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Chemistry

With Value Based Questions

Vol. I

Class XII

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Pradeep's
New Course

Chemistry

Vol. I

Strictly according to new syllabus & latest guidelines of CBSE and state boards of Punjab, Haryana, H.P., J & K, Kerala, Nagaland, Manipur, Rajasthan, Jharkhand, Bihar, Uttarakhand, Karnataka, Assam, West Bengal, A.P. etc. for class XII of +2 stage. Also for JEE-Main, JEE-Advanced, NEET and other Competitive Examinations.

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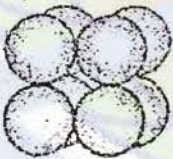
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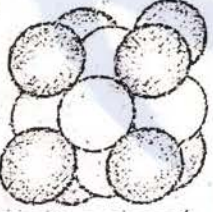
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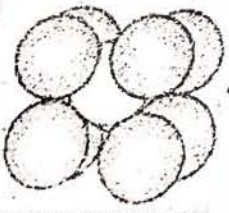
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1.1. General Introduction

The different types of substances that are present around us are solids or liquids or gases. However, solids are more common than liquids and gases. The main point in which the solids differ from liquids and gases is the fact that gases and liquids possess fluidity, i.e., they can flow and hence they are called fluids whereas solids do not possess fluidity; instead, they possess rigidity. The reason for fluidity of gases and liquids lies in the fact that their constituent particles are free to move about whereas rigidity of solids is due to the fact that their constituent particles have fixed positions and can only oscillate about their mean positions. Further, because of rigidity possessed by the solids, they have definite shape and definite volume. Hence, a solid may be defined as follows:

A solid is defined as that form of matter which possesses rigidity and hence possesses a definite shape and a definite volume.

Now, our aim will be to know the following about the solids which we shall discuss in this unit:

- Why do some substances exist as solids?
- What are the general characteristics of solids?
- How can solids be classified into amorphous and crystalline solids?
- How can crystalline solids be further classified into different types on the basis of the nature of the constituent particles and the binding forces operating between them?
- How different solids are put to different uses on the basis of their properties?
- How are the properties of the solids related to the structure of the solids?
- How does the correlation between structure and properties of solids help in the discovery of new solid materials with desired electrical or magnetic properties or biodegradable polymers for packaging, biocompliant solids for surgical implants etc.?
- How are the properties of solids modified due to structural imperfections or by the presence of impurities in very small amounts?

1.2. Why Do Some Substances Exist as Solids?

As already discussed in class XI, whether a substance will exist as a solid or a liquid or a gas depends upon the net effect of the following two opposing forces:

- Intermolecular forces.** These are the forces existing among the constituent particles which try to keep the constituent particles close together.
- Thermal energy.** This is the energy possessed by the constituent particles due to temperature. This energy tries to keep the constituent particles apart as it tends to make them move faster.

At low temperature, the thermal energy is quite low, but intermolecular forces are so strong that the particles are brought very close together. As a result, the constituent particles occupy fixed positions and are unable to move except that they can oscillate about their mean positions. Hence, the substance exists in the solid state.

1.3. General Characteristics of Solid State

As explained above, a solid has the following properties:

- The constituent particles are very closely packed, i.e., intermolecular distances are very small
- The constituent particles occupy fixed positions and can only oscillate about their mean positions.

Because of these properties, the solids possess the following characteristic properties:

- They possess rigidity.
- They have high density.
- They possess definite shape and definite volume.
- They are incompressible.

1.4. Classification into Crystalline and Amorphous Solids

The various solids are classified into the following two types:

- Crystalline solids.** All solid elements (metals and non-metals) and compounds exist in this form.
- Amorphous solids.** e.g., rubber, glass, pitch, tar, fused silica, plastics, polymers of high molecular mass etc.

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1.4.1. Points of Difference between a Crystalline solid and an Amorphous solid

(i) **Arrangement of their constituent particles.** In a crystalline solid, the constituent particles (i.e., ions, atoms or molecules) are arranged in a definite geometric pattern in all the three dimensions. The order is so regular that knowing the arrangement at any one site, that at any other site can be predicted. This is called **long range order**.

In fact, a crystalline solid consists of a large number of small crystals each of which has the same regular pattern or arrangement of particles. This arrangement repeats itself periodically over the entire crystal.

On the other hand, in an amorphous solid, there is a regular arrangement of particles in a small region only. This is called **short range order**. Thus, whereas crystalline solids possess both short range and long range order, amorphous solids possess only short range order.

For example, the structures of crystalline quartz and that of quartz glass are shown in Fig. 1.1(a) and (b) respectively.

Although both the structures look to be identical but there is no long range order in structure (b).

For this reason, whereas crystalline solids have definite geometrical shapes, amorphous solids have irregular shape (i.e., no definite geometric shape).

Thus, crystalline and amorphous solids may be defined as follows :

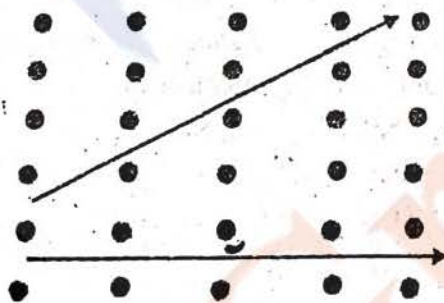
A solid is said to be crystalline if its various constituent particles (i.e. ions, atoms or molecules) are arranged in a definite geometric pattern in three dimensional space so that there is short range as well as long range order of the constituent particles. On the other hand, a solid is said to be amorphous if there is no regular arrangement of its constituent particles or at the most, there is only a short range order of its constituent particles.

(ii) **Melting points.** The crystalline substances possess sharp melting points whereas the amorphous substances melt gradually over a temperature range.

For this reason, crystalline solids have definite heats of fusion whereas amorphous solids do not have definite heats of fusion.

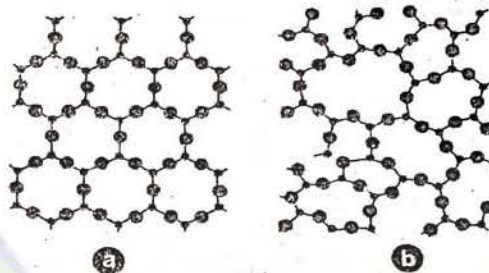
(iii) **Isotropy and Anisotropy.** In case of amorphous substances, properties like electrical conductivity, refractive index, thermal expansion etc. are identical in all directions just as in case of gases or liquids. This property is called **isotropy** and the substances showing this property are called isotropic. On the other hand, in case of crystalline substances, the properties mentioned above have different values in different directions. This type of behaviour is called **anisotropy** and the substances exhibiting this type of behaviour are called anisotropic. Thus, whereas amorphous substances are isotropic in nature, the crystalline substances are anisotropic. The anisotropy exhibited by crystalline substances is obviously due to the fact that in making measurements in different directions, different types of particles fall on the way, as shown in Fig. 1.2.

FIGURE 1.2



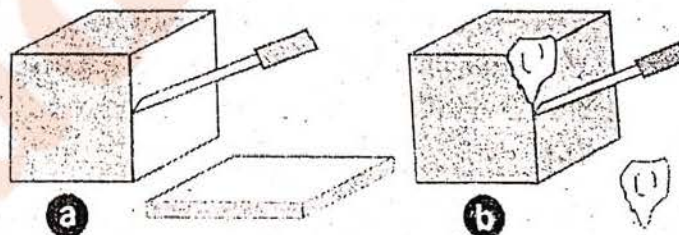
Anisotropy exhibited by crystalline substances

FIGURE 1.1



Two dimensional structure of (a) quartz and (b) quartz glass

FIGURE 1.3



(a) A crystalline solid undergoes a clean cleavage
(b) An amorphous solid undergoes an irregular cut

(iv) **Cleavage with a knife.** A crystalline solid on being cut with a sharp knife gives a clean cleavage whereas an amorphous solid undergoes an irregular breakage as shown in Fig. 1.3.

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In fact, only the crystalline solids are the true solids whereas amorphous solids are considered to be highly supercooled liquids of very high viscosity and are called pseudo solids. This is supported by the fact that the glass of the window panes of some very old houses are found to be thicker at the bottom than at the top, showing some fluidity possessed by glass.

Further, it may be pointed out that due to short range order possessed by amorphous solids, small parts of the amorphous solid may be crystalline while the rest may be non-crystalline. These crystalline parts of the amorphous solids are called crystallites.

It may also be noted that the window glass of the old buildings looks milky. This is because due to heating during the day and cooling at nights, i.e., annealing over a number of years, glass acquires some crystalline character.

Thus, the main points of difference between a crystalline solid and an amorphous solid may be summed up as follows :

TABLE 1.1 Comparison of main characteristics of crystalline and amorphous solids

- | CRYSTALLINE SOLID | AMORPHOUS SOLID |
|---|---|
| (i) The constituent particles are arranged in a regular fashion containing short range as well as long range order. | (i) The constituent particles are not arranged in any regular fashion ; there may be at the most some short range order only. |
| (ii) They have definite geometric shapes. | (ii) They have irregular shapes. |
| (iii) They have sharp melting points. | (iii) They melt over a range of temperature. |
| (iv) They are anisotropic. | (iv) They are isotropic. |
| (v) They have definite heats of fusion. | (v) They do not have definite heats of fusion. |
| (vi) They undergo a clean cleavage. | (vi) They undergo an irregular cut. |
| (vii) They are true solids. | (vii) They are pseudo solids or supercooled liquids. |

RETAIN IN MEMORY

Any material can be made amorphous or glassy either by rapidly cooling its melt or freezing its vapours. For example, silica (SiO_2) crystallizes as quartz in which SiO_4 tetrahedra are linked in a regular manner but on melting and then rapid cooling, it gives glass in which SiO_4 tetrahedra are randomly joined to each other. Thus, quartz is crystalline SiO_2 whereas silica glass is amorphous SiO_2 . Similarly, many complex materials including metallic alloys have been converted into the glassy form.

1.4.2. Uses of Amorphous Solids

Amorphous solids are very useful materials in our everyday life. A few applications are given below :

- The most widely used amorphous solids are the inorganic glasses, which find application in construction, house-ware, laboratory ware, etc.
- Another well known amorphous solid is rubber which is used in making tyres, shoe soles, etc.
- A large number of plastics which are amorphous solids are being used in articles of everyday life.
- Amorphous silica has been found to be the best material for converting sunlight into electricity (in photovoltaic cells).

1.5. Classification of Crystalline Solids

Based upon the nature of the constituent particles and the binding forces present between them, the crystalline solids are further classified into the following four categories :

- Ionic solids
- Molecular solids
- Covalent or Network solids
- Metallic solids.

Now, let us discuss each of these categories one by one.

1. Ionic solids. In these crystalline solids, the constituent particles are positive and negative ions (i.e., cations and anions), e.g., Na^+ and Cl^- ions in case of NaCl , arranged in the three dimensional space. These

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ions are held together by strong coulombic, i.e., electrostatic forces of attraction. Some of their important characteristics are below :

- (i) Because of strong electrostatic forces of attraction, they have high melting and boiling points.
- (ii) They are electrical insulators in the solid state because their ions are not free to move about. However, in the aqueous solution or in the molten state, they are good conductors of electricity because ions become free.
- (iii) They are soluble in polar solvents but insoluble in non-polar solvents.
- (iv) Because of strong electrostatic forces of attraction, the ions are closely packed and hence ionic solids are hard. However, they are brittle because their stability depends upon preservation of their geometric pattern.

2. Molecular solids. In these solids, the constituent particles are molecules. Depending upon the nature of molecules, these are further sub-divided into the following three types :

(a) **Non-polar molecular solids.** These are those crystalline solids in which the constituent particles are either atoms like those of noble gases (helium, neon, argon etc.) or non-polar molecules like H_2 , Cl_2 , I_2 , CH_4 etc. The forces operating between them are weak dispersion forces or London forces (a type of van der Waals forces), as already studied in class XI, i.e., momentary dipole-induced dipole forces as shown in Fig. 1.4 for the case of helium.

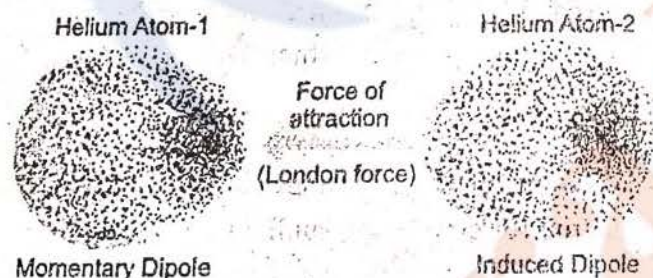
Their main characteristics are as follows :

- (i) These solids are generally soft because of weak intermolecular forces present in them.
- (ii) They are non-conductors of electricity as there are no ions present.
- (iii) As they are soft, they have low melting and boiling points.
- (iv) Due to weak intermolecular forces present in them, they are usually gaseous or liquids at room temperature and pressure.

(b) **Polar molecular solids.** These are those crystalline solids in which the constituent particles are polar molecules like HCl , SO_2 etc. The forces holding these molecules together are dipole-dipole forces of attraction (which are again a type of van der Waals forces) as shown in Fig. 1.5.

These intermolecular forces of attraction are comparatively stronger than London dispersion forces. These solids show the following characteristics :

- (i) They are soft.
- (ii) They are non-conductors of electricity.
- (iii) Their melting and boiling points are comparatively higher than non-polar molecular solids, though not so high.
- (iv) As their melting and boiling points are not so high, they also exist as gases or liquids at room temperature and ordinary pressure.

FIGURE 1.4

Weak London dispersion forces.

FIGURE 1.5

Dipole-dipole forces of attraction.

(c) **Hydrogen-bonded molecular solids.** In these solids, the constituent particles are such molecules which contain hydrogen atom linked to a highly electronegative atom small in size such as F, O or N, e.g., in H_2O , NH_3 , etc. Hence, the intermolecular forces of attraction existing among these molecules are the strong hydrogen bonds. These solids show the following characteristics :

- (i) They exist as volatile liquids or soft solids at room temperature and ordinary pressure.
- (ii) They are non-conductors of electricity.
- (iii) Their melting and boiling points are generally higher than the molecular solids of the first two types

3. Covalent or Network solids. These are those crystalline solids in which the constituent particles are non-metal atoms linked to the adjacent atoms by covalent bonds throughout the crystal. As a result, a network of covalent bonds is formed. Hence, they form giant molecules. One of the most common examples of the crystals of this type is that of diamond in which the carbon atoms are linked together by covalent bonds to give a three dimensional structure as shown in Fig. 1.6. Another very common example is that of silicon carbide (SiC).

The main characteristics of these solids are as under :

- (i) As covalent bonds are strong and directional in nature, these solids are very hard and brittle.
- (ii) They have extremely high melting points and may even decompose before melting.
- (iii) They are insulators and do not conduct electricity.

Exception. Graphite is also a covalent solid but it is soft and a good conductor of electricity. Its exceptional behaviour is due to its typical structure as shown in Fig. 1.7. In this case, carbon atoms are arranged in different layers. In each layer, every carbon atom is linked to three neighbouring carbon atoms. Thus, the fourth electron of each carbon atom is free to move about. Because of the presence of these free electrons in different layers, graphite becomes a good conductor of electricity. Further, the distance between the adjacent layers is greater than carbon-carbon bond length. Hence, these layers are not bonded to each other and can easily slip over each other. For this reason, graphite is soft and acts as a good solid lubricant.

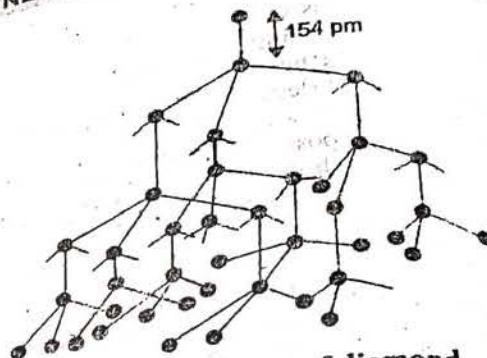
4. Metallic solids. In case of metals, the constituent particles are positively charged metal ions and free electrons. These are produced from metal atoms because metal atoms have low ionization energy and can easily lose their valence electrons to leave behind positively charged ions (called kernels). These electrons can easily flow throughout the metal crystal like water in the sea. Hence, we call it a sea of free electrons (Fig. 1.8). Each metal atom contributes one or more electrons towards this sea of mobile electrons. These mobile electrons are simultaneously attracted by the positive ions and hence hold these positive ions together.

The force that holds the metal ions together in the crystal is called metallic bond.

These solids show the following characteristic properties :

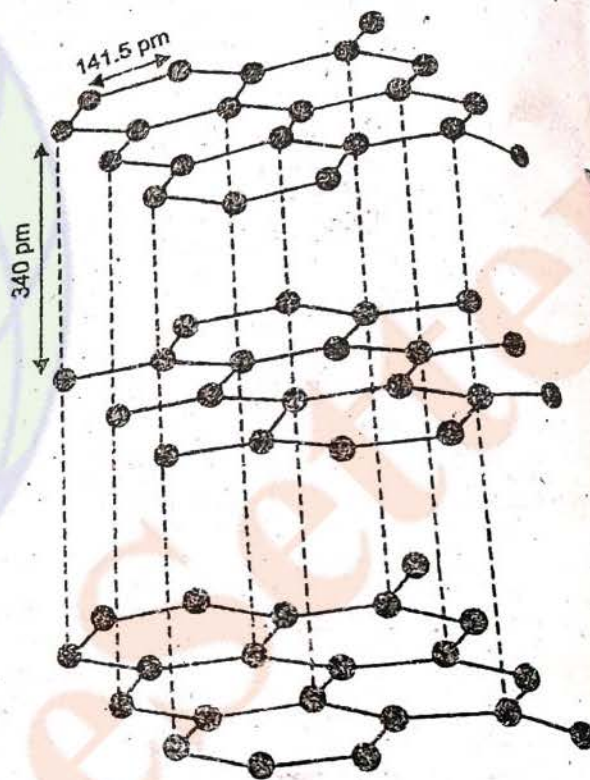
- (i) They possess high electrical and thermal conductivity. This is because on applying electric current, electrons start flowing towards positively charged electrode.

FIGURE 1.6



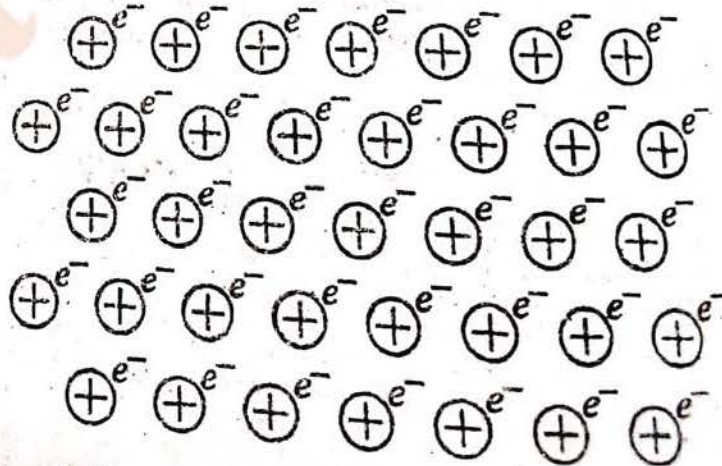
Network structure of diamond

FIGURE 1.7



Structure of graphite

FIGURE 1.8



Metallic solid-Positive ions in a sea of mobile electrons (electron sea model)

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Similarly, heat given to one part is carried by the electrons to all parts of the metal.

- (ii) They possess lustre and colour in some cases. This is also explained on the basis of free electrons.
 (iii) They are highly malleable and ductile.

This is because unlike ionic crystals, the positions of the positive ions can be altered without destroying the crystal because of uniform charge distribution provided by freely moving electrons. For this reason, metals can be easily deformed.

- (iv) As the positive ions are closely packed in the crystal, most of the metals possess high melting points and high densities.

To sum up, the various types of crystalline solids, their constituent particles occupying the points, the type of attractive forces, their properties and some examples are given in Table 1.2.

TABLE 1.2: Different types of crystalline solids

Type of solid	Constituent particles	Nature of binding forces	Examples	Physical nature	Electrical conductivity	Melting point	Other characteristics
1. Ionic solids	Positive and negative ions	Coulombic or Electrostatic forces	NaCl, LiF, MgO, ZnS, CaF ₂	Hard but brittle	Insulators in solid state but conductors in molten state or aqueous solution	High	Soluble in polar solvents, insoluble in non-polar solvents
2. Molecular solids							
(i) Non-polar	Atoms of noble gas or non-polar molecules	London dispersion forces	Ar, H ₂ , I ₂ , solid CO ₂ (dry ice) CH ₄	Soft	Insulator	Very low	Low density and volatile
(ii) Polar	Polar molecules	Dipole-dipole attractions	HCl, SO ₂	Soft	Insulator	Low	
(iii) Hydrogen bonded	Molecules containing H linked to F, O or N	Hydrogen bonding	H ₂ O (ice), NH ₃	Soft	Insulator	Low	
3. Covalent or Network solids	Atoms	Covalent bonds	C (diamond), SiO ₂ (quartz), SiC, AlN C (graphite) (Exception)	Very hard Soft	Insulators Conductor	Very high Very high	
4. Metallic solids	Positive ions in a sea of mobile electrons	Metallic bonds	All metals and alloys	Hard	Conductor in solid state as well as molten state	Fairly high	Malleable and ductile and possess lustre

SUPPLEMENT YOUR KNOWLEDGE

Isomorphism and Polymorphism. When two or more crystalline solids having similar chemical composition exist in the same crystalline form or structure, the property is called isomorphism, e.g., Na₃PO₄ and Na₃AsO₄. On the other hand, when a particular substance exists in more than one crystalline form, the property is called polymorphism, e.g., calcium carbonate exists in two crystalline forms called *calcite* and *aragonite*. In case of elements, this property is called 'allotropy'.

