ions or molecules, extends over the entire volume of the solid i.e. it possesses *long range order*.

A *polycrystalline* solid is made up of an aggregate of a large number of tiny single crystals oriented in different directions and separated by well-defined boundaries. The tiny crystals are called *grains*.

The majority of materials like minerals, alloys, organic or inorganic salts etc. in their natural form exist as polycrystalline solids.

*Amorphous* materials have no regular arrangement of atom or molecules. However, the arrangement may not be completely disordered; that they have *short range order*. Rapidly solidified liquids are amorphous materials, Example. Ordinary glass (soda lime glass), amorphous silica etc.

### 1.10 CRYSTALLINE SOLIDS

#### 1.10.1 Space Lattice and Lattice Points

A *space lattice* may be defined as a regular three-dimensional arrangement of identical points in space and these points are called as *lattice points*. (Fig. 1.6)

![Fig. 1.6 A portion of a 3-dimensional lattice and its unit cell (shaded)](image)

#### 1.10.2 Crystal Lattice

A *lattice* is an infinite periodic array of geometric points in space, without any atom. However, when we place an identical group of atoms (molecules or ions), called as *basis*, at each lattice point, it forms a *crystal lattice*.

#### 1.10.3 Unit Cells

A *unit cell* is defined as the fundamental blocks which, when repeated in the three direction, will generate the entire lattice (Fig. 1.6).
For a three-dimensional lattice (i.e. the space lattice) the unit cell is described by specifying six parameters viz. \( a, b, c \) the angles \( \alpha, \beta, \gamma \). These six parameters are called the lattice parameters.

### 1.11 BRAVIA LATTICES

#### 1.11.1 Crystal Classes (Systems)

There are 7 crystal classes or systems. These are (1) Cubic, (2) Tetragonal, (3) Orthorhombic, (4) Monoclinic, (5) Hexagonal, (6) Rhombohedral, (7) Triclinic.

![Crystal Classes](image)

Fig. 18 (a) Cubic (b) Tetragonal (c) Orthorhombic (d) Rhombohedral (e) Hexagonal (f) Monoclinic (g) Triclinic

#### 1.11.2 Types of Unit Cells

(i) A unit cell having lattice points only at the corners is called simple or primitive unit cell. A crystal lattice having primitive unit cell is called simple crystal lattice.

(ii) A unit cell having lattice points at the centre of each face, in addition to the lattice points at the corners, is called face centred unit cell.

(iii) A unit cell having lattice points at the centre of the body, in addition to the lattice points at the corners is called body centred unit cell.

(iv) In an end centred unit cell, there are lattice points in the face centres of only one set of faces, in addition to the lattice points at the corners of the unit cell.
It may be noted that all the four types of unit cells are not possible for each crystal class. The various types of unit cells possible for different crystal class are given below:

<table>
<thead>
<tr>
<th>Crystal System or Class</th>
<th>Crystal Parameter</th>
<th>Possible type of Unit cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Cubic</td>
<td>( a = b = c ) ( \alpha = \beta = \gamma = 90^\circ )</td>
<td>Primitive (SCC), Body Centred (BCC), Face Centred (FCC)</td>
</tr>
<tr>
<td>2. Tetragonal</td>
<td>( a = b \neq c ) ( \alpha = \beta = \gamma = 90^\circ )</td>
<td>Primitive, Body centred</td>
</tr>
<tr>
<td>3. Orthorhombic</td>
<td>( a \neq b \neq c ) ( \alpha = \beta = \gamma = 90^\circ )</td>
<td>Primitive, Body centred, Face centred, End centred</td>
</tr>
<tr>
<td>4. Hexagonal</td>
<td>( a = b \neq c ) ( \alpha = \beta = 90^\circ, \gamma = 120^\circ )</td>
<td>Primitive</td>
</tr>
<tr>
<td>5. Rhombohedral</td>
<td>( a = b = c ) ( \alpha = \beta = \gamma \neq 90^\circ )</td>
<td>Primitive</td>
</tr>
<tr>
<td>6. Monoclinic</td>
<td>( a \neq b \neq c ) ( \alpha = \gamma = 90^\circ, \beta \neq 90^\circ )</td>
<td>Primitive and End centred</td>
</tr>
<tr>
<td>7. Triclinic</td>
<td>( a \neq b \neq c ) ( \alpha \neq \beta \neq \gamma \neq 90^\circ )</td>
<td>Primitive</td>
</tr>
</tbody>
</table>

Thus from the table above we can say there are 7 crystal types for which 14 different types of lattices (7 primitive, 3 body centred, 2 face centred, 2 end centred) are possible.