CURIOSITY QUESTION

Q Why is glass of window panes of very old buildings found to be thicker at the bottom than at the top and why is it milky?

Ans. Glass is an amorphous solid which is a supercooled liquid of high viscosity and hence possesses fluidity. Due to this property it is thicker at the bottom than at the top. Milkiness of glass is due to the fact that it undergoes heating during the day and cooling at night, i.e., annealing over a number of years. As a result, it acquires some crystalline character.

1.6. Space Lattice or Crystal Lattice and Unit Cell

Space lattice is a regular repeating arrangement of points in space. As it is a regular repeating arrangement, to describe the space lattice completely, we can choose a small part of the lattice, which when repeated in different directions produces the complete space lattice. This small portion of the lattice is called 'unit cell'. To understand space lattice and unit cell, we shall discuss first two dimensional and then three dimensional lattices.

A. Two Dimensional Lattices. A two dimensional lattice is a regular arrangement of points in the plane of the paper as shown in Fig. 1.9 (a). We suitably choose four points and connect them to obtain the unit cell. In some cases, the unit cell may have an interior point also. Such unit cells are called centred unit cells. The unit cell that does not contain any interior point is called primitive unit cell. There are five types of two dimensional lattices as shown in Fig. 1.9 (a) with their unit cells as follows :

- (i) Square lattice
- (ii) Rectangular lattice
- (iii) Parallelogram lattice
- (iv) Rhombic lattice
- (v) Hexagonal lattice

- Square
- Rectangle
- Parallelogram
- Rectangular with interior point
- Rhombus with an angle of 60°

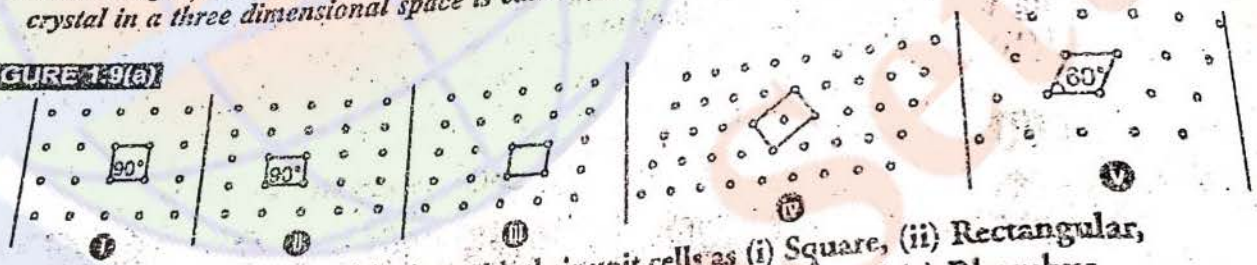
The complete lattice can be generated by repeatedly moving the unit cell in the direction of its edges by a distance equal to the cell edge, as shown in Fig. 1.9 (b).

Such two dimensional lattices are often seen in the wall papers and tiled floors.

B. Three Dimensional Crystal Lattices. As mentioned earlier, the constituent particles of a crystalline solid are arranged in a definite fashion in the three dimensional space. Representing the constituent particles by points, one such arrangement is shown in Fig. 1.9 (c).

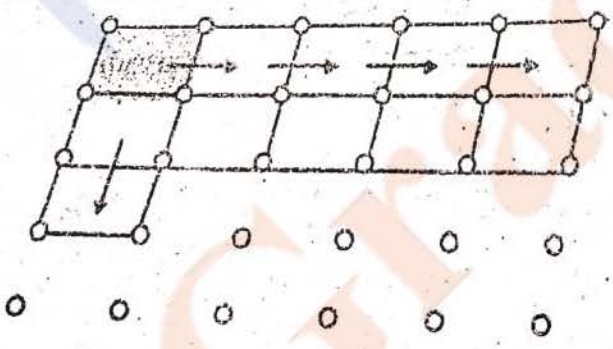
Such a regular arrangement of the constituent particles (i.e., atoms, ions or molecules) of a crystal in a three dimensional space is called crystal lattice or space lattice.

FIGURE 1.9(a)



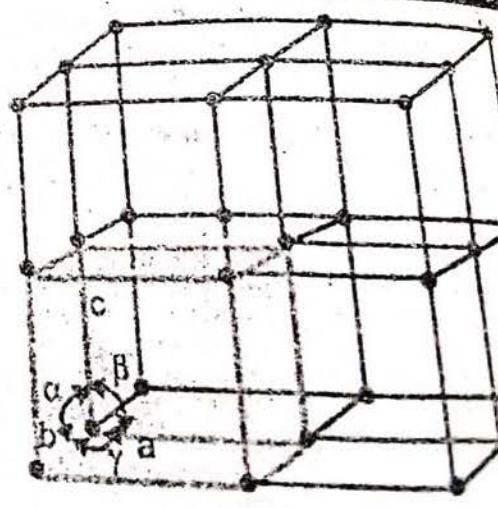
Five two dimensional lattices with their unit cells as (i) Square, (ii) Rectangular, (iii) Parallelogram, (iv) Rectangular with interior point and (v) Rhombus

FIGURE 1.9(b)



Generating complete two dimensional lattice by repeatedly moving the unit cell in the direction of the cell edges by distance equal to cell edge

FIGURE 1.9(c)



Space lattice and unit cell

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Some Characteristics of a Crystal Lattice. These are given below :

- (i) Each point in the crystal lattice represents a constituent particle which may be an atom, a molecule or an ion.
- (ii) Each point in the lattice is called lattice point or lattice site.
- (iii) The points are joined by lines just to represent the geometry of the lattice.

Unit Cell. From the complete space lattice, it is possible to select a smallest three dimensional portion (as shown by coloured lines in Fig. 1.9c) which repeats itself in different directions to generate the complete space lattice. This is called a 'unit cell'. Thus, a unit cell may be defined as follows :

The smallest three dimensional portion of a complete space lattice which when repeated over and again in different directions produces the complete space lattice is called the unit cell.

The situation may be compared with that of a thick wall made of bricks where the brick is similar to the unit cell and the wall to the complete space lattice.

The unit cell may be considered as the 'fundamental building block' of the crystal lattice because the lattice can be constructed by stacking the unit cells.

Parameters of a unit cell. A unit cell is characterised by the following parameters which decide the size and shape of the unit cell :

(i) Its dimensions (lengths) along the three edges a , b and c (as shown in Fig. 1.9c). These edges may or may not be mutually perpendicular.

(ii) Angles between the edges, i.e., angle α between the edges b and c , angle β between the edges a and c and angle γ between the edges a and b .

Thus, a unit cell is characterised by six parameters, i.e., axial lengths a , b and c and axial angles α , β and γ .

Types of Unit Cells. Based upon the parameters of the unit cells (i.e. lengths a , b and c and the angles α , β and γ), there are seven types of unit cells. These are also called *crystal systems* or *crystal habits* because any crystalline solid must belong to any one of these unit cells. These different types of crystal systems along with their characteristics and examples are listed in Table 1.3 and are shown in Fig. 1.10 on page 1/10.

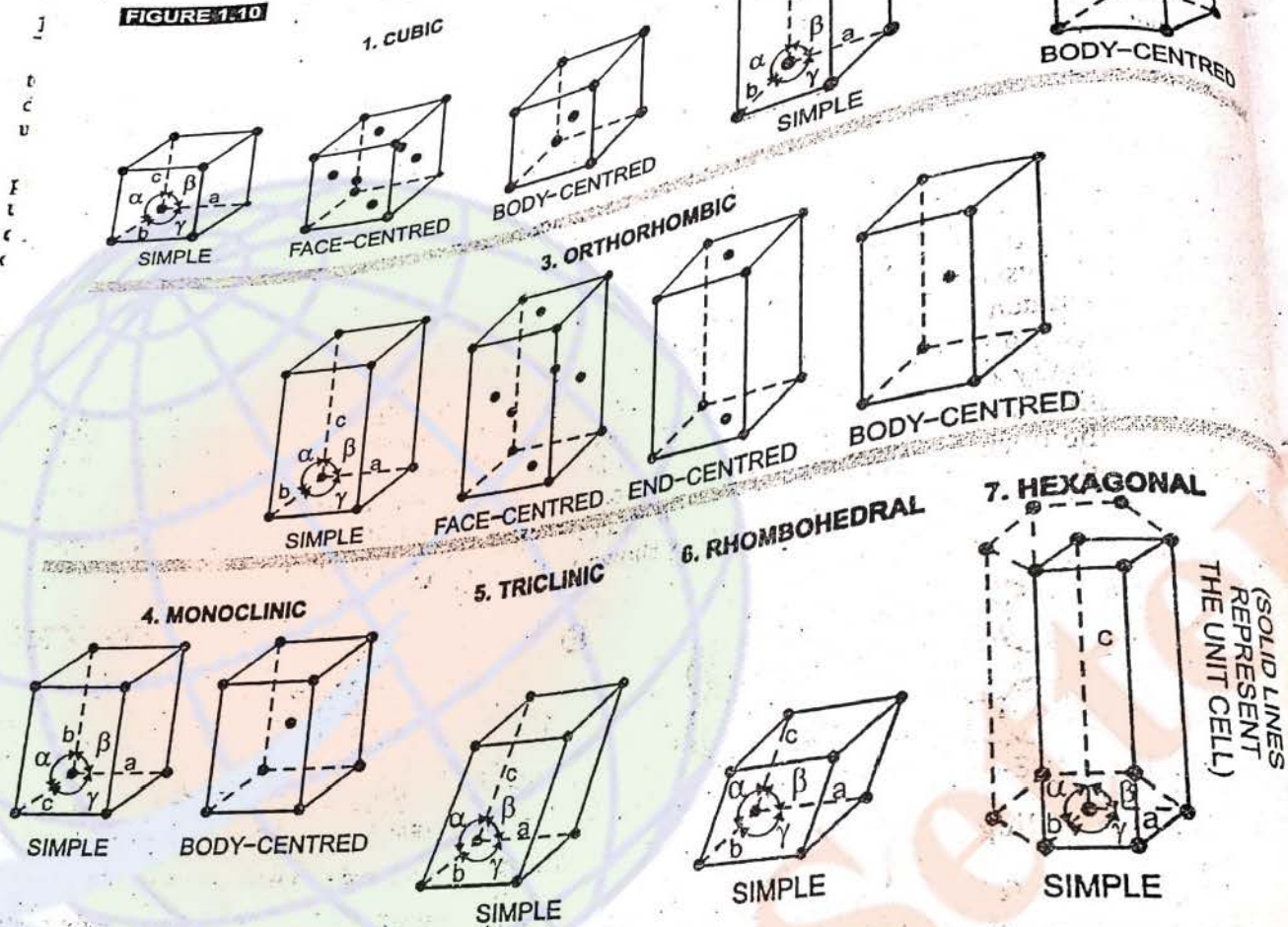
TABLE 1.3 Seven types of unit cells or crystal systems

SYSTEM	AXIAL LENGTHS	AXIAL ANGLES	EXAMPLES
1. Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	Cu, NaCl, KCl, Alums, Diamond, Zinc blende
2. Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	White tin (Sn), SnO_2 , TiO_2 , CaSO_4
3. Orthorhombic or Rhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	KNO_3 , K_2SO_4 , BaSO_4 , PbCO_3 , CaCO_3 Rhombic sulphur
4. Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta$	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, PbCrO_4 , Monoclinic sulphur
5. Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{K}_2\text{Cr}_2\text{O}_7$, H_3BO_3
6. Rhombohedral or Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	NaN_3 , ICl, As, Sb, Bi, Calcite (CaCO_3)
7. Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	Cinnabar (HgS), Ice, Graphite, Mg, Zn, Cd, ZnO , CdS , AgI, PbI_2

Note that cubic is the most symmetrical while triclinic is the most unsymmetrical system.

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FIGURE 1.10



Seven types of Unit cells or Crystal systems

Types of Lattices. In the various types of unit cells described above, it was assumed that the particles are present only at the corners of the unit cells. However, it has been observed that the particles may be present not only at the corners but may also be present at some other special positions within the unit cell. Hence, unit cells may broadly be divided into the following two categories :

(a) Primitive unit cells.

The unit cells in which the constituent particles are present only at the corners are called 'simple unit cells' or 'primitive unit cells'.

Thus, there are seven types of primitive unit cells as given in Table 1.3.

(b) Non-primitive or centred unit cells.

Those unit cells in which the constituent particles are present not only at the corners of the unit cells but also at some other positions are called non-primitive unit cells or centred unit cells.

There are three types of non-primitive unit cells* as follows :

- (i) **Face-centred.** When the particles are present not only at the corners but also at the centre of each face of the unit cell, it is called face-centred unit cell.
- (ii) **End-Centred.** When in addition to the particles at the corners, there are particles at the centres of any two opposite faces, it is called end-face centred.
- (iii) **Body-Centred.** When in addition to the particles at the corners, there is one particle present at the centre within the body of the unit cell, it is called body-centred unit cell.

Every crystal system does not have all the four types of unit cells, i.e., simple, face-centred, end-centred and body-centred. Hence, there are only 14 types of space lattices corresponding to seven crystal systems as shown in Fig. 1.10.

The fourteen lattices (shown in Fig. 1.10) corresponding to seven crystal systems are known as Bravais lattices.

1.7. A More Realistic Picture of a Unit cell (Open Structures and Space-filling Structures)

It has been explained above that the unit cells are represented by points connected by lines. The points represent the constituent particles, i.e., atoms, ions or molecules whereas the lines help to visualize the symmetry of the crystal. These are called **open structures** (as shown in Fig. 1.10). In actual practice, the particles occupy much more space of the crystal lattice and are held together by one or the other type of force. For example, a more realistic picture of simple, face-centred and body-centred cubic showing how the particles actually pack within the solid is given in Fig. 1.11 (a) with actual particle sizes. These are called **space-filling structures**. As-mentioned above, the structures as given in Fig. 1.10 are called **open structures**. In the open structures, quite often, instead of points, we draw small spheres, the centre of the sphere representing the centre of the particle as shown in Fig. 1.11 (b).

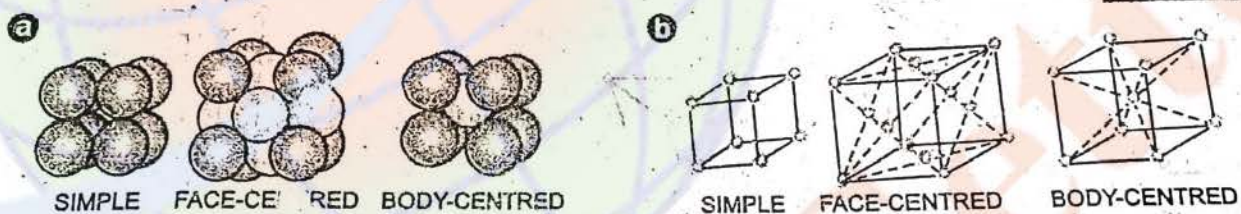


FIGURE 1.11

It is important to note that the spheres (atoms) at the corners of the face-centred and body-centred cubes do not touch each other. However, in the body-centred cube, all the spheres at the corners touch the central sphere. Similarly, in the face-centred cube, each sphere at the corner touches three spheres present at the face-centres of three adjoining faces.

This type of arrangement extends in the three dimensional space. In general, for any crystal system, the number of spheres which are touching a particular sphere is called its **coordination number**.

In ionic crystals, the coordination number may be defined as the number of oppositely charged ions surrounding a particular ion.

In general, the coordination number of any constituent particle in a crystal is the number of its nearest neighbours.

1.8. Calculation of Number of Particles per Unit Cell of a Cubic Crystal System

As explained earlier, in a crystal lattice, each unit cell is touching a number of other unit cells. Thus, a particle present at the lattice point may be shared by a number of unit cells. Let us, therefore, first find out the portion or the fraction of the particle that belongs to a particular unit cell and then we shall calculate the

*Besides these, we also have edge-centred unit cell in which the particles are present not only at the corners but one particle is present on each edge-centre. Also remember that a cube has 12 edge centres.

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number of particles in the unit cell of different lattices of a cubic crystal system. For simplicity, we shall assume that the constituent particles are atoms.

1.8.1. Calculation of the contribution of atoms present at different lattice sites

(i) An atom at the corner is shared by eight unit cells [see Fig. 1.12 (a)]. Hence,

[as shown in Fig. 1.12 (b)]

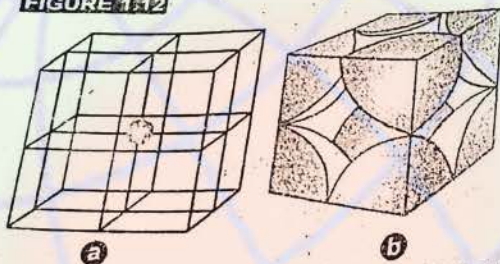
Contribution of each atom present at the corner = $\frac{1}{8}$

(ii) An atom on the face is shared between two unit cells [see Fig. 1.13 (a)]. Hence,

[as shown in Fig. 1.13 (b)]

Contribution of each atom on the face = $\frac{1}{2}$

FIGURE 1.12



An atom at the lattice point shared by 8 unit cells

(iii) An atom present within the body of the unit cell is shared by no other unit cell [see Fig. 1.14 (a)]. Hence,

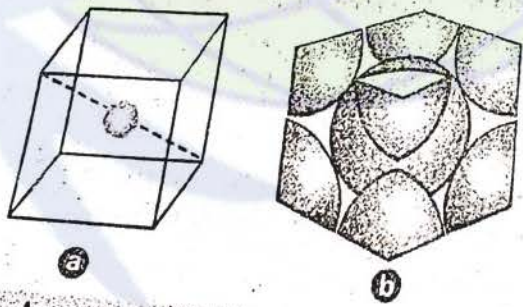
[as shown in Fig. 1.14 (b)]

Contribution of each atom within the body = 1

(iv) An atom present on the edge is shared by four unit cells (see Fig. 1.15). Hence,

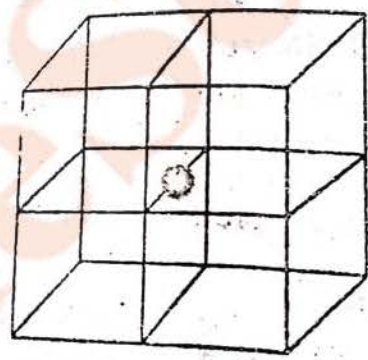
Contribution of each atom on the edge = $\frac{1}{4}$

FIGURE 1.14



An atom at the body centre not shared by any other unit cell

FIGURE 1.15



An atom at the edge centre shared by 4 unit cells

1.8.2. Calculation of Number of Atoms per Unit Cell

(a) Number of atoms in a unit cell of Simple (Primitive) Cubic Lattice. A simple cubic lattice has only eight atoms on the corners. As contribution by each = $\frac{1}{8}$, therefore, number of atoms present in the unit cell = $\frac{1}{8} \times 8 = 1$.

(b) Number of atoms in a unit cell of Body Centred Cubic (BCC). This lattice has 8 atoms on the corners and one atom within the body.

$$\therefore \text{Contribution by 8 atoms present on the corners} = \frac{1}{8} \times 8 = 1$$

$$\text{Contribution by the atom present within the body} = 1$$

$$\therefore \text{Number of atoms present in the unit cell} = 1 + 1 = 2.$$

(c) **Number of atoms in a unit cell of the Face Centred Cubic (FCC).** This lattice has 8 atoms on the corners and 6 atoms on the faces (one on each face).

$$\text{Contribution by atoms on the corners} = \frac{1}{8} \times 8 = 1$$

$$\text{Contribution by atoms on the faces} = \frac{1}{2} \times 6 = 3$$

$$\therefore \text{Number of atoms present in the unit cell} = 1 + 3 = 4.$$

Remember that in case of compounds, the number of atoms per unit cell are in the same ratio as the stoichiometry of the compound. Hence, it helps to predict the formula of the compound.

FORMULAS USED

(i) Contribution by a particle on the corner of a unit cell = $\frac{1}{8}$

Contribution by a particle on the face of a unit cell = $\frac{1}{2}$

Contribution by a particle within the body of a unit cell = 1

Contribution by a particle on the edge of a unit cell = $\frac{1}{4}$

(ii) The ratio of the number of particles A and B present per unit cell gives the formula of the compound formed between A and B.

PROBLEMS BASED ON

Calculation of particles per unit cell and formula of compound

Problem 1 Calculate the number of atoms per unit cell present in simple, fcc and bcc unit cells.

(Assam Board 2012)

Solution. See calculations given above.

Problem 2 A compound formed by elements A and B has a cubic structure in which A atoms are at the corners of the cube and B atoms are at the face centres. Derive the formula of the compound.