These 14 different types of crystal lattices are known as Bravais Lattices.

### 1.12 NUMBER OF ATOMS IN A UNIT CELL

An atom at the corner of a unit cell is shared by eight unit cells in the lattice and contributes 1/8 to a particular unit cell.
The atom at the face centre is shared by two unit cells and contributes 1/2 to a particular unit cell.
The atom at the body centre belongs entirely to one unit cell and contributes 1 atom to the unit cell.

By using the above rules let us calculate the number of atom in the 4 types of unit cells.

1. **Simple or Primitive Unit Cell**
   
   \[
   \text{No. of atoms per unit cell} = 8 \times \frac{1}{8} = 1 \text{ atom}
   \]

2. **Face Centred Unit Cell**
   
   \[
   \text{No. of atoms per unit cell} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4 \text{ atoms}
   \]

3. **Body Centred Unit Cell**
   
   \[
   \text{No. of atoms per unit cell} = 8 \times \frac{1}{8} + 1 = 2 \text{ atom}
   \]

4. **End Centred Unit Cell**
   
   \[
   \text{No. of atoms per unit cell} = 8 \times \frac{1}{8} + 2 \times \frac{1}{2} = 2 \text{ atom}
   \]

**1.13 Close Packing in Crystals**

In the formation of crystals the atoms (molecules or ions) try to pack as closely as possible so as to attain a state of maximum possible density and stability.

**1.13.1 Close Packing in Three Dimensions**

Since in different crystals, the units of pattern have different shapes and sizes, the actual mode of closest packing is different for different crystals. Here we will discuss two most efficient close packing, hexagonal close packing (hcp) and cubic close packing (ccp).

The atoms are assumed as solid spheres. First consider a first layer, in which atoms are placed such that they have hexagonal close packing (2 dimension). Fig. (1.10 (a))

![Close packing of spheres](image)

For close packing each sphere in the second layer rests in the hollow at the centre of the three touching spheres in the layers as shown in Fig. 1.10 (b). The spheres in the first layer are shown by solid lines while those in second layer are shown by broken lines.
Now there are two alternative ways in which the third layer can be arranged over the second layer. The third layer can lie vertically above the first if the spheres in the third layer rest in one set of hollows (marked by 'a' in first layer) on the top of second layer. Alternatively, the third layer can be different from the first layer if the spheres in the third layer lie on the other set of hollows (marked by 'c' in the first layer).

These two arrangements are equally efficient. In either type packing factor is 74% (Section 1.3.2). The first arrangement is called ABAB..... type, while the second is ABCABC..... type.

The ABAB..... type has hexagonal symmetry and is known as hexagonal close packing (hcp) Fig. 1.11(a).

The ABCABC..... type packing has cubic symmetry and is known as cubic close packing (Fig. 1.11(b)) has face centred cubic unit cell.

1.13.2 Packing Factor

Packing factor is a measure of how closely the atoms are packed in a crystal. It is defined as

\[
\text{Packing factor} = \frac{\text{Volume occupied by the atoms in a unit cell}}{\text{Volume of the unit cell}}.
\]

(i) Packing factor of a simple cubic lattice.
In simple cubic unit cell there is $8 \times \frac{1}{8} = 1$ atom per unit cell. Let $R$ be the radius of the atom and $a$ be the edge length of the cube.

Volume occupied by the atoms = $1 \times \frac{4}{3} \pi R^3$
Volume of unit cell = $a^3 = (2R)^3$

Packing factor = $\frac{\frac{4}{3} \pi R^3}{(2R)^3} = 0.52$

Therefore, % Packing factor = 52%.

(ii) Packing factor of face centred cubic lattice

There are 4 atoms per unit cell in a FCC lattice.

Volume occupied by 4 atoms = $4 \times \frac{4}{3} \pi R^3 = \frac{16 \pi R^3}{3}$

Diagonal $AC = 4R$ but in right angled triangle $ABC$, $AC = \sqrt{AB^2 + BC^2}$
\[ a = \sqrt{a^2 + a^2} = \sqrt{2} \ a \]

Therefore \( \sqrt{2} \ a = 4R \) or \( a = 2\sqrt{2} \ R \)

Volume of the unit cell \( a^3 = (R)^3 \)

Packing factor \( \frac{16}{3} \pi R^3 \frac{2}{\sqrt{2}R} = 0.74 \) or 74%

(iii) Packing factor of body centre cubic lattice

![Diagram of Unit cell of body centred cubic lattice](a) ![Diagram of Unit cell of body centred cubic lattice](b)

*Fig. 1.14 Unit cell of body centred cubic lattice*

There are 2 atoms per unit cell in a bcc lattice.