Solution. As A atoms are present at the 8 corners of the cube, therefore, number of atoms of A in the unit cell = $\frac{1}{8} \times 8 = 1$.

As B atoms are present at the face centres of the 6 faces of the cube, therefore, number of atoms of B in the unit cell = $\frac{1}{2} \times 6 = 3$.

$$\therefore \text{Ratio of atoms A : B} = 1 : 3.$$

Hence, the formula of the compound is AB_3 .

Problem 3 A cubic solid is made up of two elements X and Y. Atoms Y are present at the corners of the cube and atoms X at the body centre. What is the formula of the compound? What are the coordination numbers of X and Y?

Solution. As atoms Y are present at the 8 corners of the cube, therefore, number of atoms of Y in the unit cell = $\frac{1}{8} \times 8 = 1$.

As atoms X are present at the body centre, therefore, number of atoms of X in the unit cell = 1

$$\therefore \text{Ratio of atoms X : Y} = 1 : 1.$$

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Hence, the formula of the compound is XY
 Coordination number of each of X and Y=8.

Problem 4 An ionic compound made up of atoms A and B has a face-centred cubic arrangement in which atoms A are at the corners and atoms B are at the face-centres. If one of the atoms is missing from the corner, what is the simplest formula of the compound?

Solution. No. of atoms of A at the corners = 7 (because one A is missing)
 \therefore Contribution atoms of A towards unit cell = $7 \times \frac{1}{8} = \frac{7}{8}$

No. of atoms B at face-centres = 6

\therefore Contribution of atom B towards unit cell = $6 \times \frac{1}{2} = 3$

Ratio of A : B = $\frac{7}{8} : 3 = 7 : 24$ \therefore Formula is A_7B_{24}

Problem 5 Calculate the approximate number of unit cells present in 1 g of gold. Given that gold crystallizes in the face-centred cubic lattice. (Atomic mass of gold = 197 u)

Solution. 1 mole of gold = 197 g = 6.02×10^{23} atoms
 \therefore No. of atoms present in 1 g of gold = $\frac{6.02 \times 10^{23}}{197}$

As face-centred cubic unit cell contains 4 atoms, therefore, number of unit cells present = $\frac{6.02 \times 10^{23}}{197 \times 4} = 7.64 \times 10^{20}$

PROBLEMS FOR PRACTICE

1. A compound formed by elements X and Y crystallizes in the cubic structure where Y atoms are at the corners of the cube and X atoms are at the alternate faces. What is the formula of the compound?
2. Calculate the number of atoms in a cubic based unit cell having one atom on each corner and two atoms on each body diagonal.
3. A compound made up of elements A and B crystallises in the cubic structure. Atoms A are present on the corners as well as face centres whereas atoms B are present on the edge centres as well as body centre. What is the formula of the compound? Draw the structure of its unit cell.
4. If three elements P, Q and R crystallize in a cubic solid lattice with P atoms at the corners, Q atoms at the cube centre and R atoms at the centre of the faces of the cube, then write the formula of the compound.
5. Sodium crystallizes in a bcc unit cell. Calculate the approximate number of unit cells in 9.2 g of sodium (Atomic mass of Na = 23)

ANSWERS

1. XY
2. 9
3. AB, structure is same as that of NaCl (See Fig. 1.35 (a), page 1/41)
4. PQR_3
5. 1.204×10^{23}

HINTS FOR DIFFICULT PROBLEMS

1. As there are 8 Y atoms at the corners and contribution of each = $\frac{1}{8}$, therefore, no. of Y atoms/unit cell = $8 \times \frac{1}{8} = 1$. There can be only two X atoms on alternate faces. As contribution of each of them = $\frac{1}{2}$, therefore, atoms/unit cell = $2 \times \frac{1}{2} = 1$. Hence, formula is XY.

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2. There are four body diagonals. Thus, there are 8 atoms within the body of the unit cell which are not shared by any other unit cell. Contribution by atoms at the corners $= 8 \times \frac{1}{8} = 1$.
Hence, total atoms/unit cell $= 8 + 1 = 9$.

3. Atoms A/unit cell $= 8 \times \frac{1}{8}$ + $6 \times \frac{1}{2} = 4$
(corners) (face-centres)
Atoms B/unit cell $= 12 \times \frac{1}{4}$ + $1 = 4$
(edge-centres) (body-centre)

$\therefore A : B = 4 : 4 = 1 : 1$. So the formula is AB.

4. Atoms P per unit cell $= 8 \times \frac{1}{8} = 1$, Atoms Q per unit cell $= 1$, Atoms R per unit cell $= 6 \times \frac{1}{2} = 3$.
Hence, the formula is PQR_3 .
5. BCC has 2 atoms per unit cell. Proceed as in Solved Problem 3 above.

1.9. Close Packing in Crystals

In order to understand the packing of the constituent particles in a crystal, it is assumed that these particles are hard spheres of identical size (e.g., those of a metal). The packing of these spheres takes place in such a way that they occupy the maximum available space and there is minimum empty space and hence the crystal has maximum density. This type of packing is called *close packing*.

The packing of spheres of equal size may be discussed in the following three steps :

(a) **Close-Packing in One Dimension.** There is only one way in which the spheres can be arranged in one dimensional close packed structure, i.e., these spheres should be touching each other in a row as shown in Fig. 1.16. In this arrangement, each sphere is touching two neighbouring spheres. Hence, in this arrangement, coordination number is 2.

FIGURE 1.16



Close packing of spheres in one dimension

(b) **Close-Packing in Two Dimensions.** When the rows are stacked over each other, a two dimensional close-packed structure (called *crystal plane*) is produced. This stacking can be done in two different ways as follows :

(i) The spheres in the second row may be placed in such a way that they are touching the spheres of the first row and are exactly above the spheres of the first row, i.e., there is horizontal as well as vertical alignment of the spheres in the two rows. If the first row is called 'A' type row, the second row, being exactly same, will also be 'A' type. Further rows may also be built up exactly in the same way. Hence, we call this arrangement as AAA type of arrangement (Fig. 1.17a).

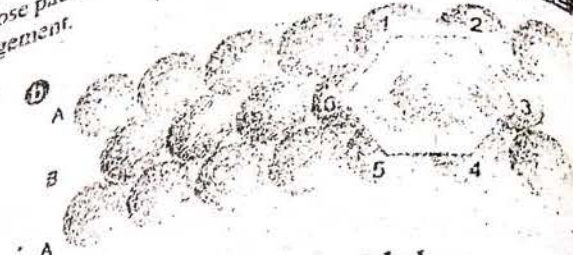
In this arrangement, each sphere is touching four other spheres. Hence, in this arrangement, the coordination number is 4. Further, on joining the centres of the four spheres touching the particular sphere, a square is formed as shown in Fig. 1.17 (a). Hence, this packing is called **square close packing in two dimensions**.

(ii) The spheres in the second row may be placed in the depressions of the first row as shown in Fig. 1.17 (b). This produces a row different from the first row. Hence, if we call first row as 'A' type, the second

row may be called as 'B' type. When the spheres in the third row are placed in the depressions of the second row, the third row formed is exactly similar to the first row, i.e., 'A' type. The fourth row formed again 'B' type and so on. Hence, this arrangement is called as ABAB type of arrangement. In this arrangement each sphere is touching six other spheres. Hence, the coordination number is 6. Further, on joining the centres of the six spheres touching a particular sphere, a hexagon is formed as shown in Fig. 1.17. Hence, this arrangement is called two dimensional hexagonal close packing.

The second mode of packing (i.e., hexagonal close packing) is more efficient as more space is occupied by the spheres and empty space is less in this arrangement.

I
t
d
w
p
u
c
o



Close packing of spheres in two dimensions (a) Square close packing (b) Hexagonal close packing

(c) Close-Packing in Three Dimensions. We have discussed above that two dimensional packing can be square close packing or hexagonal close packing. Now let us see how a three dimensional packing can be obtained from each of these.

(i) Three dimensional close packing from two dimensional square close packed layers. Starting from the square close packed layer, the second layer and all further layers will be built up such that they are horizontally as well as vertically aligned with each other. Hence, if we call the first layer as 'A' type, the lattice generated will be AAA...type. This will be a simple cubic lattice and its unit cell will be a primitive cubic unit cell, as shown in Fig. 1.18.

(ii) Three dimensional packing from two dimensional hexagonal close packed layers. We have seen that for two dimensional packing, a more efficient packing is given by hexagonal close packing. Let us now consider a three dimensional packing keeping a hexagonal close packed pattern for layers. In the base layer shown in Fig. 1.19, the spheres are marked as A and the voids between the spheres are marked as 'a' and 'b' alternately.

FIGURE 1.18

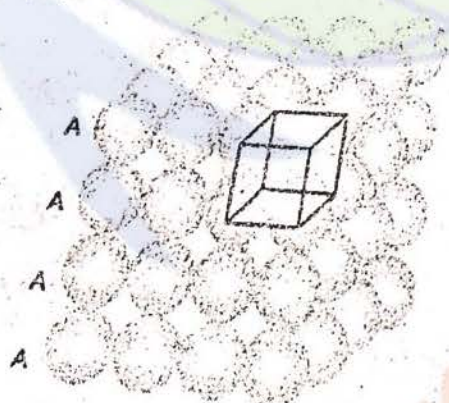
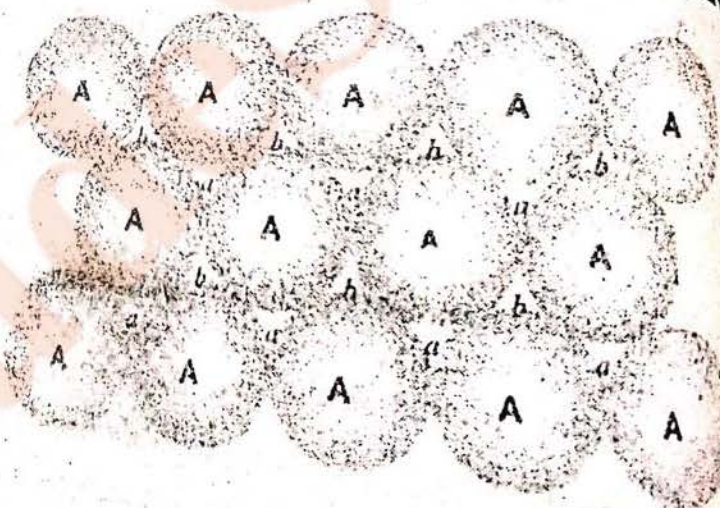


FIGURE 1.19



Three dimensional packing of square close packed layers forming simple cubic lattice with AAA-arrangement

Representing the two types of triangular voids in hexagonal close packed layer

Both 'a' and 'b' voids are triangular in shape. They differ only in the fact that whereas apex of the 'a' voids point downwards, those of voids 'b' point upwards.

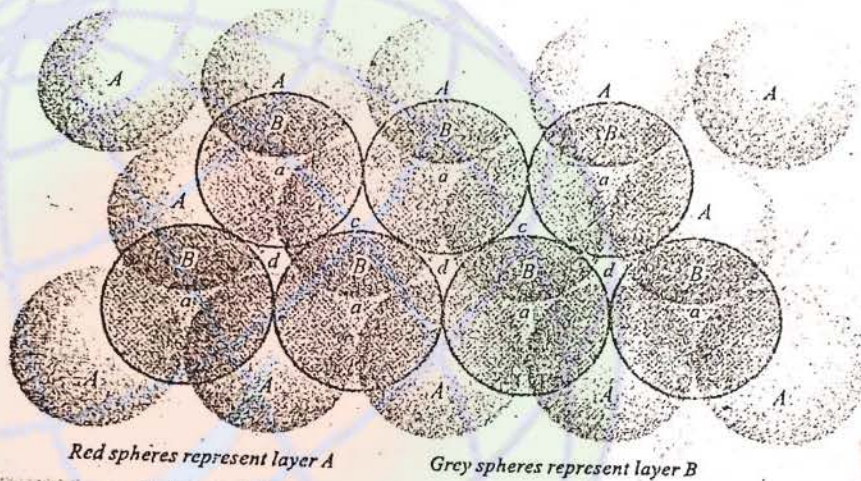
SOLID STATE

When a second layer is placed with spheres vertically aligned with those in the first layer, its voids will come above the voids in the first layer. This is an inefficient way of filling the space.

When the second layer is placed in such a way that its spheres find place in the 'a' voids of the first layer, the 'b' voids will be left unoccupied since under this arrangement no sphere can be placed in them [Fig. 1.20].

Now, there are two types of voids in the second layer. These are marked as voids 'c' and voids 'd'. The voids 'c' are ordinary voids which lie above the spheres of the first layer whereas voids 'd' lie on the voids of the first layer and hence are combinations of two voids, one of the first layer and second of the second layer.

FIGURE 1.20



Red spheres represent layer A Grey spheres represent layer B
Close packing of two layers with hexagonal close packed base layer

The 'a' and 'b' voids of the first layer are both triangular while only 'c' voids of the second layer are triangular. The 'd' voids of the second layer are combinations of two triangular voids (one each of first layer and second layer) with the vertex of one triangle upwards and the vertex of the other triangle downwards.

A simple triangular void like 'c' in a crystal is surrounded by four spheres and is called a **tetrahedral void** or a **hole** [Fig. 1.21. (a)]. A double triangular void like 'd' is surrounded by six spheres and is called **octahedral void** [Fig. 1.21. (b)].

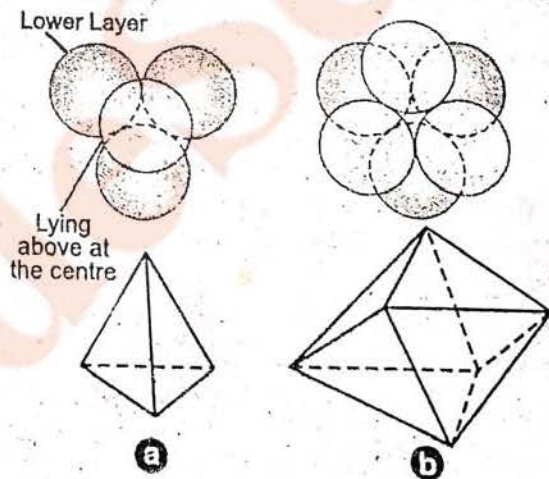
The voids or holes in crystals are also called **interstices**.

Now, there are two ways to build up the third layer.

(i) When a third layer is placed over the second layer in such a way that the spheres cover the tetrahedral or 'c' voids, a three dimensional closest packing is obtained where the spheres in every third or alternate layers are vertically aligned (i.e., the third layer is directly above the first, the fourth above the second layer and so on). Calling the first layer as layer A and second layer as layer B, the arrangement is called **ABAB.....** pattern or **hexagonal close packing (hcp)** [Fig. 1.22a (i) or b (i)].

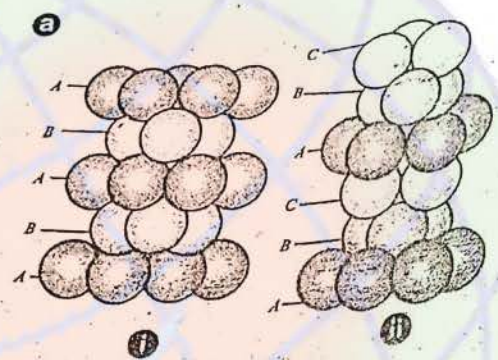
Molybdenum, magnesium and beryllium crystallise in *hcp* (hexagonal close packing) structure.

FIGURE 1.21

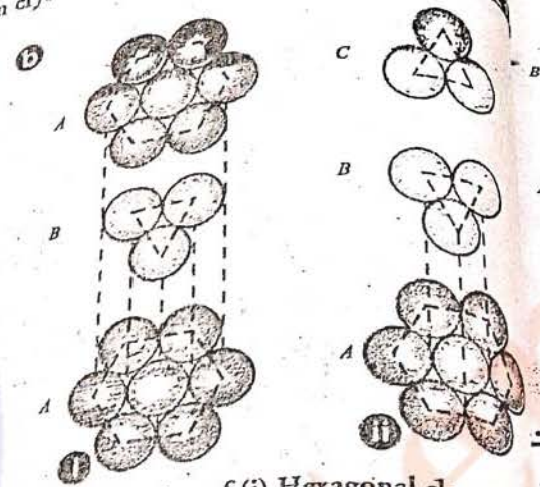


Two types of voids in crystals
(a) tetrahedral void (b) octahedral void

(ii) When the third layer is placed over the second layer in such a way that spheres cover the octahedral or 'd' voids, a layer different from layers A and B is produced. Let us call it as layer C. Continuing this stacking spheres in every fourth layer will be vertically aligned. This pattern of stacking spheres is called ABCABC..... pattern or cubic close packing (ccp). It is similar to face-centred cubic (fcc) packing [Fig. 1.22a (ii) or 1.22b (ii)].
Iron, nickel, copper, silver, gold and aluminium crystallise in ccp (cubic close packing) structure.



Actual view of (i) Hexagonal close packing (ii) Cubic close packing



A simplified view of (i) Hexagonal close packing (AB AB pattern) (ii) Cubic close packing (ABC ABC pattern)

Both the above patterns of stacking spheres, though different in form, are equally efficient. They occupy the maximum possible space which is about 74% of the available volume (the empty space is only 26%). Hence, they are called close packings.

Further, in both hcp and ccp methods of stacking, a sphere is in contact with 6 other spheres in its layer. It also touches directly 3 spheres in the layer above and three spheres in the layer below. Thus, a sphere has 12 close neighbours. It is said to have a coordination number of 12. As readily defined,

The number of closest (or nearest) neighbours of any constituent particle in the crystal lattice is called its coordination number.

The common coordination numbers in different types of crystals are 4, 6, 8 and 12. In crystals with directional bonds, coordination number is lower than that of the crystals with non-directional bonds as metals and ionic compounds.

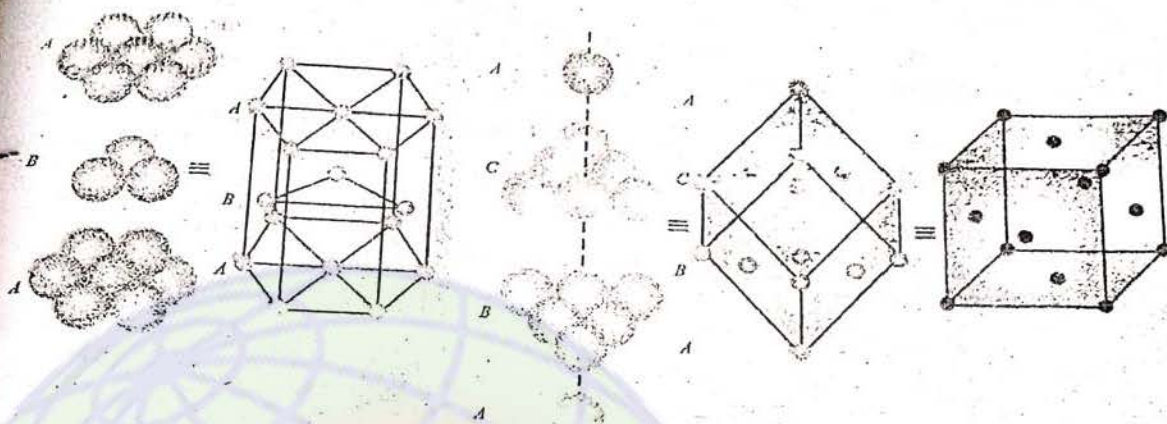
To understand as to why they are called hexagonal close packing and cubic close packing, arrangement of the layers may be represented as shown in Fig. 1.23 next page.

In addition to these two types of arrangements, a third type of arrangement found in metals is body-centred cubic (bcc) in which space occupied is about 68%.

Lithium, sodium, potassium, rubidium and caesium crystallize in the bcc structure. The coordination number of each atom in the bcc structure is 8. Further, it is not as closely packed as the first two as the empty space is about 32%.

SOLID STATE

FIGURE 1.23



(a) HEXAGONAL CLOSE PACKING (HCP)

(b) CUBIC CLOSE PACKING (CCP) ≡ FACE-CENTRED CUBIC (FCC)

(a) ABAB..... type is hexagonal close packing (b) ABC ABC..... type is cubic close packing

1.10. Calculation of the Spaces Occupied, i.e., Packing Efficiency or Packing Fractions

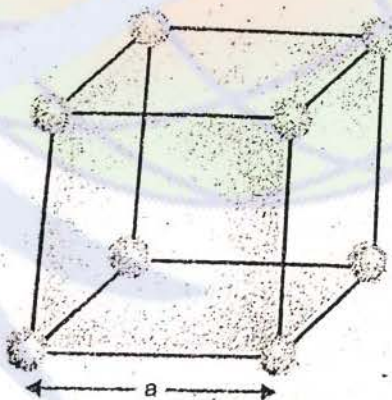
We have seen above that in any type of packing, some voids (empty spaces) are always present.

The percentage of the total space filled by the particles is called packing efficiency or the fraction of the total space filled is called packing fraction.

The calculations for different types of structures are described below :

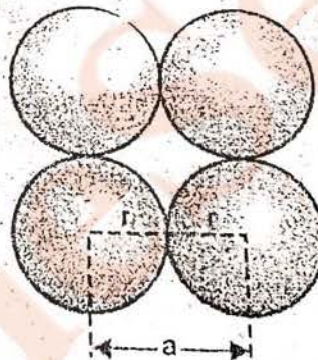
(1) In a simple cubic unit cell.

FIGURE 1.24



Simple cubic unit cell

FIGURE 1.25



Top/Bottom/Side view of simple cubic unit cell

Suppose the edge length of the unit cell = a and radius of the sphere = r
 As spheres are touching each other, evidently, $a = 2r$. (Fig. 1.25)

$$\text{No. of spheres per unit cell} = \frac{1}{8} \times 8 = 1$$

$$\text{Volume of the sphere} = \frac{4}{3} \pi r^3$$

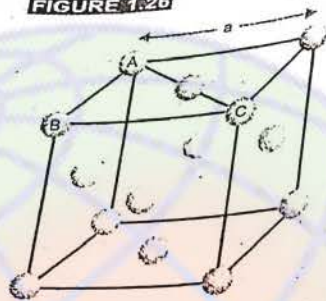
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Volume of the cube = $a^3 = (2r)^3 = 8r^3$

∴ Fraction occupied, i.e., packing fraction = $\frac{4 \pi r^3}{8r^3} = \frac{\pi}{6} = 0.524$ or % occupied = 52.4%.

(2) In face-centred cubic structure (cubic close packing).

FIGURE 1.26



Face-centred cubic unit cell

As sphere on the face centre is touching the spheres at the corners*,
But from right angled triangle ABC,

$$AC = \sqrt{AB^2 + BC^2} = \sqrt{a^2 + a^2} = \sqrt{2}a$$

$$\therefore \text{Volume of the unit cell} = a^3 = \left(\frac{4}{\sqrt{2}}r\right)^3 = \frac{32}{\sqrt{2}}r^3$$

$$\text{No. of spheres in the unit cell} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

$$\text{Volume of 4 spheres} = 4 \times \frac{4}{3} \pi r^3 = \frac{16}{3} \pi r^3$$

$$\therefore \text{Fraction occupied, i.e., packing fraction} = \frac{16 \pi r^3 / 3}{32 r^3 / \sqrt{2}} = \frac{\pi \sqrt{2}}{6} = 0.74 \text{ or } \% \text{ occupied} = 74\%.$$

Packing efficiency of hcp and ccp structures. Cubic close packing (ccp) is same as face-centred cubic packing. Hence, packing efficiency is 74%. Further, ccp and hcp are equally efficient. Hence, hcp also has a packing efficiency of 74%. **

(3) In body centred cubic structure.

As the sphere at the body centre touches the spheres at the corners*, body diagonal, $AD = 4r$ (Fig. 1.28)

Further, face diagonal, $AC = \sqrt{AB^2 + BC^2} = \sqrt{a^2 + a^2} = \sqrt{2}a$

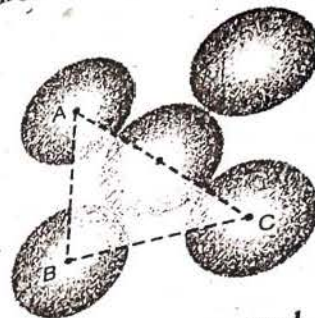
and body diagonal, $AD = \sqrt{AC^2 + CD^2} = \sqrt{2a^2 + a^2} = \sqrt{3}a$

$$\therefore \sqrt{3}a = 4r \text{ or } a = \frac{4r}{\sqrt{3}}$$

*The spheres at the corners are not touching each other.

**Remember that packing in rhombohedral is similar to hexagonal close packing with 12 nearest neighbours and a packing fraction of 0.74.

FIGURE 1.27



Top view of face-centred cubic unit cell

$AC = 4r$ (Fig. 1.27)

$$\therefore \sqrt{2}a = 4r \text{ or } a = \frac{4}{\sqrt{2}}r$$

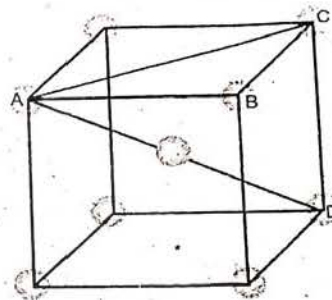
$$\therefore \text{Volume of the unit cell} = a^3 = \left(\frac{4r}{\sqrt{3}}\right)^3 = \frac{64r^3}{3\sqrt{3}}$$

$$\text{No. of spheres per unit cell} = 8 \times \frac{1}{8} + 1 = 2$$

$$\text{Volume of 2 spheres} = 2 \times \frac{4}{3} \pi r^3 = \frac{8}{3} \pi r^3$$

$$\therefore \text{Fraction occupied, i.e., packing fraction} = \frac{\frac{8}{3} \pi r^3}{\frac{64r^3}{3\sqrt{3}}} = \frac{\pi\sqrt{3}}{8} = 0.68$$

\therefore % occupied = 68%.



Body-centred cubic unit cell

FIGURE 1.28

1.11. Sizes of Tetrahedral and Octahedral Voids

As already discussed, in the close packing structure, (hcp or ccp), there are following two types of voids present in the crystal :

- (i) Tetrahedral voids
- (ii) Octahedral voids

The radii of the voids in these close packed structures are related to the sizes of the spheres present in the packing.

If R is the radius of the spheres in the close packed arrangement, then

$$\text{Radius (r) of the tetrahedral void} = 0.225 R$$

$$\text{Radius (r) of the octahedral void} = 0.414 R$$

In case of ionic compounds, as usually anions are present in the packing and cations occupy the voids, hence we can also write

$$(i) \text{ For cations occupying the tetrahedral voids, } r_+ = 0.225 r_-$$

$$(ii) \text{ For cations occupying the octahedral voids, } r_+ = 0.414 r_-$$

Thus, a tetrahedral void is much smaller than the octahedral void. Further, the maximum size of the sphere occupying the void is 0.414 R. If the smaller spheres to occupy the voids have size larger than this, the arrangement will no longer be close packed.

Their size acquires importance in the formation of transition metal hydrides, borides, carbides and nitrides in which the respective non-metal atoms, i.e., H, B, C and N are accommodated in the interstices. That is why these compounds are called **interstitial compounds**.

1.11.1. Derivation of the relationship between the radius (r) of the octahedral void and the radius (R) of the atoms in close packing.

A sphere fitting into the octahedral void is shown by a small circle. A sphere above and a sphere below this small sphere have not been shown in the Fig.

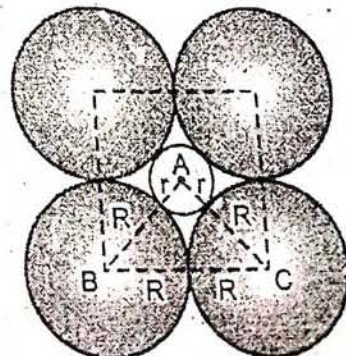
Obviously, ABC is a right angled triangle. Applying Pythagoras theorem,

$$BC^2 = AB^2 + AC^2$$

$$(2R)^2 = (R+r)^2 + (R+r)^2 = 2(R+r)^2 \quad \text{or} \quad \frac{(2R)^2}{2} = (R+r)^2$$

$$\text{or} \quad 2R^2 = (R+r)^2 \quad \text{or} \quad (\sqrt{2}R)^2 = (R+r)^2 \quad \text{or} \quad \sqrt{2}R = R+r$$

$$\text{or} \quad r = \sqrt{2}R - R = R(\sqrt{2} - 1) = R(1.414 - 1) = 0.414 R$$



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1.11.2. Derivation of the relationship between radius (r) of the tetrahedral void and the radius (R) of the atoms in close packing.

To simplify calculations, a tetrahedral void may be represented in a cube as shown in the fig. below, in which three spheres A, E and F form the triangular base, the fourth (B) lies at the top and the grey colour sphere occupies the tetrahedral void.

Suppose the length of the side of the cube = a
From right angled triangle ABC, face diagonal

$$AB = \sqrt{AC^2 + BC^2} = \sqrt{a^2 + a^2} = \sqrt{2}a$$

As spheres A and B are actually touching each other in the close packing, face diagonal AB = 2R

Hence, $2R = \sqrt{2}a$ or $R = \frac{1}{\sqrt{2}}a$

Again from the right angled triangle ABD,

$$\text{body diagonal AD} = \sqrt{AB^2 + BD^2} = \sqrt{(\sqrt{2}a)^2 + a^2} = \sqrt{3}a$$

But as grey coloured sphere touches other spheres, evidently, body diagonal AD = 2(R + r)

$$\therefore 2(R+r) = \sqrt{3}a \text{ or } R+r = \frac{\sqrt{3}}{2}a$$

Dividing eqn. (ii) by eqn. (i), we get.

$$\frac{R+r}{R} = \frac{\sqrt{3}a/2}{a/\sqrt{2}} = \frac{\sqrt{3}}{\sqrt{2}}$$

or $1 + \frac{r}{R} = \frac{\sqrt{3}}{\sqrt{2}}$ or $\frac{r}{R} = \frac{\sqrt{3}}{\sqrt{2}} - 1$

$$= \frac{\sqrt{3} - \sqrt{2}}{\sqrt{2}} = \frac{1.732 - 1.414}{1.414} = 0.225$$

or $r = 0.225 R$.

Calculation of ideal radius of the cation fitting into the voids. The radius of the tetrahedral or octahedral void can be calculated if the radius of the ions in the packing is known. This gives the ideal radius of the ion fitting into the void.

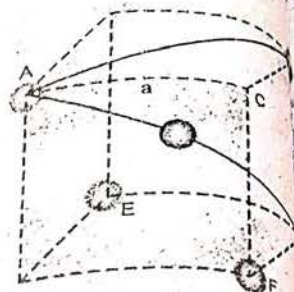
Sample Problem: A solid A^+B^- has NaCl type close packed structure. If the anion has a radius of 241.5 pm, what should be the ideal radius of the cation? Can a cation C^+ having radius of 50 pm be fitted into the tetrahedral hole of the crystal A^+B^- ?

Solution. As A^+B^- has NaCl structure, A^+ ions will be present in the octahedral voids. Ideal radius of the cation will be equal to the radius of the octahedral void because in that case, it will touch the anions and the arrangement will be close packed. Hence,

Radius of the octahedral void = $r_{A^+} = 0.414 \times r_{B^-} = 0.414 \times 241.5 \text{ pm} = 100.0 \text{ pm}$

Radius of the tetrahedral void = $0.225 \times r_{B^-} = 0.225 \times 241.5 \text{ pm} = 54.3 \text{ pm}$

As the radius of the cation C^+ (50 pm) is smaller than the size of the tetrahedral void, it can be placed into the tetrahedral void (but not exactly fitted into it).



SOLID STATE

1. A solid AB h
2. A solid AB l radius of the

ANSWERS

1. 241 pm

1. As NaCl h
2. The formu

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- (i) As r = smaller packin
- (ii) Each sphere
- (iii) In the conta it and form tetra tetra tetra sph

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SOLID STATE

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PROBLEMS FOR PRACTICE

1. A solid AB has NaCl structure. If the radius of the cation A is 100 pm, what is the radius of the anion B?
2. A solid AB has NaCl structure. If the radius of cation A^+ is 170 pm, calculate the maximum possible radius of the anion B^- .

ANSWERS

1. 241 pm
2. 410.6 pm

HINTS FOR DIFFICULT PROBLEMS

1. As NaCl has octahedral structure, $r_{A^+} = 0.414 \times r_{B^-}$.
2. The formula $r_+ = 0.414 \times r_-$ gives maximum possible radius of anion for a given cation for close packing.

Summing up the Main Features of the Tetrahedral and Octahedral voids

TETRAHEDRAL VOIDS

- (i) As $r = 0.225 R$, tetrahedral void is much smaller than the size of the spheres in the packing.
- (ii) Each tetrahedral void is surrounded by 4 spheres. Hence, its coordination number is 4.
- (iii) In the hcp or ccp packing, each sphere is in contact with three spheres in the layer above it and three spheres in the layer below it, thus forming one tetrahedral void above and one tetrahedral void below. Hence, there are two tetrahedral voids per sphere, i.e., number of tetrahedral voids is double the number of spheres in the packing.

OCTAHEDRAL VOIDS

- (i) As $r = 0.414 R$, the size of the octahedral void is smaller than that of the spheres in the packing but larger than the tetrahedral voids.
- (ii) Each octahedral void is surrounded by 6 spheres. Hence, its coordination number is 6.
- (iii) As octahedral void is a combination of two voids of the two layers, number of octahedral voids is equal to half the number of tetrahedral voids and hence equal to the number of spheres in the packing.

1.12. Number of Voids Filled and Formula of the Compound

As already discussed, in a close packed structure (hcp or ccp), there are two types of voids present in the lattice, i.e., tetrahedral voids and octahedral voids. It is found that

(i) Number of octahedral voids = Number of particles present in the close packing.

(ii) Number of tetrahedral voids = $2 \times$ Number of octahedral voids.

In case of ionic compounds, it is found that the bigger ions (usually anions) are present in the packing whereas smaller ions (usually cations) occupy the voids.

If the cations are small in size, they may occupy tetrahedral voids (because they are smaller than octahedral voids). However, if the cations are large enough to occupy the tetrahedral voids, they may occupy octahedral voids. Further, it is not necessary that only tetrahedral or only octahedral voids may be occupied. Also, it is not necessary that all the voids must be occupied. Only a fraction of the total voids may be occupied.

Knowing the fraction of the voids occupied, the formula of the compound can be calculated or vice-versa. This will become clear from the following solved problems.

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Sample Problem 1 A compound is formed by two elements X and Y. Atoms of the element X (as cations) occupy all the octahedral voids. What is the formula of the compound?

Solution. Suppose number of atoms Y in ccp = n
 As number of octahedral voids = No. of atoms in ccp
 \therefore No. of octahedral voids = n
 As all the octahedral voids are occupied by atoms X, therefore, number of atoms X = n.
 \therefore Ratio of X : Y = n : n = 1 : 1
 Hence, the formula of the compound is XY.

Sample Problem 2 Atoms of element B form hcp lattice and those of the element A occupy 2/3rd of tetrahedral voids. What is the formula of the compound formed by these elements A and B?

Solution. Suppose number of atoms B in hcp lattice = n
 As number of tetrahedral voids is double the number of atoms in the close packing, therefore, number of tetrahedral voids = 2n
 As atoms A occupy 2/3rd of the tetrahedral voids, therefore, number of atoms A in the lattice

$$= \frac{2}{3} \times 2n = \frac{4n}{3}$$

$$\therefore \text{Ratio of A : B} = \frac{4n}{3} : n = \frac{4}{3} : 1 = 4 : 3$$

Hence, the formula of the compound is A_4B_3 .

Sample Problem 3 In a crystalline solid, anions B are arranged in a cubic close packing. Cations A are equally distributed between octahedral and tetrahedral voids. If all the octahedral voids are occupied, what is the formula of the solid?

Solution. Suppose the number of anions B = n. Then number of octahedral voids = n
 Number of tetrahedral voids = 2n
 As octahedral and tetrahedral voids are equally occupied by cations A and all the octahedral voids are occupied (given), therefore n cations A are present in octahedral voids and n cations A are present in tetrahedral voids. In other words, corresponding to n anions B, there are n + n = 2n cations A. Thus, cations A and anions B are in the ratio 2n : n = 2 : 1. Hence, the formula of the solid will be A_2B .

Sample Problem 4 In the mineral, spinel, having the formula $MgAl_2O_4$, oxide ions are arranged in the cubic close packing, Mg^{2+} ions occupy the tetrahedral voids while Al^{3+} ions occupy the octahedral voids.

- (i) What percentage of tetrahedral voids is occupied by Mg^{2+} ions?
- (ii) What percentage of octahedral voids is occupied by Al^{3+} ions?

Solution. According to the formula $MgAl_2O_4$, if there are 4 oxide ions, there will be 1 Mg^{2+} ion and 2 Al^{3+} ions. But if the 4 O^{2-} ions are in ccp arrangement, there will be 4 octahedral voids and 8 tetrahedral voids. Thus, 1 Mg^{2+} ion is present in one of the 8 tetrahedral voids

$$\therefore \% \text{ of tetrahedral voids occupied by } Mg^{2+} = \frac{1}{8} \times 100 = 12.5\%$$

Similarly, 2 Al^{3+} ions are present in two octahedral voids out of 4 available.

$$\therefore \% \text{ of octahedral voids occupied by } Al^{3+} = \frac{2}{4} \times 100 = 50\%$$



PROBLEMS FOR PRACTICE

1. In corundum, oxide ions are arranged in hexagonal close packing and aluminium ions occupy two-third of the octahedral voids. What is the formula of corundum ?
2. In a solid, oxide ions are arranged in ccp. One-sixth of the tetrahedral voids are occupied by the cations A while one-third of the octahedral voids are occupied by the cations B. What is the formula of the compound ?
3. A solid is made up of two elements P and Q. Atoms Q are in ccp arrangement while atoms P occupy all the tetrahedral sites. What is the formula of the compound ?
4. In chromium (III) chloride, CrCl_3 , chloride ions have cubic close packed arrangement and Cr (III) ions are present in the octahedral holes. What fraction of the octahedral holes is occupied ? What fraction of total number of holes is occupied ?

ANSWERS

1. Al_2O_3

2. ABO_3

3. P_2Q

4. $1/3, 1/9$

HINTS FOR DIFFICULT PROBLEMS

1. Suppose oxide ions = n . Then octahedral voids = n . Hence, Al^{3+} ions = $\frac{2}{3} \times n = \frac{2n}{3}$.
 \therefore Ratio $\text{Al}^{3+} : \text{O}^{2-} = \frac{2n}{3} : n = 2 : 3$, i.e., formula is Al_2O_3 .
2. Suppose O^{2-} ions = n . Then octahedral voids = n and tetrahedral voids = $2n$. Cations $\text{A} = \frac{1}{6} \times 2n = \frac{n}{3}$ and cations $\text{B} = \frac{1}{3} \times n = \frac{n}{3}$.
 \therefore Ratio $\text{A} : \text{B} : \text{O}^{2-} = \frac{n}{3} : \frac{n}{3} : n = 1 : 1 : 3$, i.e., formula is ABO_3 .
3. Suppose number of atoms $\text{Q} = n$.
 Then number of tetrahedral sites = $2n$
 \therefore Number of atoms $\text{P} = 2n$
 \therefore Ratio $\text{P} : \text{Q} = 2n : n = 2 : 1$, i.e., formula is P_2Q .
4. See Solved Problem 4 above.

1.13. Location of Voids in a Crystal

In a close-packed structure (ccp or hcp), if there are n spheres (atoms or ions) in the packing, then

Number of octahedral voids = n

Number of tetrahedral voids = $2n$

For example, in the cubic close packing (ccp), i.e., face-centred cubic (fcc) unit cell, there are 4 atoms or ions per unit cell, therefore, there are 4 octahedral voids and 8 tetrahedral voids. These are located at different positions as shown in Fig. 1.29 and explained below :

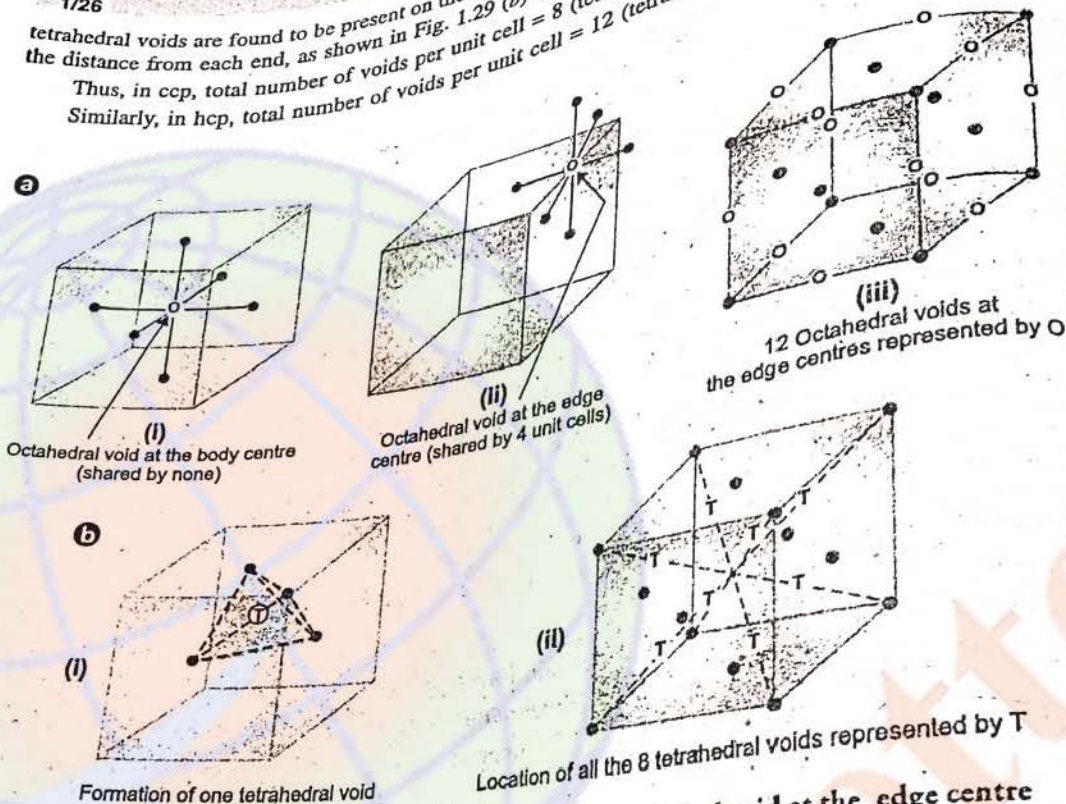
(a) **Octahedral voids.** One octahedral void is present at the body centre of the cube and 12 octahedral voids are present on the centres of the 12 edges of the cube. But each void on the edge centre is shared by 4 unit cells. Hence, its contribution in the unit cell = $1/4$. Therefore, the effective number of octahedral voids in the ccp structure = $1 + 12 \times 1/4 = 1 + 3 = 4$.