Volume occupied by 2 atoms \( 2 \left( \frac{4}{3} \pi R^3 \right) \)

Face diagonal \( AC = \sqrt{AB^2 + BC^2} = \sqrt{2a^2} \)

Body diagonal \( AD = \sqrt{BD^2 + a^2} = \sqrt{BD^2 + a^2} = \sqrt{3a} \)

Also \( AD = 4R \)

or \( = 4R \) or \( a = \frac{4}{\sqrt{3}} \ R \)

Volume of unit cell \( a^3 = \)

Packing factor \( \frac{8}{3} \pi R^3 \frac{2}{\sqrt{6}R} = 0.68 \) or 68%

Some examples of metallic solids having hcp, fcc and bcc crystal structures or arrangements are given belows.
1.14 SOME SPECIAL CRYSTAL STRUCTURES

1.14.1 Sodium Chloride Structure (Rock-Salt Structure)

Sodium chloride (NaCl) and many other ionic crystals crystallize in the rock salt structure, which is also known as sodium chloride structure.

In sodium chloride, chloride ion (Cl–) are considered as having cubic close packed structure (i.e. face centred cubic (fcc)). And the sodium ion (Na+) occupy octahedral voids in the cubic close packed type lattice of chloride ions.

![Unit cell of sodium chloride structure](image)

Each Cl– ion is surrounded by six Na+ ions. Similarly, each Na+ ion is surrounded by six Cl– ions. Therefore NaCl crystal has 6 : 6 co-ordination.

Radius ratio \( r_{\text{Na}}/r_{\text{Cl}} \) for sodium chloride is 0.54.

The unit cell of sodium chloride has 4 Na+ ion and 4 Cl– ion as calculated below:

Number of Na+ ion = 12 (at edge centres) \( \times \) 1/4 + 1 (at body centre) = 4

Number of Cl– ion = 8 (at corners) \( \times \) 1/8 + 6 (at face centre) = 4.

Examples: Other alkali halides that crystallize in this structure are KCl, KBr, NaI, RbI, RbF. Examples of oxides with this structure are MgO, CaO, SrO, BaO, CdO, MnO, FeO, CoO and NiO.

1.14.2 Cesium Chloride (CsCl) Structure

In this structure, the Cl– ions are at the corners whereas Cs+ ion is at body centre or vice versa. The structure can be viewed as a body centred cubic lattice (BCC).
Fig. 1.16  Unit cell of cesium chloride structure

This structure has 8 : 8 co-ordination.

Radius ratio for CsCl is 0.91.

The unit cell of CsCl has one Cs\(^+\) ion and one Cl\(^-\) ion per unit cell as calculated below

\[
\text{No. of Cl}^- \text{ ions} = \frac{1}{8} \times 8 = 1
\]

\[
\text{No. of Cs}^+ \text{ ions} = 1 \times 1 = 1
\]

**Examples:** Examples of compounds that crystallize in this structure, besides CsCl, are Ag, Mg, CuZn (brass), AlNi, CaBr, Cal, TICl, TIBr etc.

1.14.3 Diamond Structure

The diamond cubic structure is a very important structure as besides diamond, the elemental semiconductors silicon (Si) and germanium (Ge) also crystallize in this structure.

Fig. 1.17  Unit cell of diamond cubic structure
The unit cell in this case is identified with the cubic structure. This structure can be viewed as two interpenetrating FCC lattices, which are displaced by one quarter of a body diagonal, along the body diagonal direction.

Although there are atoms at each corner and at the centre of each face, indicating an FCC structure, there are four atoms within the unit cell as well. Thus the structure is not a true FCC. Two atoms form a basis positioned at (0, 0, 0) and $(0, 0, 0)$. Each atom has four nearest neighbours in a tetrahedral coordination with a bond angle of 109.5°. The tetrahedral bonding is shown in the figure by thick dark lines.

Packing factor of diamond cubic lattice:
No. of atoms in the unit cell = $1/8 \times 8$ (at corner) + $\times 6$ (at face centre) + 4 (at body centre) = 8

Volume occupied by the 8 atom = $8 \times \frac{4}{3} \pi R^3$

From Fig. 1.17 $2R = \sqrt{a^2 + a^2 + a^2}$ or $2R = a$ or $a = R$.