(b) **Tetrahedral voids.** The 8 tetrahedral voids present in the ccp arise from the fact that there are 8 spheres at the corners of the unit cell and each sphere at the corner touches three spheres present on the face-centres of the three adjoining faces, each giving rise to one tetrahedral void (see Fig. 1.11 on page 1/11). These

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tetrahedral voids are found to be present on the body diagonals, two on each body diagonal at one-fourth of the distance from each end, as shown in Fig. 1.29 (b) (ii).
 Thus, in ccp, total number of voids per unit cell = 8 (tetrahedral) + 4 (octahedral) = 12.
 Similarly, in hcp, total number of voids per unit cell = 12 (tetrahedral) + 6 (octahedral) = 18.

FIGURE 1.29



(a) Representing (i) Octahedral void at the body-centre (ii) Octahedral void at the edge centre (iii) All the 12 octahedral voids of ccp unit cell each shared by 4 other unit cells,
 (b) (i) Formation of a tetrahedral void (ii) Representing the location of all the 8 tetrahedral voids on the body diagonals

SUPPLEMENT YOUR KNOWLEDGE

1. Structures of some common ionic compounds. Most of the ionic compounds have close-packed arrangement in which one type of ions (usually larger ones) form the close packed arrangement and the other type of ions (smaller ones) occupy the voids. A few examples are given below :

Compound	Ions forming the close-packed arrangement	Ions occupying the voids
(i) NaCl	Cl ⁻ ions (fcc)	Na ⁺ ions in all octahedral voids
(ii) ZnS	S ²⁻ ions (fcc)	Zn ²⁺ ions in alternate tetrahedral voids.
(iii) CaF ₂	Ca ²⁺ ions (fcc)	F ⁻ ions in all tetrahedral voids.

It is further interesting to mention here that

- (i) In NaCl, there are 4 Cl⁻ ions in the unit cell. Therefore, there are 4 octahedral voids, all of which are occupied by Na⁺ ions. Hence, there are 4 NaCl units per unit cell.
- (ii) In ZnS, there are 4 S²⁻ ions in the unit cell. Therefore, there are 8 tetrahedral voids, half of which are occupied by Zn²⁺ ions. Hence, again there are 4 ZnS units per unit cell.
- (iii) In CaF₂, there are 4 Ca²⁺ ions in the unit cell. Therefore, there are 8 tetrahedral voids all of which are occupied by F⁻ ions. Hence, there are 4 CaF₂ units per unit cell.

Note. (i) In CsCl unit cell, 8 Cl⁻ ions are present at the corners of the cube and Cs⁺ ion is present at the body centre. Hence, number of Cl⁻ ions per unit cell = $8 \times \frac{1}{8} = 1$. As Cs⁺ ion at the body centre is not shared by any other unit cell, this means that there is one CsCl unit per unit cell.

(ii) In fact, zinc sulphide exists in two forms, called zinc blende and wurtzite. Both have a close packed arrangement of S²⁻ ions. In both, Zn²⁺ ions occupy the tetrahedral voids. Both have 4 : 4 structure. They differ only in the fact that zinc blende has ccp or fcc arrangement whereas wurtzite has hcp arrangement of S²⁻ ions. As a result, unit cell of wurtzite has 6 formula units of ZnS (whereas zinc blende has 4 formula units).

2. Ferrites. In the structure of Fe₃O₄ (magnetite), if Fe²⁺ ions are replaced by divalent cations such as Mg²⁺, Zn²⁺, etc., the compounds obtained are called ferrites. Thus, ferrites are the compounds having the general molecular formula AFe₂O₄ where A is a divalent cation such as Mg²⁺ or Zn²⁺, i.e., these are obtained by replacing Fe²⁺ ions in the structure of Fe₃O₄ by divalent cations. These belong to the general category of compounds having the formula AB₂O₄ where A is a divalent cation and B is a trivalent cation, e.g., B³⁺, Fe³⁺ or Al³⁺. In these compounds, divalent cations occupy tetrahedral voids whereas trivalent cations occupy octahedral voids. This type of arrangement is called spinel structure. Most of the ferrites having spinel structure are used in telephone as well as in memory loops of computers.

3. Spinel is the mineral MgAl₂O₄ in which oxide ions are arranged in ccp with dipositive Mg²⁺ ions occupying tetrahedral voids and tripositive Al³⁺ ions in the octahedral voids. There are certain compounds in which the dipositive ions are present in the octahedral voids and tripositive ions are distributed equally between tetrahedral and octahedral voids. Such compounds are called inverse spinels. An important example of this

class is magnetite, Fe₃O₄ (i.e., FeO.Fe₂O₃). These are usually represented as B [AB] O₄, e.g. Fe ^{III} [Fe ^{II} Fe ^{III}] O₄, Fe [Ni Fe] O₄ etc.

1.14. Radius Ratio Rules

For the stability of an ionic compound, each cation should be surrounded by maximum number of anions and vice versa (for maximum electrostatic forces of attraction).

The number of oppositely charged ions surrounding each ion is called its coordination number.

Since ionic bond is non-directional, the arrangement of ions within the ionic crystal is determined by the sizes of the ions.

The ratio of the radii of the cation to that of the anion is called radius ratio, i.e.,

$$\text{Radius Ratio} = \frac{\text{Radius of the cation } (r_+)}{\text{Radius of the anion } (r_-)}$$

Evidently, greater is the radius ratio, the larger is the size of the cation and hence greater is its coordination number. The relationships between the radius ratio and the coordination number and the structural arrangement are called radius ratio rules, and are given in Table 1.4.

TABLE 1.4 Radius ratio rules for AB type structures

Radius Ratio	Coordination no.	Structural arrangement	Structure type	Examples
0.155 — 0.225	3	Planar triangular	—	B ₂ O ₃
0.225 — 0.414	4	Tetrahedral	Sphalerite, ZnS	CuCl, CuBr, CuI, BaS, HgS
0.414 — 0.732	6	Octahedral	Sodium chloride (Rock salt)	NaBr, KBr, MgO, MnO, CaO, CaS
0.732 — 1	8	Body-centred cubic	Caesium chloride	CsI, CsBr, TlBr, TlCl

*NH₄Br is a borderline case between NaCl and CsCl type structure. This is because $r_{\text{NH}_4^+} = 1.43 - 1.50 \text{ \AA}$,

$r_{\text{Br}^-} = 1.96 \text{ \AA}$. If we take $r_{\text{NH}_4^+} = 1.43 \text{ \AA}$, $r_+/r_- = 0.729$. For higher values of $r_{\text{NH}_4^+}$, $r_+/r_- > 0.732$.

RETAIN IN MEMORY

In NaCl, for exact fitting of Na⁺ ions in the octahedral voids, the radius ratio r_+/r_- should be 0.414. Actual ratio is 0.525 which shows that Cl⁻ ions move apart, i.e., they do not touch each other. Same situation exists for CsCl and ZnS.

Sample Problem 1 The two ions A⁺ and B⁻ have radii 88 and 200 pm respectively. In the close packed crystal of compound AB, predict the coordination number of A⁺.

Solution. $\frac{r_+}{r_-} = \frac{r(A^+)}{r(B^-)} = \frac{88 \text{ pm}}{200 \text{ pm}} = 0.44$

It lies in the range 0.414 to 0.732
Hence, the coordination number of A⁺ = 6.

Sample Problem 2 Br⁻ ions form a close packed structure. If the radius of Br⁻ ion is 195 pm, calculate the radius of the cation that just fits into the tetrahedral hole. Can a cation A⁺ having a radius of 82 pm be slipped into the octahedral hole of the crystal A⁺Br⁻?

Solution. (i) Radius of the cation just fitting into the tetrahedral hole = Radius of the tetrahedral hole
= $0.225 \times r_{Br^-} = 0.225 \times 195 = 43.875 \text{ pm}$

(ii) For the cation A⁺ with radius = 82 pm

Radius ratio = $\frac{r_+}{r_-} = \frac{82 \text{ pm}}{195 \text{ pm}} = 0.4205$

As it lies in the range 0.414 – 0.732, hence the cation A⁺ can be slipped into the octahedral hole of the crystal A⁺Br⁻.
Note. In case (ii), radius of octahedral void in which the cation can be fitted exactly = $0.414 \times r_{Br^-} = 0.414 \times 195 \text{ pm} = 80.73 \text{ pm}$

This is the minimum size of the octahedral void in which if the cation is placed, it will touch all the anions and the anions also touch each other (Refer to lower Fig. on page 1/21). However, if cation bigger than the above size is slipped into the octahedral void, cation will continue to touch all the anions but anion-anion contact will vanish. The arrangement extends octahedral upto the maximum size of the octahedral void viz. $0.732 \times r_{Br^-}$. Hence, in such cases, we apply radius ratio rules to find the range of the void, for a particular arrangement. (Refer to Problem for Practice 5 below).

PROBLEMS FOR PRACTICE

- If the radius of Mg²⁺ ion, Cs⁺ ion, O²⁻ ion, S²⁻ ion and Cl⁻ ion are 72 Å, 1.69 Å, 1.40 Å, 1.84 Å and 1.81 Å respectively, calculate the coordination numbers of the cations in the crystals of MgS, MgO and CsCl.
- Predict the structure of MgO crystal and coordination number of cation in which cation and anion radii are equal to 65 pm and 140 pm respectively.
- Predict the close packed structure of an ionic compound A⁺B⁻ in which the radius of the cation = 148 pm and radius of anion = 195 pm. What is the coordination number of the cation?
- If the close packed cations in an AB type solid with NaCl structure have a radius of 75 pm, what would be the maximum and minimum sizes of the anions filling the voids?
- A solid A⁺B⁻ has NaCl type close packed structure. If the anion has a radius of 250 pm, what should be the ideal radius of the cation? Can a cation C⁺ having a radius of 180 pm be slipped into the tetrahedral site of the crystal A⁺B⁻? Give reason for your answer.

ANSWERS

- 4, 6, 6
- 102.5 pm, 181 pm
- 6, octahedral
- 103.4 pm. No
- 8, 12, cubic

SOLID STATE

4. For close pack

∴ Minimum

Maximum

5. $\frac{r_+(C^+)}{r_-(B^-)}$
It does 1

1.15. Rel: e

1. Si

elements,

2. I

Bu

FIGURE

HINTS FOR DIFFICULT PROBLEMS

4. For close packed AB type solid with NaCl structure, $\frac{r_+}{r_-} = 0.414 - 0.732$

$$\therefore \text{Minimum value of } r_- = \frac{r_+}{0.732} = \frac{75}{0.732} \text{ pm} = 102.5 \text{ pm}$$

$$\text{Maximum value of } r_- = \frac{r_+}{0.414} = \frac{75}{0.414} = 181.2 \text{ pm.}$$

5. $\frac{r_+(C^+)}{r_-(B^-)} = \frac{180 \text{ pm}}{250 \text{ pm}} = 0.72$

It does not lie in the range 0.225 - 0.414. Hence, C^+ cannot be slipped into the tetrahedral site.

1.15. Relationship between the nearest neighbour distance (d), edge of the unit cell (a) and radius of the atom (r) for pure elements

1. Simple cubic unit cell (Fig. 1.30). Distance between nearest neighbours (d) = AB = a. For pure elements, radius $r = \frac{d}{2}$ (because atoms are touching each other).

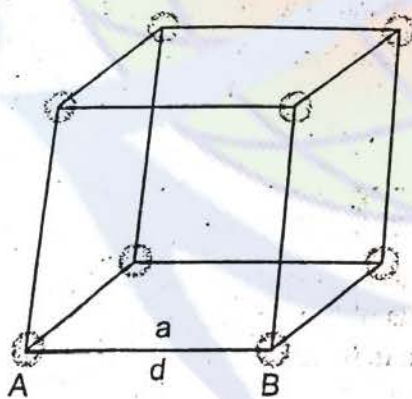
2. Face-centred cubic (Fig. 1.31). Distance between nearest neighbours (d) = $\frac{1}{2}AC$
But $AC^2 = AB^2 + BC^2 = a^2 + a^2 = 2a^2$

$$\therefore AC = \sqrt{2}a$$

$$\therefore d = \frac{\sqrt{2}a}{2} = \frac{a}{\sqrt{2}}$$

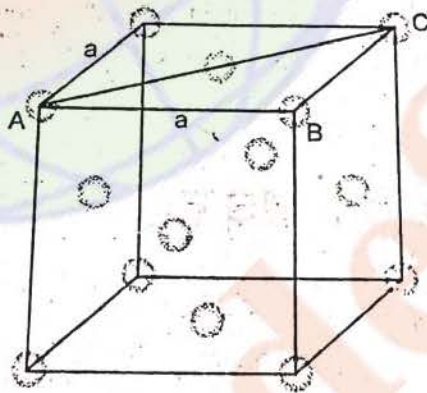
$$r = \frac{d}{2} = \frac{a}{2\sqrt{2}}$$

FIGURE 1.30



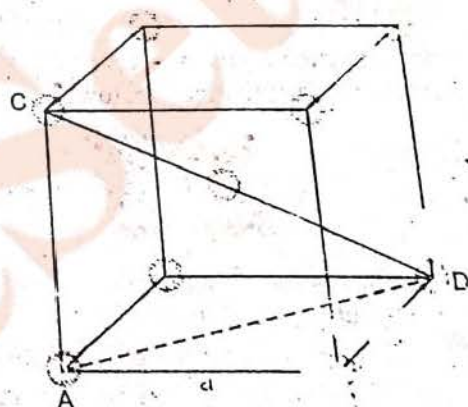
Simple cubic unit cell

FIGURE 1.31



Face-centred cubic unit cell

FIGURE 1.32



Body-centred cubic unit cell

3. Body-centred cubic (Fig. 1.32). Distance between nearest neighbours (d) = $\frac{1}{2}CD$

In the right angled triangle ABD, right angled at B, $AD = \sqrt{AB^2 + BD^2}$

Now, in the right angled triangle ACD, right angled at A,

$$CD = \sqrt{AC^2 + AD^2} = \sqrt{a^2 + 2a^2} = \sqrt{3}a$$

$$\therefore d = \frac{1}{2}CD = \frac{\sqrt{3}a}{2} \quad \text{and} \quad r = \frac{d}{2} = \frac{\sqrt{3}a}{4}$$

1/30

A. Relationships between the nearest neighbour distance (d) and the edge (a) of a unit cell of a cubic crystal

Simple	Face-centred	Body-centred
$d = a$	$d = \frac{a}{\sqrt{2}}$ $= 0.707 a$	$d = \frac{\sqrt{3}}{2} a$ $= 0.866 a$

B. Relationships between atomic radius (r) (which is $= \frac{d}{2}$ for crystals of elements) and the edge (a) of the unit cell of a cubic crystal.

Simple	Face-centred	Body-centred
$r = \frac{a}{2}$	$r = \frac{a}{2\sqrt{2}}$ $= 0.3535 a$	$r = \frac{\sqrt{3}}{4} a$ $= 0.433 a$

1. If the the u
2. The l
3. A se
4. An der

ANS

Sample Problem 1 Xenon crystallises in the face-centred cubic lattice and the edge of the unit cell is 620 pm. What is the nearest neighbour distance and what is the radius of xenon atom?

Solution. Here, $a = 620$ pm, $d = ?$, $r = ?$
 For the face-centred cubic $d = \frac{a}{\sqrt{2}} = \frac{620}{1.414} = 438.5$ pm
 $r = \frac{d}{2} = \frac{438.5}{2} = 219.25$ pm

Sample Problem 2 CsCl has bcc arrangement and its unit cell edge length is 400 pm. Calculate the interionic distance in CsCl.

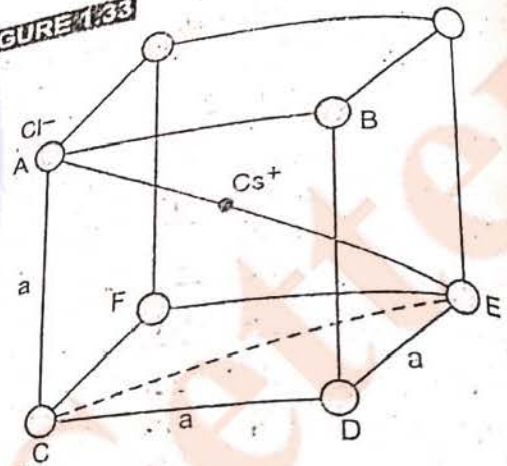
Solution. The bcc arrangement of CsCl is shown in the Fig. 1.33, where black circle is Cs^+ ion and coloured circles are Cl^- ions. The aim is to find half of the body diagonal AE. If the edge of the unit cell is 'a', then

$$CE = \sqrt{a^2 + a^2} = \sqrt{2}a$$

$$\therefore AE = \sqrt{(\sqrt{2}a)^2 + a^2} = \sqrt{3}a = \sqrt{3} \times 400$$

$$\therefore \text{Interionic distance} = \frac{1}{2} AE = \frac{\sqrt{3}}{2} \times 400 = 346.4 \text{ pm}$$

FIGURE 1.33



CsCl structure

Sample Problem 3 Sodium metal crystallises in body centred cubic lattice with the cell edge, 4.29 Å. What is the radius of sodium atom? What is the length of the body diagonal of the unit cell?

Solution. For body centred cubic lattice, the relationship between the cell edge (a) and the radius of the atom is

$$r = \frac{\sqrt{3}}{4} a = \frac{1.732}{4} \times 4.29 = 1.86 \text{ Å}$$

$$\text{Length of the body diagonal} = 4r = 4 \times 1.86 \text{ Å} = 7.44 \text{ Å}$$

Sample Problem 4 In face-centred cubic (fcc) crystal lattice, edge length is 400 pm. Find the diameter of the greatest sphere which can be fitted into the interstitial void without distortion of the lattice.

Solution. For fcc, radius of atom (R) = $\frac{a}{2\sqrt{2}} = \frac{400}{2\sqrt{2}}$ pm = 141.4 pm

As octahedral void is bigger in size than the tetrahedral void, the greatest sphere will fit into octahedral void.
 Radius of octahedral void (r) = $0.414 R = 0.414 \times 141.4$ pm = 58.54 pm
 \therefore Diameter of the greatest sphere fitting into the void = 2×58.54 pm = 117.08 pm.

PROBLEMS FOR PRACTICE

1. If the radius of an atom of an element is 75 pm and the lattice type is body-centred cubic, what is the edge of the unit cell ?
2. The radius of an atom of an element is 500 pm. If it crystallizes as a face centred cubic lattice, what is the length of the side of the unit cell ?
3. A solid AB has CsCl type structure. The edge length of the unit cell is 404 pm. Calculate the distance of closest approach between A⁺ and B⁻ ions ?
4. An element E crystallizes in body centred cubic structure. If the edge length of the cell is 1.469×10^{-10} m and the density is 19.3 g cm^{-3} , calculate the atomic radius of this element.

ANSWERS

1. 173.2 pm 2. 1414 pm 3. 349.9 pm 4. 6.361×10^{-11} m

HINTS FOR DIFFICULT PROBLEMS

1. For BCC, $r = \frac{\sqrt{3}}{4} a$ or $a = \frac{4r}{\sqrt{3}} = \frac{4 \times 75}{1.732} = 173.2 \text{ pm}$.
2. For FCC, $r = \frac{a}{2\sqrt{2}}$ or $a = 2\sqrt{2} r = 2 \times 1.414 \times 500 \text{ pm} = 1414 \text{ pm}$.
3. Distance of closest approach is equal to the distance between the nearest neighbours (d). As CsCl has BCC lattice,
 $d = \frac{\sqrt{3}}{2} a = \frac{1.732}{2} \times 404 \text{ pm} = 349.9 \text{ pm}$.
4. For BCC, $r = \frac{\sqrt{3}}{4} a = \frac{1.732}{4} \times 1.469 \times 10^{-10} \text{ m} = 6.361 \times 10^{-11} \text{ m}$.

1.16. Calculation of Density of a Cubic Crystal from its Edge

Knowing the edge of a cubic crystal from X-ray studies and knowing the type of crystal structure possessed by it so that the number of particles per unit cell is known, the density of the crystal can be calculated.

Case I. For cubic crystals of elements.