Hence volume of a unit cell = $a^3 = \frac{8}{3} \pi R^3$

Packing factor = $\frac{8 \times \frac{4}{3} \pi R^3}{(8 + 6 + 4) \pi R^3} = 0.34$ or 34%.

Thus the atoms are loosely packed in diamond crystal structure.

1.14.4 Zinc Blend Structure (or ZnS structure)

This structure is similar to a diamond cubic structure except that there are two different atoms. For example in cubic zinc sulphide structure one atom is zinc and the other sulphur.

In zinc sulphide structure, a sulphide ion has cubic closed packed (or face centred cubic (fcc)) lattice and zinc ions occupy half of the total number of tetrahedral voids.
Each sulphide ion is tetrahedrally surrounded by four zinc ions and each zinc ion is surrounded by four sulphide ions. Thus ZnS has 4:4 coordination.

There are 4 Zn\(^{2+}\) ions and 4 S\(^{2-}\) ions per unit cell as calculated below.

No. of S\(^{2-}\) ion = 1/8 \times 8 (at corner) + 1/2 \times 6 (at face centre) = 4
No. of Zn\(^{2+}\) ions = 4 (within the body) \times 1 = 4

This number of ZnS units per unit cell is equal to 4

Co-ordinates of S\(^{2-}\) ions are – (0, 0, 0) \(\ldots\) (0, , ) \(\ldots\) (0, , 0)

Co-ordinates of Zn\(^{2+}\) ions are – (, , ) \(\ldots\) (, , ) \(\ldots\) (, , )

**Example:** Most important compound semiconductors have this crystal structure, GaAs being the most commonly known. Examples of other materials that crystallize in this structure are CuF, CuCl, CuBr, AgI, CdS, SiC, InSb, CuCl etc.

### 1.15 Bonding in Solids

The attractive force which holds various constituents (atoms, ions etc.) together to form a solid is called chemical bond. According to strength, chemical bonds can be grouped into primary and secondary bonds.

Primary bonds are stronger than the secondary bonds. Ionic, covalent and metallic bonds are all primary bonds. Secondary bonds includes Van der Waals bond and hydrogen bond.

Depending upon the nature of interparticle forces (chemical bonding), solids are broadly classified into four different categories

- **Ionic Solids:** Ionic bonding
- **Covalent Solids:** Covalent bonding
- **Metallic Solids:** Metallic bonding
- **Molecular Solids:** Molecular bonding.

#### 1.15.1 Ionic Bond

Ionic bond is formed by the transference of one or more electrons from one atom to the other. This type of bond usually comes into existence between a metal and a non-metal atom.

The metallic atom (electropositive) loses its valence electrons and changes into a positive ion (cation), while non-metallic atom (electronegative) gains electrons and get converted into negative ion (anion). The oppositely charged ions are held together by electrostatic force of attraction.

For example: Consider the formation of sodium chloride (NaCl).

Sodium Na (2, 8, 1) has only 1 electron in its valence shell. In order to acquire the configuration of nearest noble gas Ne (2, 8) it has to loose its valence electron.

Chlorine atom, Cl (2, 8, 7) on the other hand, has seven electrons in its valence shell. It can acquire the configuration of nearest noble gas Ar (2, 8, 8) by gaining one electron.

Thus sodium atom transfers its valence electron to chlorine atom resulting in the formation of sodium ion (Na\(^{+}\)) and chloride ion (Cl\(^{-}\)) respectively. The electrostatic force of attraction holds these oppositely charged ions together. The reaction is represented as
It may be noted that ion has a uniform field of influence around it, so the binding force between the ions is same in all directions. Hence the ionic bonding is non-directional in nature.

Thus ionic solids are those in which the constituent particles are ions of opposite charges and interparticle forces among them are ionic bonds. Ions of opposite charges are closely packed in a definite geometric pattern so that each positive ion is surrounded by many negative ions and vice versa. This regularly ordered three-dimensional arrangement of ions is called ionic crystal. For example, solid NaCl (discussed in Section 1.14).

1.15.2 Covalent Bond

A force, which binds atoms of same or different elements by mutual sharing of electrons, is called a covalent bond. The atoms involved in bond formation contribute equal number of electrons for sharing. The shared electrons become a common property of both the atoms and contribute a bond between them.

When the atoms share one electron pair, the bond formed is called single covalent bond. However, if two electron pairs are shared, the bond formed is called double covalent bond. Similarly, where the atoms share three electron pairs, the bond is called triple covalent bond. The double and triple covalent bonds are collectively called multiple covalent bonds.