Suppose the edge of the unit cell = a pm
 Number of atoms present per unit cell = Z
 Atomic mass of the element = M

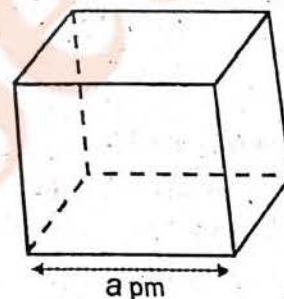
\therefore Volume of the unit cell = $(a \text{ pm})^3$
 $= (a \times 10^{-10} \text{ cm})^3 = a^3 \times 10^{-30} \text{ cm}^3$

Density of the unit cell = $\frac{\text{Mass of the unit cell}}{\text{Volume of the unit cell}}$

Mass of the unit cell = Number of atoms in the unit cell \times Mass of each atom = $Z \times m$

where m = mass of each atom = $\frac{\text{Atomic mass}}{\text{Avogadro's number}} = \frac{M}{N_0}$. Substituting this value,

FIGURE 1.34



A cubic unit cell

1/32

$$\text{Density of the unit cell} = \frac{Z \times M / N_0}{a^3 \times 10^{-30}}$$

$$\rho = \frac{Z \times M}{a^3 \times N_0 \times 10^{-30}} \text{ g/cm}^3$$

i.e.,

where edge, a , is in pm and molar mass, M , is in g mol^{-1} .
The density of the substance is same as the density of the unit cell.
The above equation involves five parameters. Knowing any four, the fifth can be calculated.

Case II. For cubic crystals of ionic compounds. The formula is the same except that now Z is number of formula units present in one unit cell and M is formula mass.

RETAIN IN MEMORY

(i) If a is taken in cm and M is molar mass in g mol^{-1} , the above expression becomes

$$\rho = \frac{Z \times M}{a^3 \times N_0} \text{ g/cm}^3$$

(ii) In terms of SI units, M is in kg mol^{-1} , a is in meters, then

$$\rho = \frac{Z \times M}{a^3 \times N_0} \text{ kg m}^{-3}$$

(iii) In case of ionic compounds $A^+ B^-$ having fcc structure like NaCl, Edge (a) = $2 \times$ Distance between A^+ and B^- ions

PROBLEMS BASED ON

Relation between density and edge of cubic crystals

FORMULAS USED

(i) For an element, the density of the unit cell and hence the density of a crystal is given by

$$\rho = \frac{Z \times M}{a^3 \times N_0 \times 10^{-30}}$$

where Z = Number of particles present per unit cell, viz., 1 for simple, 2 for BCC and 4 for FCC.

M = Atomic mass of the element, a = Edge of the unit cell in pm (Note carefully)

N_0 = Avogadro's number, ρ = Density of the crystal in g/cm^3 (when M is in g mol^{-1})

(ii) For ionic compounds

Z = No. of formula units in one unit cell, e.g., 4 for NaCl and ZnS, 1 for CsCl, etc.

M = Formula mass (molecular mass) of the compound

a = Edge which is $2 \times$ Distance between Na^+ and Cl^- in case of NaCl

(iii) In SI units, $\rho = \frac{Z \times M}{a^3 \times N_0}$ where M = molar mass in kg mol^{-1} , a = edge in metres, ρ = density in kg m^{-3}

Remember. For BCC structure of an element (like alkali metals), $Z = 2$

For BCC structure of ionic compounds (like CsCl), $Z = 1$.

TYPE I: Calculation of density of a cubic crystal from the edge/nearest neighbour distance/radius

Problem 1 Silver forms ccp lattice and X-ray studies of its crystals show that the edge length of its unit cell is 408.6 pm. Calculate the density of silver (Atomic mass = 107.9 u).

NCERT Solved Example

$$\text{Solution. } \rho = \frac{Z \times M}{a^3 \times N_0}$$

For ccp lattice (which is equivalent to fcc lattice), $Z = 4$ atoms/unit cell.

Also we are given that $M = 107.9 \text{ g mol}^{-1}$

$$a = 408.6 \text{ pm} = 408.6 \times 10^{-12} \text{ cm}$$

$$\therefore \rho = \frac{4 \text{ atoms} \times 107.9 \text{ g mol}^{-1}}{(408.6 \times 10^{-12} \text{ cm})^3 (6.022 \times 10^{23} \text{ atoms mol}^{-1})} = 10.5 \text{ g cm}^{-3}$$

Problem 2 Sodium has a bcc structure with nearest neighbour distance 365.9 pm. Calculate its density (Atomic mass of sodium = 23).

Solution. For the bcc structure, nearest neighbour distance (d) is related to the edge (a) as $d = \frac{\sqrt{3}}{2} a$

$$\text{or } a = \frac{2}{\sqrt{3}} d = \frac{2}{1.732} \times 365.9 = 422.5 \text{ pm}$$

For bcc structure, $Z = 2$

For sodium, $M = 23$

$$\therefore \rho = \frac{Z \times M}{a^3 \times N_0} = \frac{2 \times 23 \text{ g mol}^{-1}}{(422.5 \times 10^{-10} \text{ cm})^3 \times (6.02 \times 10^{23} \text{ mol}^{-1})} = 1.51 \text{ g/cm}^3$$

Problem 3 Gold (atomic mass 197 u, atomic radius = 0.144 nm) crystallizes in a face centred unit cell. Determine the density of gold. (Assam Board 2013)

$$\text{Solution. For fcc unit cell, } r = \frac{a}{2\sqrt{2}}$$

$$\text{or } a = 2\sqrt{2} r = 2 \times 1.414 \times 0.144 \text{ nm} = 0.407 \text{ nm} = 0.407 \times 10^{-7} \text{ cm}$$

$$\rho = \frac{Z \times M}{a^3 \times N_0} = \frac{4 \times 197 \text{ g mol}^{-1}}{(0.407 \times 10^{-7} \text{ cm})^3 \times (6.02 \times 10^{23} \text{ mol}^{-1})} = 19.4 \text{ g cm}^{-3}$$

TYPE II: Calculation of edge/interionic distances/radius from density

Problem 4 CsCl has cubic structure. Its density is 3.99 g cm^{-3} . What is the distance between Cs^+ and Cl^- ions? (At. mass of Cs = 133)

Solution. CsCl has BCC structure. It has one formula unit in the unit cell. So $Z = 1$.

$$\rho = \frac{Z \times M}{a^3 \times N_0} \quad \text{or} \quad a^3 = \frac{Z \times M}{\rho \times N_0} = \frac{1 \times (133 + 35.5) \text{ g mol}^{-1}}{3.99 \text{ g cm}^{-3} \times 6.02 \times 10^{23} \text{ mol}^{-1}} = 70.15 \times 10^{-24} \text{ cm}^3$$

$$a = (70.15)^{1/3} \times 10^{-8} \text{ cm} = (70.15)^{1/3} \times 10^2 \text{ pm} \quad (1 \text{ pm} = 10^{-10} \text{ cm})$$

$$= 4.124 \times 10^2 \text{ pm} = 412.4 \text{ pm}$$

$$\text{Interionic distance} = \frac{\sqrt{3} a}{2} = \frac{1.732}{2} \times 412.4 = 357 \text{ pm}$$

(See Solved Problem 2, page 1/30).

[To solve $(70.15)^{1/3}$, put $x = (70.15)^{1/3}$. Then $\log x = \frac{1}{3} \log 70.15 = \frac{1}{3} \times 1.8460 = 0.6153$
 $x = \text{Antilog } 0.6153 = 4.124$]

Problem 5 The density of aluminium is 2700 kg m^{-3} . Aluminium crystallises in a cubic lattice. Calculate the radius of aluminium atom in metres (Atomic mass of Al = 27)

Solution. $\rho = \frac{Z \times M}{a^3 \times N_0}$ or $a^3 = \frac{Z \times M}{\rho \times N_0} = \frac{4 \times 0.027 \text{ kg mol}^{-1}}{2700 \text{ kg m}^{-3} \times 6.02 \times 10^{23} \text{ mol}^{-1}}$
 $= 66.4 \times 10^{-30} \text{ m}^3$ or $a = (66.4)^{1/3} \times 10^{-10} \text{ m}$
 $\therefore x = 4.050 \therefore a = 4.05 \times 10^{-10} \text{ m}$
 Putting $(66.4)^{1/3} = x$, $\log x = \frac{1}{3} \log 66.4 = \frac{1.8222}{3} = 0.6074 \therefore x = 4.050$
 For fcc, $r = \frac{a}{2\sqrt{2}} = \frac{4.05 \times 10^{-10} \text{ m}}{2 \times 1.414} = 1.43 \times 10^{-10} \text{ m}$

TYPE III Calculation of Avogadro's Number

Problem 6 Calculate the value of Avogadro's number from the following data :
 Density of NaCl = 2.165 g cm^{-3} . Distance between Na^+ and Cl^- in NaCl = 281 pm . (P.N.)

Solution. A unit cell of NaCl contains 4 NaCl units, therefore, $Z = 4$.
 $M = 23 + 35.5 = 58.5 \text{ g mol}^{-1}$, $\rho = 2.165 \text{ g cm}^{-3}$
 As distance between Na^+ and $\text{Cl}^- = 281 \text{ pm}$
 \therefore Edge of the unit cell = $2 \times 281 = 562 \text{ pm}$
 (Edge is the distance from Na^+ to Na^+ ion or Cl^- to Cl^- ion. See Fig. 1.35a)

Substituting these values in the expression, $\rho = \frac{Z \times M}{a^3 \times N_0}$
 $2.165 \text{ g cm}^{-3} = \frac{4 \times 58.5 \text{ g mol}^{-1}}{(562 \times 10^{-10} \text{ cm})^3 \times N_0}$ or $N_0 = 6.09 \times 10^{23}$

TYPE IV Calculation of atomic mass and no. of atoms in a given mass

Problem 7 An element has a body-centred cubic (bcc) structure with cell edge of 288 pm . density of the element is 7.2 g/cm^3 . How many atoms are present in 208 g of the element?

Solution. For the BCC structure, $Z = 2$
 Edge of the unit cell, $a = 288 \text{ pm}$, Density of the element, $\rho = 7.2 \text{ g/cm}^3$

Substituting the values in the expression $\rho = \frac{Z \times M}{a^3 \times N_0}$

$7.2 \text{ g cm}^{-3} = \frac{2 \times M}{(288 \times 10^{-10} \text{ cm})^3 \times (6.02 \times 10^{23} \text{ mol}^{-1})}$ or $M = 51.8 \text{ g mol}^{-1}$

By mole concept, 51.8 g of the element contains = 6.02×10^{23} atoms

$\therefore 208 \text{ g}$ of the element contains = $\frac{6.02 \times 10^{23}}{51.8} \times 208 \text{ atoms} = 24.17 \times 10^{23} \text{ atoms}$

Problem 8 X-ray diffraction studies show that copper crystallizes in an fcc unit cell with edge length of $3.608 \times 10^{-8} \text{ cm}$. In a separate experiment, copper is determined to have a density of 8.92 g/cm^3 . Calculate the atomic mass of copper.

NCERT Solved Example

$$\text{Solution. } \rho = \frac{Z \times M}{a^3 \times N_0} \quad \text{or} \quad M = \frac{\rho \times a^3 \times N_0}{Z}$$

For fcc lattice, $Z = 4$.

$$\text{Hence, } M = \frac{(8.92 \text{ g cm}^{-3})(3.608 \times 10^{-8} \text{ cm})^3 (6.022 \times 10^{23} \text{ atoms mol}^{-1})}{4 \text{ atoms}} = 63.1 \text{ g mol}^{-1}$$

∴ Atomic mass of copper = 63.1

TYPE V Calculation of no. of atoms per unit cell/type of lattice (Simple/BCC/FCC).

Problem 9 Density of Li atom is 0.53 g/cm^3 . The edge length of Li is 3.5 \AA . Find out the number of Li atoms in a unit cell ($N_0 = 6.023 \times 10^{23}$, $M = 6.94$)

Solution. The aim is to find Z in the formula $\rho = \frac{Z \times M}{a^3 \times N_0}$

$$\therefore Z = \frac{\rho \times a^3 \times N_0}{M} = \frac{0.53 \text{ g cm}^{-3} \times (3.5 \times 10^{-8} \text{ cm})^3 \times (6.023 \times 10^{23} \text{ mol}^{-1})}{6.94 \text{ g mol}^{-1}} = 1.97 \approx 2.$$

Problem 10 The density of KBr is 2.75 g cm^{-3} . The length of edge of the unit cell is 654 pm . Predict the type of cubic lattice to which unit cell of KBr belongs. ($N_0 = 6.023 \times 10^{23} \text{ mol}^{-1}$, At. mass: K = 39, Br = 80)

Solution. For cubic crystals, $\rho = \frac{Z \times M}{a^3 \times N_0}$

$$\text{or } Z = \frac{\rho \times a^3 \times N_0}{M} = \frac{(2.75 \text{ g cm}^{-3})(654 \times 10^{-10} \text{ cm})^3 \times (6.023 \times 10^{23} \text{ mol}^{-1})}{(39 + 80) \text{ g mol}^{-1}} = 3.89 \approx 4$$

Thus, there are four formula units of KBr present per unit cell. Hence, it has face-centred cubic lattice (similar to that of NaCl).

Problem 11 The density of copper metal is 8.95 g cm^{-3} . If the radius of copper atom is 127.8 pm , is the copper unit cell a simple cubic, a body-centred cubic or a face-centred cubic? (Given At. mass of Cu = 63.54 g mol^{-1} and $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$) (CBSE 2010)

Solution. If copper atom were simple cubic,

$$a = 2r = 2 \times 127.8 \text{ pm} = 255.6 \text{ pm}$$

$$Z = 1$$

$$\rho = \frac{Z \times M}{a^3 \times N_0} = \frac{1 \times 63.54 \text{ g mol}^{-1}}{(255.6 \times 10^{-10} \text{ cm})^3 \times (6.02 \times 10^{23} \text{ mol}^{-1})} = 6.34 \text{ g cm}^{-3}$$

Actual $\rho = 8.95 \text{ g cm}^{-3}$.

Hence, copper atom is not simple cubic.

If copper atom were body-centred,

$$a = \frac{4r}{\sqrt{3}} = \frac{4 \times 127.8}{1.732} \text{ pm} = 295.15 \text{ pm}$$

$$Z = 2$$

$$\rho = \frac{Z \times M}{a^3 \times N_0} = \frac{2 \times 63.54 \text{ g mol}^{-1}}{(295.15 \times 10^{-10} \text{ cm})^3 \times 6.02 \times 10^{23} \text{ mol}^{-1}} = 8.21 \text{ g cm}^{-3}$$

Hence, copper atom is not body-centred.

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If copper atom were face-centred

$$a = 2\sqrt{2}r = 2 \times 1.414 \times 127.8 \text{ pm} = 361.4 \text{ pm}$$

$$Z = 4$$

$$\rho = \frac{Z \times M}{a^3 \times N_0} = \frac{4 \times 63.54 \text{ g mol}^{-1}}{(361.4 \times 10^{-10} \text{ cm})^3 \times 6.02 \times 10^{23} \text{ mol}^{-1}} = 8.94 \text{ g cm}^{-3}$$

Hence, copper is face-centred cubic.

PROBLEMS FOR PRACTICE

TYPE I Calculation of density from the edge/interionic distance/radius

- Gold crystallizes in a face-centred cubic lattice. If the length of the edge of the unit cell is 407 pm, calculate the density of gold as well as its atomic radius assuming it to be spherical. Atomic mass of gold = 197.
- The effective radius of an iron atom is 1.42 Å. It has rock salt like structure. Calculate its density (Fe = 56).
- The edge length of NaCl unit cell is 564 pm. What is the density of NaCl in g cm^{-3} ? ($N_A = 6.02 \times 10^{23}$)
- The compound CuCl has ZnS structure and the edge length of its unit cell is 500 pm. Calculate its density. (Atomic masses : Cu = 63, Cl = 35.5. Avogadro's constant = $6.02 \times 10^{23} \text{ mol}^{-1}$).
- KF has NaCl structure. If the distance between K^+ and F^- is 269 pm, find the density of KF. (Atomic masses : K = 39, F = 19 amu)
- Copper crystal has a face-centred cubic lattice structure. Atomic radius of copper atom is 128 pm. Calculate the density of copper. Atomic mass of copper = 63.5.
- Copper crystallises into a fcc lattice. Its edge length is $3.62 \times 10^{-8} \text{ cm}$. Calculate the density of copper. (atomic mass of Cu = 63.5 u, $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$).
- Calculate the density of silver which crystallizes in a face-centred cubic structure. The distance between nearest silver atoms in this structure is 287 pm. (Molar mass of Ag = 107.87 g mol^{-1} , $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$)

TYPE II Calculation of edge/interionic distance/radius from density

- The compound CuCl has ZnS (cubic) structure. Its density is 3.4 g cm^{-3} . What is the length of the edge of the unit cell? (At masses Cu = 63.5, Cl = 35.5).
- The density of a face centred cubic element (atomic mass = 60.2 amu) is 6.25 g cm^{-3} . Calculate the length of the edge of the unit cell.
- The density of lead is 11.35 g cm^{-3} and the metal crystallizes with fcc unit cell. Estimate the radius of lead atom. (At. mass of lead = 207 g mol^{-1} and $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$).

TYPE III Calculation of Avogadro's number

- Calculate the value of Avogadro's number from the following data : Density of KF = 2.48 g cm^{-3} . Distance between K^+ and F^- in KF = 269 pm. (Atomic masses : K = 39 and F = 19 amu)
- Calculate the Avogadro's number from the following data of AB when AB has NaCl type structure : Density of AB = 2.48 g cm^{-3} , M = 58. Distance between A^+ and B^- in AB = 269 pm.
- Iron has a body centred cubic unit cell with a cell edge of 286.65 pm. The density of iron is 7.87 g cm^{-3} . Use this information to calculate Avogadro's number (At. mass of Fe = 56 g mol^{-1}) (CBSE 2009, 2012)
- The well known mineral fluorite is chemically calcium fluoride. It is well known that in one unit of this mineral, there are 4 Ca^{2+} ions and 8 F^- ions, and that Ca^{2+} ions are arranged in a fcc lattice. The F^- ions fill all the tetrahedral holes in the face-centred cubic lattice of Ca^{2+} ions. The edge of the unit cell is $5.46 \times 10^{-8} \text{ cm}$ in length. The density of the solid is 3.18 g cm^{-3} . Use this information to calculate Avogadro's number (Molar mass of $\text{CaF}_2 = 78.08 \text{ g mol}^{-1}$). (CBSE 2010)

SOLID STATE

TYPE IV

- What is the ...
- Lead (Pb) has a ...
- KBr has a ...

TYPE V

- Use the ...
- Thallium ...
- Iron ...

TYPE VI

- Silver ...
- (a) A ...
- (b) F ...
- Cop ...

Miscellaneous

- An ...
- An ...
- A c ...
- The ...
- Tur ...
- The ...
- A ...
- A ...
- A ...
- A ...

TYPE IV. Calculation of interionic distance

15. What is the distance between Na^+ and Cl^- in a NaCl crystal if its density is 2.165 g cm^{-3} ? NaCl crystallises in the fcc lattice.
16. Lead (II) sulphide crystal has NaCl structure. What is the distance between Pb^{2+} and S^{2-} in PbS if its density is 12.7 g cm^{-3} ? (At. mass of Pb = 207).
17. KBr has fcc structure. The density of KBr is 2.75 g cm^{-3} . Find the distance between K^+ and Br^- . (At mass of Br = 80.0).

TYPE V. Calculation of the type of lattice

18. Use the data given below to find the type of cubic lattice to which the crystal of iron belongs :
 $a/\text{pm} = 286$, $\rho/\text{g cm}^{-3} = 7.86$.
19. Thallium chloride (TlCl) crystallizes in a cubic lattice whose edge length is found to be 385 pm. If the density of the solid is found to be 7.0 g cm^{-3} , predict the type of lattice to which the crystals of TlCl belong. (Atomic mass of Tl = 204, Cl = 35.5)
20. Iron (II) oxide has a cubic structure and each unit cell has side 5 Å. If the density of the oxide is 4 g cm^{-3} , calculate the number of Fe^{2+} and O^{2-} ions present in each unit cell (Molar mass of FeO = 72 g mol^{-1} , $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$)

TYPE VI. Calculation of atomic mass/molar mass

21. Silver crystallises in a fcc lattice. The edge length of the unit cell is $4.077 \times 10^{-8} \text{ cm}$ and its density is 10.5 g cm^{-3} . Calculate on this basis the atomic mass of silver ($N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$). (CBSE 2008, 2010)
22. (a) An element crystallises in BCC structure. The edge length of its unit cell is 288 pm. If the density of the crystals is 7.2 g cm^{-3} , what is the atomic mass of the element?
 (b) How many atoms of this element are present in 100 g?
23. Copper crystallises in FCC unit cell with cell edge of $3.608 \times 10^{-8} \text{ cm}$. Its density is 8.92 g cm^{-3} . Find its atomic mass.