Thus in covalent solids, the constituent particles are atoms of same or different elements (having similar electronegativities) and the interparticle forces are covalent bonds or we can say the covalent solids have crystal made up of giant network of atoms linked to each other by covalent bonds.

**Example:** Diamond is a covalent solid (discussed in Section 1.14) containing carbon atoms. Similarly carborundum (silicon carbide SiC) is a covalent solid containing silicon and carbon atoms. Other covalently bonded solids are Si, Ge etc.

Covalent bond energy is highest for all bond types, leading to very high melting points and very hard solids: diamond is one of the hardest known materials. The highly directional nature and strength of covalent bond make these materials non-ductile (or non-malleable).
1.15.3 Metallic Bond

Metals constitute about three fourth of all the known elements. The attractive force, which bonds various metal atoms together, is called metallic bond.

Let us understand the nature of bonding in metals.

Metal atoms have only a few valence electrons, which are loosely held by the nucleus (because of small ionisation energy of metals). Since the valence electrons are loosely held, they can easily leave the field of influence of one metal ion and enter the field of influence of the other. Thus the electrons become collectively shared by all the ions. The valence electrons therefore become delocalised and form an electron gas or electron cloud. This simultaneous force of attraction between the “free” electrons and the positive ions is responsible for holding the metal atoms and is known as metallic bond. Because of collective sharing of electrons the bond is non-directional.

![Metallic bonding](image)

Metallic crystal, due to non-directional nature of bonding, consists of closely packed metal atoms in three dimensions. The positive ion cores occupy fixed positions called lattice points while space between the ion cores is occupied by free valence electrons.

Thus most metals crystallize in FCC and HCP structures. The close packing with strong metallic bonds leads to high melting point and high modulus of elasticity. Due to non-directional nature of bonds pure metals are ductile and malleable. The high electrical and thermal conductivity of metals are due to presence of free electrons (also discussed in Chap. 2).

1.15.4 Secondary Bonding

Van der Waals Bonding

The cohesive energy in a Van der Waals bond is due to the interaction between two dipoles. Van der Waals bonding exists in non-polar molecules i.e. those in which centres of positive and negative charge cloud coincide and therefore have no permanent dipole moment.

To understand this bonding let us consider a monatomic molecule of Neon (Ne). Each Ne atom has its electron cloud symmetrically distributed around the nucleus. But as a result of momentary fluctuations in the charge distribution around the atom, the electron distribution of the atom may become unsymmetrical with slight increase of electron density on one side.
This would lead to the separation of positive and negative charge clouds at a particular instant. In other words, the molecule develops a temporary induced dipole moment. This induced dipole influences the electron distribution of other molecules in its close vicinity and induces dipole moment in them also. The attraction forces between the induced dipoles are called Van der Waals forces. The dipole-induced-dipole attraction is non-directional in nature.

Solids in which constituent molecules (or atoms) have been bonded by Van der Waals forces are known as molecular solids. Examples: O\textsubscript{2}, H\textsubscript{2}, CH\textsubscript{4} and solid inert gases.

**Hydrogen Bonding**

In many molecules, the centres of the positive and negative charges do not coincide i.e. they have permanent dipole moment.

Consider the example of water molecule (H\textsubscript{2}O). Since the electronegativity of oxygen is greater than hydrogen, therefore, the oxygen atom pulls the bonding electrons (negative charge) to itself more strongly than hydrogen does. These results in a net negative charge at the oxygen end and a net positive charge at the hydrogen end of the molecule. Due to this imbalance in electrical charge, the water molecule possesses a permanent dipole moment.

The bond that is formed between water molecules due to attraction between the positively charged hydrogen end of a molecule and the negatively charged oxygen end of another molecule is called the hydrogen bond (Fig. 1.22).

![Fig. 1.21 Hydrogen bonding](image-url)

![Fig. 1.22 Hydrogen bond between water molecules.](image-url)
Hydrogen bonds are evidently directional. Hydrogen bond between water molecules is responsible for the unusual properties of ice and water.

**Examples:** Hydrogen bonding is found in component containing hydrogen.

Typical examples of hydrogen bond are the bonding in HF, HCl, ice etc.

![Diagram of Hydrogen Bond in HF](image)

Fig. 1.23  *Hydrogen bond in HF*

Many other inorganic materials containing groups such as – COOH, – OH and – NH$_2$ exhibit hydrogen bonding.