Miscellaneous

24. An element crystallizes in a structure having f.c.c. unit cell of an edge 200 pm. Calculate the density if 200 g of this element contains 24×10^{23} atoms.
25. An element (density 6.8 g cm^{-3}) occurs in the BCC structure with cell edge of 290 pm. Calculate the number of atoms present in 200 g of the element.
26. A crystal of Lead (II) sulphide has NaCl structure. In this crystal the shortest distance between the Pb^{2+} ion and S^{2-} ion is 297 pm. What is the length of the edge of the unit cell in lead sulphide? Also calculate the unit cell volume.
27. The unit cube length for LiCl (NaCl structure) is 5.14 Å. Assuming anion-anion contact, calculate the ionic radius for chloride ion.
28. Tungsten has a density of 19.35 g cm^{-3} and the length of the side of the unit cell is 316 pm. The unit cell in the most important crystalline form of tungsten is the body centred cubic unit cell. How many atoms of the element does 50 g of the element contain?
29. A compound AB crystallises in bcc lattice with the unit cell edge length of 380 pm. Calculate
 (i) the distance between oppositely charged ions in the lattice
 (ii) radius of B^- if the radius of A^+ is 190 pm.
30. An element A crystallises in fcc structure. 200 g of this element has 4.12×10^{24} atoms. The density of A is 7.2 g cm^{-3} . Calculate the edge length of the unit cell.
31. Sodium crystallises in the cubic lattice and the edge of the unit cell is 430 pm. Calculate the number of atoms in a unit cell. [Atomic mass of Na = 23.0 amu, Density of sodium = 0.9623 g cm^{-3} , $N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$]
32. A metal (atomic mass = 50) has a body centred cubic crystal structure. The density of the metal is 5.96 g cm^{-3} . Find the volume of the unit cell ($N_0 = 6.023 \times 10^{23} \text{ atoms mol}^{-1}$).
33. Aluminium metal forms a cubic close-packed crystal structure. Its atomic radius is $125 \times 10^{-12} \text{ m}$. (a) Calculate length of the side of the unit cell. (b) How many

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34. A uni-univalent ionic crystal AX is composed of the following radii (arbitrary units):
 A^+ 1.0 X^- 2.0
 Assuming that ions are hard spheres, predict giving reasons whether the crystal will have sodium chloride (Manipur Board) cesium chloride structure. Calculate the volume of the unit cell.

ANSWERS

- | | | |
|--|---|---|
| 1. 19.4 g/cm ³ , 143.9 pm | 2. 5.74 g cm ⁻³ | 3. 2.16 g cm ⁻³ |
| 4. 5.24 g/cm ³ | 5. 2.48 g cm ⁻³ | 6. 8.9 g cm ⁻³ |
| 7. 10.71 g cm ⁻³ | 8. 578 pm | 9. 400 pm |
| 10. 174.7 pm | 11. 6.0 × 10 ²³ | 12. 6.0 × 10 ²³ |
| 13. 6.04 × 10 ²³ | 14. 6.033 × 10 ²³ | 15. 281 pm |
| 16. 250 pm | 17. 330 pm | 18. BCC |
| 19. BCC | 20. Z = 4, i.e., 4 Fe ²⁺ and 4 O ²⁻ ion | 23. 63.0 g mol ⁻¹ |
| 21. 107.09 g mol ⁻¹ | 22. (a) 51.8 (b) 11.62 × 10 ²³ | 28. 1.638 × 10 ²³ |
| 24. 41.67 g cm ⁻³ | 25. 24.12 × 10 ²³ atoms | 32. 2.786 × 10 ⁻²³ cm ³ |
| 26. a = 5.94 × 10 ⁻⁸ cm, V = a ³ = 2.096 × 10 ⁻²² cm ³ | 27. 1.81 Å | |
| 29. (i) 329 pm (ii) 139 pm | 31. 2, i.e., BCC | |
| 33. (a) 354 pm (b) 2.25 × 10 ²³ | 34. NaCl, 216 (au) ³ | |

HINTS FOR DIFFICULT PROBLEMS

- For fcc lattice, Z = 4. Radius $r = \frac{a}{2\sqrt{2}} = 0.3535a$.
- Rock salt type structure means fcc for which $r = \frac{a}{2\sqrt{2}} = 0.3535a$ or $a = \frac{r}{0.3535} = \frac{142 \text{ pm}}{0.3535} = 401.7 \text{ pm}$
 For fcc, Z = 4.
- For fcc, $r = \frac{a}{2\sqrt{2}}$ or $a = 2\sqrt{2}r = 2 \times 1.414 \times 128 \text{ pm} = 362 \text{ pm}$

$$\rho = \frac{Z \times M}{a^3 \times N_0} = \frac{4 \times 63.5 \text{ g mol}^{-1}}{(362 \times 10^{-10} \text{ cm})^3 \times 6.02 \times 10^{23} \text{ mol}^{-1}} = 8.9 \text{ g cm}^{-3}$$
 Alternatively,
$$\rho = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}} = \frac{4 \times (63.5 \text{ g mol}^{-1} / 6.02 \times 10^{23} \text{ mol}^{-1})}{(362 \times 10^{-10} \text{ cm})^3} = 8.9 \text{ g cm}^{-3}$$
- For FCC, $d = \frac{a}{\sqrt{2}}$ or $a = \sqrt{2}d = 1.414 \times 287 \text{ pm} = 406 \text{ pm}$, Z = 4, M = 107.87 g mol⁻¹

$$\rho = \frac{Z \times M}{a^3 \times N_0} = \frac{4 \times 107.87 \text{ g mol}^{-1}}{(406 \times 10^{-10} \text{ cm})^3 \times (6.02 \times 10^{23} \text{ mol}^{-1})} = 10.71 \text{ g cm}^{-3}$$
- $$\rho = \frac{Z \times M}{a^3 \times N_A}$$
 or
$$a^3 = \frac{Z \times M}{N_A \times \rho} = \frac{4 \times 207 \text{ g mol}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-1} \times 11.35 \text{ g cm}^{-3}} = 12.118 \times 10^{-23} = 121.18 \times 10^{-24}$$
 or
$$a = (121.18)^{1/3} \times 10^{-8}$$
 Let $x = (121.18)^{1/3}$ ∴ $\log x = \frac{1}{3} \log 121.18 = \frac{1}{3} (2.083) = 0.694$ or $x = \text{antilog } 0.694 = 4.943$
 ∴ $a = 4.943 \times 10^{-8} \text{ cm} = 494.3 \times 10^{-10} \text{ cm} = 494.3 \text{ pm}$

For fcc,
 13. For BCC un
 $N_0 = \frac{Z \times M}{a^3 \times \rho}$
 16. Distance b
 18. Calculate
 19. Calculate
 has body-
 24. Calculate
 mass of
 25. Calculate
 26. Edge 'a'
 27. Interioni
 ∴ BC
 Radius
 29. (i) For
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SOLID STATE

For fcc, $r = \frac{a}{2\sqrt{2}} = 0.3535 a = 0.3535 \times 494.3 \text{ pm} = 174.7 \text{ pm}$

13. For BCC unit cell of the element Fe, $Z = 2$

$$N_0 = \frac{Z \times M}{a^3 \times \rho} = \frac{2 \times 56 \text{ g mol}^{-1}}{(286.65 \times 10^{-10} \text{ cm})^3 \times (7.87 \text{ g cm}^{-3})} = 6.04 \times 10^{23} \text{ mol}^{-1}$$

16. Distance between Pb^{2+} and S^{2-} ions = $\frac{a}{2}$ (as it has NaCl structure).

18. Calculate Z ($Z = 2$ means BCC).

19. Calculate Z . It comes out to be 1. This shows that a unit cell of TlCl has one formula unit of TlCl . Hence, it has body-centred cubic lattice (similar to that of CsCl).

24. Calculate the mass (m) of an atom and then substitute in $\rho = \frac{Z \times m}{a^3}$. Take $Z = 4$ or first calculate M , i.e., mass of Avogadro's no. of atoms.

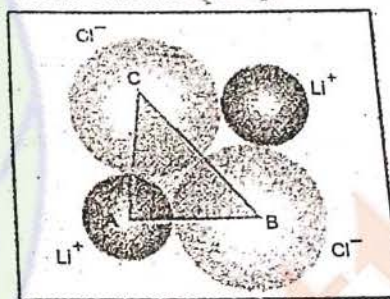
25. Calculate the atomic mass, M . Then M grams contain 6.023×10^{23} atoms. Calculate atoms present in 200 g.

26. Edge ' a ' of unit cell = $2 \times$ Distance between Pb^{2+} and S^{2-} ions.

27. Interionic distance of $\text{LiCl} = \frac{5.14}{2} = 2.57 \text{ \AA}$

$$\therefore BC = \sqrt{AB^2 + AC^2} = \sqrt{(2.57)^2 + (2.57)^2} = 3.63$$

Radius of Cl^- ion = $\frac{1}{2} \times 3.63 \text{ \AA} = 1.81 \text{ \AA}$.



29. (i) For bcc, distance between A^+ and $\text{B}^- = \frac{\sqrt{3}}{2} a$, i.e., it is half of body diagonal (See Fig. 1.33 on page 1/30)

(ii) As the cations and the anions touch each other,

$$r_{\text{A}^+} + r_{\text{B}^-} = 329 \text{ pm} \quad \therefore r_{\text{B}^-} = 329 - 190 = 139 \text{ pm}$$

30. $\rho = \frac{Z \times m}{a^3 \times 10^{-30}}$

$$\text{or } a = \left(\frac{Z \times m}{\rho \times 10^{-30}} \right)^{1/3} = \frac{4 \times 200 / (4.12 \times 10^{24})}{7.2 \times 10^{-30}} \text{ pm} = 299.9 \text{ pm}$$

32. Mass of the unit cell = Mass of one atom \times No. of atoms present in the unit cell

$$= \left(\frac{50}{6.023 \times 10^{23}} \text{ g} \right) \times 2 \quad [\text{For BCC, } Z = 2]$$

$$\text{Volume of the unit cell} = \frac{\text{Mass}}{\text{Density}} = \frac{50 \times 2}{6.023 \times 10^{23}} \text{ g} \times \frac{1}{5.96 \text{ g cm}^{-3}} = 2.786 \times 10^{-23} \text{ cm}^3$$

33. $\text{ccp} = \text{fcc}$. For fcc, $r = \frac{a}{2\sqrt{2}}$ or $a = 2\sqrt{2} r = 2 \times 1.414 \times 125 \times 10^{-2} \text{ m} = 354 \times 10^{-12} \text{ m} = 354 \text{ pm}$

$$\text{Volume of one unit cell} = (354 \times 10^{-12} \text{ m})^3 = 4.436 \times 10^{-29} \text{ m}^3$$

$$\therefore \text{No. of unit cells in } 1 \text{ m}^3 = \frac{1}{4.436 \times 10^{-29}} = 2.25 \times 10^{28}$$

34. $r_+/r_- = 2/1 = 0.5$ which lies in the range $0.414 - 0.732$ (See page 1/27)

$$\text{Edge} = 2(r_+ + r_-) = 6 \text{ au. Volume} = (6 \text{ au})^3 = 216 \text{ (au)}^3$$

SUPPLEMENT YOUR KNOWLEDGE

TABLETS

Main characteristics and examples of some simple ionic solids

Crystal Structure	Brief description	Examples	Coordination no.	Number of units per unit cell
Type AB (i) Rock salt (NaCl) type	It has fcc arrangement in which Cl ⁻ ions occupy the corners and face centres of a cube while Na ⁺ ions are present at the edge centres and body centre. (Refer to Fig. 1.35)	Halides of Li, Na, K, Rb, AgF, AgBr, NH ₄ Cl, NH ₄ Br, NH ₄ I, etc.	Na ⁺ = 6 Cl ⁻ = 6	4 (Na ⁺ ions = 8 × $\frac{1}{8}$ corners + 1 body centre) Cl ⁻ ions = 8 × $\frac{1}{2}$ face centres + 6 × $\frac{1}{2}$ edge centres + 1 body centre
(ii) Caesium chloride (CsCl) type	It has the bcc arrangement with Cs ⁺ at the body centre and Cl ⁻ ions at the corners of a cube or vice versa. (Refer to Fig. 1.36)	CsCl, CsBr, CsI, CsCN, TlCl, TlBr, TlI and TlCN	Cs ⁺ = 8 Cl ⁻ = 8	1 (Cs ⁺ ions = 1 at body centre) Cl ⁻ ions = 8 × $\frac{1}{8}$ corners
(iii) Zinc blende (ZnS) type	It has ccp arrangement in which S ²⁻ ions form fcc and each Zn ²⁺ ion is surrounded tetrahedrally by four S ²⁻ ions and vice versa. (Refer to Fig. 1.37) Note. The structure of diamond is similar to that of ZnS in which in place of Zn ²⁺ and S ²⁻ ions, there are C-atoms at each place (Refer to Fig. 1.37)	CuCl, CuBr, CuI, AgI, BeS	Zn ²⁺ = 4 S ²⁻ = 4	4 S ²⁻ ions = 8 × $\frac{1}{8}$ corners Zn ²⁺ ions = 4 face centres (present on the body diagonal)
Type AB₂ (i) Fluorite (CaF ₂) type	It has ccp arrangement in which Ca ²⁺ ions form fcc with each Ca ²⁺ ion surrounded by 8 F ⁻ ions and each F ⁻ ion by 4 Ca ²⁺ ions. F ⁻ ions occupy all the tetrahedral voids. (Refer to Fig. 1.38)	BaF ₂ , BaCl ₂ , SrF ₂ , SrCl ₂ , CdF ₂ , PbF ₂	Ca ²⁺ = 8 F ⁻ = 4	4 Ca ²⁺ ions = 8 × $\frac{1}{8}$ corners F ⁻ ions = 8 (present within the body)
(ii) Antifluorite type (A ₂ B type)	Here negative ions form the ccp arrangement so that each positive ion is surrounded by 4 negative ions and each negative ion by 8 positive ions. The cations occupy half of the tetrahedral voids.	Na ₂ O	Na ⁺ = 4 O ²⁻ = 8	4

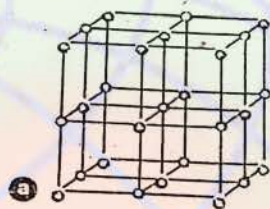
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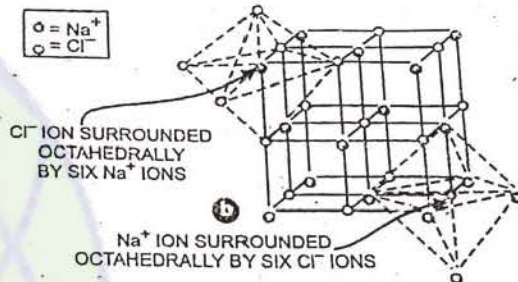
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Remember that CsCl lattice is slightly (about 1%) more stable than NaCl lattice because in CsCl, each ion is surrounded by more oppositely charged ions. The question arises then why halides of Li, Na, K and Rb do not have CsCl type lattice. This is answered by their radius ratio values as small cations cannot accommodate 8 halide ions.

Effect of Temperature and Pressure on Crystal Structure — Conversion of NaCl into CsCl Structure and Vice-versa. On applying high pressure, NaCl structure having 6 : 6 coordination changes to CsCl structure having 8 : 8 coordination. Similarly, CsCl having 8 : 8 coordination on heating to 760 K changes to NaCl structure having 6 : 6 coordination. Thus, increase of pressure increases the coordination number whereas increase of temperature decreases the coordination number.



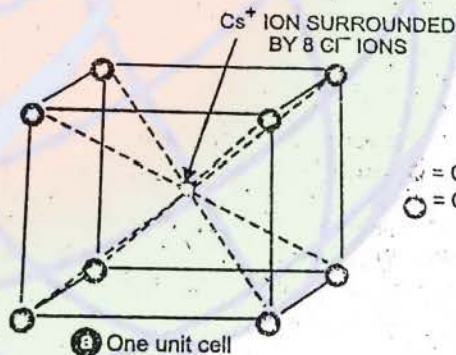
Structure of NaCl (Rock salt)



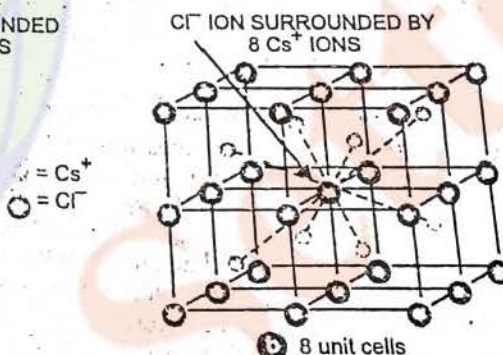
Showing coordination number of Na⁺ and Cl⁻ ions

FIGURE 1.35

NaCl structure (6 : 6 coordination)
 Pressure ↑ ↓ 760 K
 CsCl structure (8 : 8 coordination)



(a) One unit cell

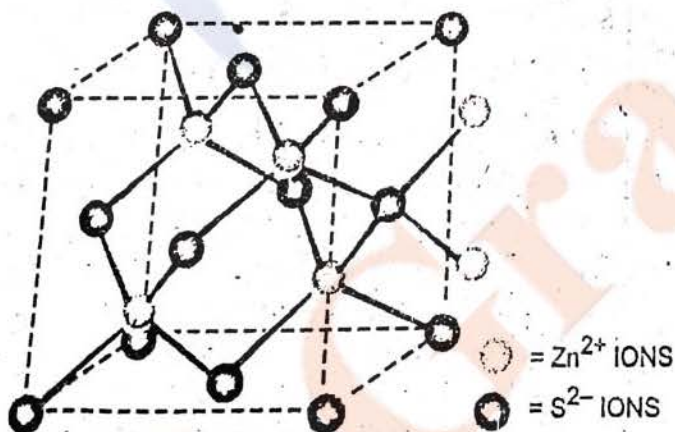


(b) 8 unit cells

Structure of CsCl

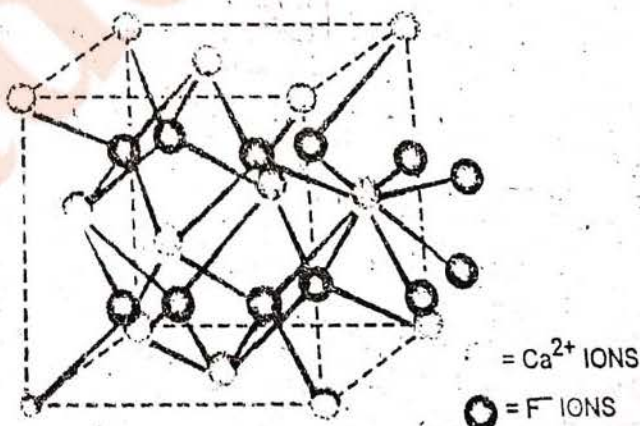
FIGURE 1.36

FIGURE 1.37



Structure of ZnS (Zinc blende)

FIGURE 1.38



Structure of CaF₂ (Fluorite)

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Calculation of number of unit cells in a given mass. Remembering that 1 mole of an ionic compound contains Avogadro's number of formula units and also knowing the number of formula units per unit cell, the number of unit cells in a given mass can be calculated.

Sample Problem: Calculate the approximate number of unit cells present in 1 g of ideal NaCl crystal.

Solution: 1 mole of NaCl = 58.5 g = 6.02×10^{23} formula units.

$$\therefore \text{No. of formula units in 1 g of NaCl} = \frac{6.02 \times 10^{23}}{58.5}$$

As one unit cell of NaCl contains 4 NaCl formula units, therefore, number of unit cells present in 1 g of NaCl is

$$= \frac{6.02 \times 10^{23}}{58.5 \times 4} = 2.57 \times 10^{21}$$

1.17. Imperfections or Defects In Solids

As discussed in the beginning of this unit, in a crystalline solid, there is a regular arrangement of constituent particles. However, this arrangement is generally not found to be perfect. This is because a solid contains a large number of small crystals and some of these may not have a perfect regular arrangement of the constituent particles. This happens when crystallisation takes place at fast or moderate rate because the constituent particles may not get sufficient time to arrange themselves in a perfect order. Even if we prepare single crystals by carrying out the crystallisation at extremely slow rate, these single crystals may not have a perfect arrangement.

Any departure from perfectly ordered arrangement of constituent particles in crystal is called imperfection or defect.

The defects may also arise due to the heat absorbed by the crystals from the surroundings* or due to the presence of impurities in the crystals.

Broadly speaking, there are two types of defects called point defects and line defects.

When the deviations or irregularities exist from the ideal arrangement around a point or an atom in a crystalline substance, the defect is called point defect. However, when the deviation from the ideal arrangement exists in the entire row of lattice points, the defect is called line defect.

It is not possible to explain many properties of solids such as the electrical conductivity and mechanical strength in terms of structure alone. Imperfections not only modify the properties but also sometimes impart new properties to the solids.

Here, we shall discuss only the point defects.

Types of Point Defects. Point defects in a crystal may be classified into the following three types:

- (A) Stoichiometric defects
- (B) Non-stoichiometric defects
- (C) Impurity defects

Now, we shall discuss each of these defects one by one.

(A) Stoichiometric Defects. If imperfections in the crystal are such that the ratio between the cations and anions remains the same as represented by the molecular formula, i.e., stoichiometry of the solid is not disturbed, the defects are called stoichiometric defects.

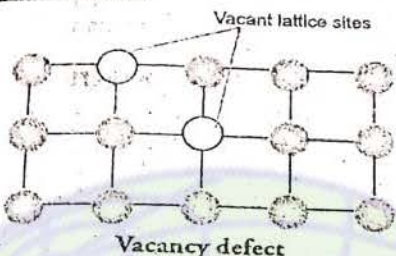
These are also called intrinsic defects or thermodynamic defects. Basically, these defects are of the following two types:

(i) **Vacancy defect.** When in a crystalline substance, some of the lattice sites are vacant, the crystal is said to have vacancy defect (Fig. 1.39). This generally arises due to absorption of heat from the surroundings (That is why it is a thermodynamic defect). It results in the decrease in the density of the substance (because mass in the same volume of the crystal decreases).

*There is a perfect ordered arrangement of constituent particles in a crystalline substance only at 0 K (Third law of thermodynamics).

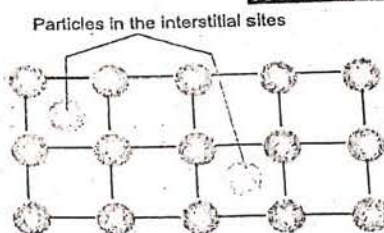
SOLID STATE

FIGURE 1.39



Vacancy defect

FIGURE 1.40



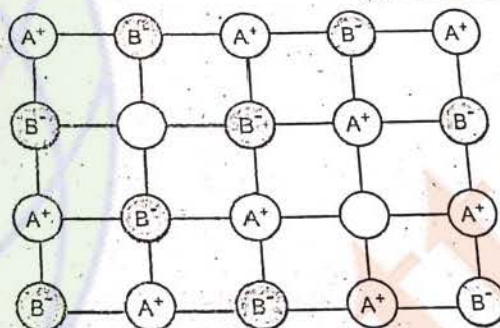
Interstitial defect

(ii) **Interstitial defect.** When some extra constituent particles are present in the interstitial sites, the crystal is said to have interstitial defect (Fig. 1.40). This defect results in the increase in the density of the substance (because mass increases but volume remains the same).

The above two types of defects are generally shown by non-ionic solids. Ionic solids do not show simple vacancy and interstitial defects. Instead, they show these defects as Schottky and Frenkel defects, as explained below :

FIGURE 1.41

(iii) **Schottky defect.** If in an ionic crystal of the type A^+B^- , equal number of cations and anions are missing from their lattice sites so that the electrical neutrality is maintained, it is called Schottky defect. The Schottky defect containing one pair of holes due to missing of one cation and one anion is shown in Fig. 1.41. Thus, basically, it is a vacancy defect.



Schottky defect

Types of compounds exhibiting Schottky defects. This type of defect is shown by highly ionic compounds which have

- (i) high coordination number, and
- (ii) small difference in the size of cations and anions

A few examples of ionic compounds exhibiting Schottky defect are NaCl, KCl, KBr, AgBr and CsCl.

Effect on density. As the number of ions decreases as a result of this defect, the mass decreases whereas the volume remains the same. Hence, like vacancy defect, the density of the solid decreases.

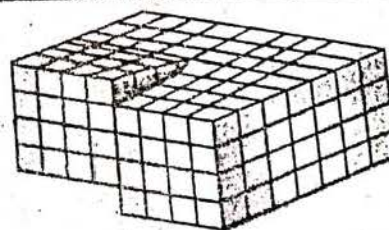
It is observed that in NaCl crystal at room temperature, there are about 10^{22} ions and 10^6 Schottky pairs per cm^3 . This means that there is one Schottky pair defect per 10^{16} ions. Thus, there are large number of holes present in the crystal. This results in the decrease in the density.

(iv) **Frenkel defect.** If an ion is missing from its lattice site (causing a vacancy or a hole there) and it occupies the interstitial site, electrical neutrality as well as the stoichiometry of the compound are maintained. This type of defect is called Frenkel defect. Thus, this defect is a combination of vacancy defect and interstitial defect. Since cations are usually smaller, it is more common to find the cations occupying interstitial sites. This defect is also called **dislocation defect*** because smaller ion (usually cation) is dislocated from its normal site to an interstitial site.

*The line defects are also called **dislocations**. The two main line defects are called **edge dislocations** and **screw dislocations**. If the edge of an atomic plane terminates within the crystal instead of passing all the way through, it is called edge dislocation. However, if parallel atomic planes normal to the axis are converted into a kind of spiral (helical) ramp, it is called screw dislocation.



(a) Edge dislocation



(b) Screw dislocation (small cubes represent atoms or molecules)

The Frenkel defect in which one cation is missing from the lattice site and is occupying the interstitial site is shown in Fig. 1.42.

Types of compounds exhibiting Frenkel defects. This type of defect is present in those compounds which have

- (i) low coordination number and
- (ii) large difference in the size of cations and anions

Frenkel defects are found in silver halides (AgCl, AgBr and AgI) due to small size of Ag^+ ion. It is also shown by ZnS due to small size of Zn^{2+} ion. They are not found in alkali metal halides as the alkali metal ions cannot fit into the interstitial sites.

There are some ionic solids which show both Schottky and Frenkel defects, e.g., AgBr. Effect on density. Since no ions are missing from the crystal as a whole, therefore density of the solid remains unchanged.

Some other consequences of Schottky and Frenkel defects.

- (i) Solids having these defects conduct electricity to a small extent. This is because if an ion moves from its lattice site to occupy a 'hole', it creates a new 'hole'. In this way, a hole moves across the crystal which as a result moves the charge in the opposite direction.
- (ii) Due to presence of holes, the stability (or the lattice energy) of the crystal decreases
- (iii) In Frenkel defect, similar charges come closer. This results in the increase of dielectric constant of the crystals.

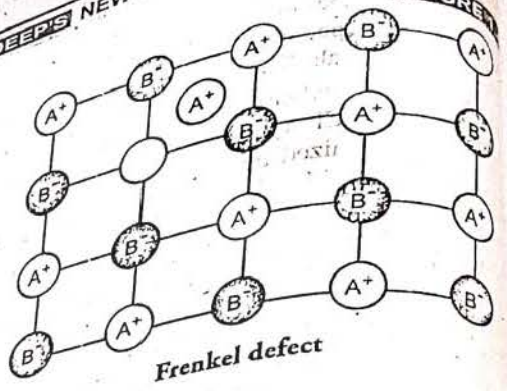
Difference between Schottky and Frenkel defects. The main points of difference are listed below:

TABLE 1.6 Main points of difference between Schottky defect and Frenkel defect

SCHOTTKY DEFECT	FRENKEL DEFECT
(i) It is due to equal number of cations and anions missing from the lattice sites.	(i) It is due to the missing of ions (usually cation) from the lattice sites and these occupy the interstitial sites.
(ii) This results in the decrease in the density of the crystal.	(ii) It has no effect on the density of the crystal.
(iii) This type of defect is found in highly ionic compounds with high coordination number and having cations and anions of similar sizes, e.g., NaCl, CsCl etc.	(iii) This type of defect is found in crystals with low coordination number and in which the difference in the size of cations and anions is very large, e.g., silver halides.

(B) Non-stoichiometric Defects*. If, as a result of the imperfection in the crystal, the ratio of the cations to the anions becomes different from that indicated by the ideal chemical formula, the defects are called non-stoichiometric defects. These defects result in either excess of the metal atoms or excess of non metal atoms (or deficiency of the metal atoms). These can occur as follows:—

*Non-stoichiometric substances are sometimes called berthollides after Berthollet who studied such compounds.



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SOLID STATE

(a) **Metal excess.** This may occur in either of the following two ways :—

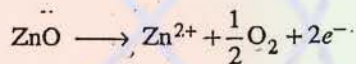
(i) **By anion vacancies.** A negative ion may be missing from its lattice site, leaving a hole which is occupied by an electron, thereby maintaining the electrical balance (Fig. 1.43). The sites containing the electrons thus trapped in the anion vacancies are called **F-centres** because they are responsible for imparting colour to the crystals (F=Farbe which is a German word for 'colour').

For example, when NaCl is heated in an atmosphere of Na vapour, the excess of Na atoms deposit on the surface of NaCl crystal. Cl⁻ ions then diffuse to the surface where they combine with the Na atoms which become ionized by losing electrons. These electrons diffuse back into the crystal and occupy the vacant sites created by the Cl⁻ ions. These electrons absorb some energy of the white light, giving yellow colour to NaCl. Similarly, excess of Li in LiCl makes it pink and excess of K in KCl makes it violet.

This defect is similar to Schottky defect and is found in crystals having Schottky defects.

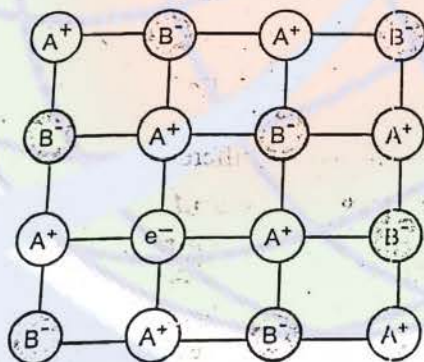
(ii) **By the presence of extra cations in the interstitial sites.** Metal excess may also be caused by an extra cation occupying the interstitial site. Electrical neutrality is maintained by an electron present in another interstitial site (Fig. 1.44). This defect is similar to Frenkel defect and is found in crystals having Frenkel defects.

For example, when ZnO is heated, it loses oxygen and turns yellow due to following reaction :



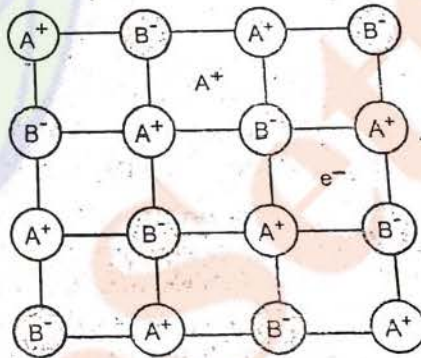
The excess of Zn²⁺ ions thus formed get trapped into the vacant interstitial sites and the electrons in the neighbouring interstitial sites.

FIGURE 1.43



Metal excess defect due to anion vacancy

FIGURE 1.44



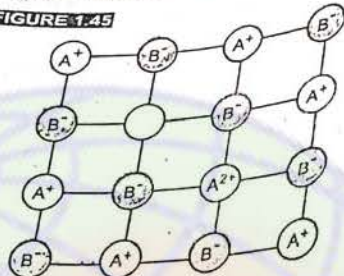
Metal excess defect caused by extra cation in the interstitial site

Crystals with either type of metal excess defects contain some free electrons. Hence, they act as semi-conductors.

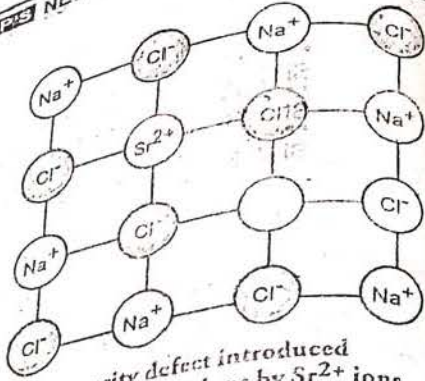
(b) **Metal Deficiency.** This defect occurs when the metal shows variable valency, i.e., in transition metals. The defect usually occurs due to the missing of a cation from its lattice site and the presence of the cation having higher charge (e.g., + 2 instead of + 1) in the adjacent lattice site. Examples include FeO, FeS and NiO. A general case where a metal A shows variable valency of + 1 and + 2 is shown in Fig. 1.45. Two monovalent cations are replaced by one divalent cation to maintain electrical neutrality.

Due to metal deficiency, the compounds obtained are non-stoichiometric. For example, it is difficult to prepare ferrous oxide with the ideal composition, FeO. What we actually obtain is Fe_{0.95}O or Fe_xO with x = 0.93 to 0.96.

FIGURE 1.45



Metal deficiency defect due to missing of a cation of a lower valency and another lattice site occupied by a cation of higher valency



Impurity defect introduced by substituting Na+ ions by Sr2+ ions

(C) Impurity Defects. These defects arise when foreign atoms are present at the lattice site in place of host atoms (as shown in Figs. 1.46, 1.47 and 1.48) or at the vacant interstitial sites (e.g. in steel, which is carbide of iron, C-atoms are present at the interstitial sites in the lattice of Fe atoms). In the former case, we get substitutional solid solutions while in the latter case, we get interstitial solid solutions. The formation of the former depends upon the electronic structure of the impurity while that of the latter on the size of the impurity.

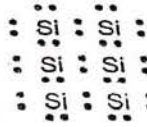
Addition of impurities changes the properties of the crystal.

The process of adding impurities to a crystalline substance so as to change its properties is called doping.

(i) Introducing impurity defect in ionic solids. In case of ionic solids, the impurities are introduced by adding impurity of ions. If the impurity ions are in a different valence state from that of the host ions, vacancies are created. For example, if molten NaCl, containing a little SrCl₂ as impurity is allowed to cool, in the crystals of NaCl formed, at some lattice sites, Na⁺ ions are substituted by Sr²⁺ ion. For every Sr²⁺ ion thus introduced, two Na⁺ ions are removed to maintain electrical neutrality. One of these lattice sites is occupied by Sr²⁺ ion and the other remains vacant. These vacancies result in the higher electrical conductivity of the solid. Similar defect and behaviour is observed when CdCl₂ is added to AgCl.

(ii) Introducing impurity defects in covalent solids. In case of covalent solids such as silicon or germanium (Group 14 elements) which have 4 valence electrons, the impurities added may be of the elements which may have more than 4 valence electrons (e.g., Group 15 elements like P or As which have five valence electrons) or of the elements which have less than 4 valence electrons (e.g., Group 13 elements like B, Al or Ga which have 3 electrons in the valence shell). Thus, the impurities added may be electron rich or electron deficit. The defects thus introduced in the crystals are called electronic defects*. Each of these is briefly described below :

*Electronic defects or imperfections may also be present in pure covalent or ionic crystals. This is because in these crystals, the electrons occupy fully the lowest energy states only at 0 K. For example, in the covalent crystal of silicon, at 0 K, all the electrons occupy the position of covalent bonds and in an ionic crystal like NaCl, the electrons are mostly concentrated around the more electronegative element. That is why pure silicon or NaCl at 0 K are bad conductors of electricity. Above 0 K, some of the electrons are likely to occupy higher energy states. For example, in silicon, some of the electrons from the covalent bonds get thermally released, creating an electron deficient site called a 'hole'. The released electrons are free to move and hence pure silicon above 0 K becomes a semiconductor. The holes in an electric field move in a direction opposite to that of electrons.



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(a) Doping in the valence 1.47a). When lattice sites are after forming free and gets germanium (or germanium

(b) Do Group 13 el or Ga. Now with the ne (Fig. 1.48) can jump t jumped. A Now, whe electron h Hence, sil

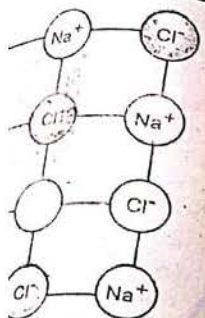
EL HO



(a)

ion v can l

FIGURE 1.48



roduced by Sc^{2+} ions
 free site in place of in steel, which is the former case, we see. The formation in the size of the

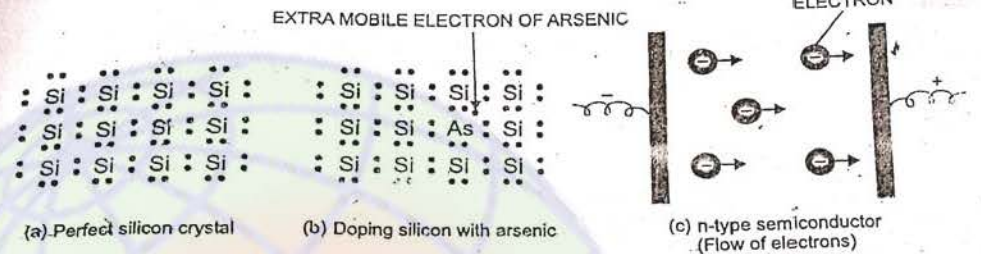
properties is
 re introduced the host ions, added to cool, every Sr^{2+} ion in the lattice sites is conductivity

silicon or one of the elements which have 4 valence electrons each of

use in the crystal of electrons bad e, in called The ons.

SOLID STATE

FIGURE 1.47

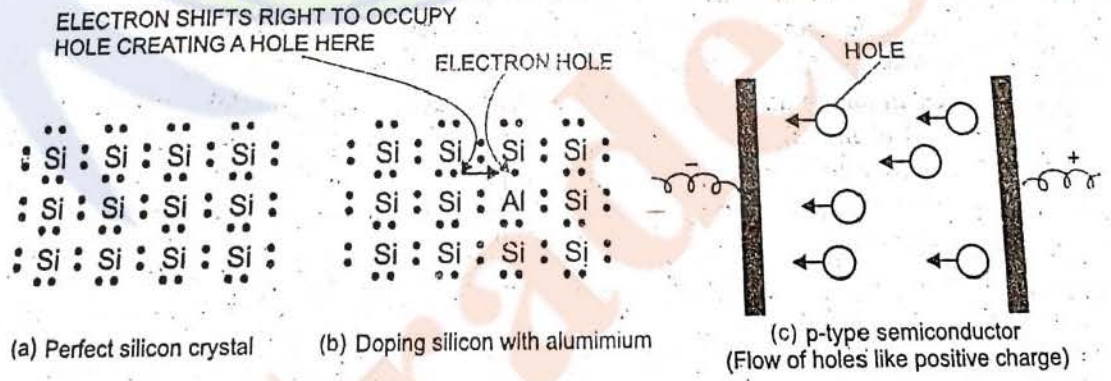


Doping of silicon with Group 15 elements to produce n-type semiconductors

(a) **Doping with electron rich impurities.** Group 14 element like silicon or germanium has 4 electrons in the valence shell. Hence, it normally forms four covalent bonds with the neighbouring atoms (Fig. 1.47a). When it is doped with Group 15 element like P or As, the silicon or germanium atoms at some lattice sites are substituted by atoms of P or As. Now, as these atoms have 5 electrons in the valence shell, after forming normal four covalent bonds with the neighbouring silicon atoms, the fifth extra electron is free and gets delocalized (Fig. 1.47b). These delocalized electrons increase the conductivity of silicon or germanium (Fig. 1.47c). As the increase in conductivity is due to negatively charged electrons, the silicon or germanium crystals doped with electron rich impurities are called **n-type semiconductors**.

(b) **Doping with electron deficit impurities.** When Group 14 element like Si or Ge is doped with Group 13 element like B, Al or Ga, the Si or Ge atom at some lattice sites are substituted by those of B, Al or Ga. Now, as Group 13 elements have only three valence electrons, they can form three covalent bonds with the neighbouring silicon atoms. Thus, a hole is created at the site where fourth electron is missing (Fig. 1.48 b). This is called **electron hole** or **electron vacancy**. An electron from the neighbouring atom can jump to fill up this electron hole but then an electron hole is created at the site from where electron has jumped. As it continues, the electron holes will move in a direction opposite to that of the flow of electrons. Now, when an electric field is applied, the electrons move towards the positively charged plate and the electron holes move towards the negatively charged plate as if they carry positive charge (Fig. 1.48 b). Hence, silicon and germanium doped with electron-deficit impurities are called **p-type semiconductors**.

FIGURE 1.48



Doping of silicon with group 13 elements to produce p-type semiconductors with flow of holes like positive charge

Calculation of cation vacancies. A metal ion with higher valency replaces more than one metal ion with lower valency, thereby creating vacancies. Depending upon their charges, number of vacancies can be calculated.

1/48

Sample Problem 1 If NaCl is doped with 10^{-3} mol % SrCl_2 , what is the concentration of vacancies?

Solution. Doping of NaCl with 10^{-3} mol % SrCl_2 means that 100 moles of NaCl are doped with 10^{-3} mole SrCl_2 .

\therefore 1 mole of NaCl is doped with $\text{SrCl}_2 = \frac{10^{-3}}{100}$ mole = 10^{-5} mole
As each Sr^{2+} ion introduces one cation vacancy, therefore, concentration of cation vacancies = 10^{-5} mol/mol of NaCl = $10^{-5} \times 6.02 \times 10^{23} \text{ mol}^{-1} = 6.02 \times 10^{18} \text{ mol}^{-1}$

Sample Problem 2 If Al^{3+} replaces Na^+ at the edge centre of NaCl lattice then calculate the concentration of vacancies in 1 mole NaCl. (AIPMT Mains 2000)

Solution. 1 mole of NaCl contains 1 mole of Na^+ ions, i.e., $6.023 \times 10^{23} \text{ Na}^+$ ions. NaCl has fcc arrangement of Cl^- ions and Na^+ ions are present at the edge centres and body-centre. As there are 12 edge centres and each edge centre is shared by 4 unit cells, their contribution per unit cell = $\frac{1}{4} \times 12 = 3$.

Contribution of Na^+ ion at the body-centre = 1.

Thus, for every 4 Na^+ ions, the ions present at the edge centres = 3. This means that Na^+ ions which have

been replaced = $\frac{3}{4} \times 6.023 \times 10^{23} = 4.517 \times 10^{23}$

1 Al^{3+} ion will replace 3 Na^+ ions to maintain electrical neutrality. One vacancy will be occupied by Al^{3+} ion and the remaining 2 will be vacant.

This means that $\frac{1}{3}$ rd of these positions will be occupied by Al^{3+} ions and $\frac{2}{3}$ rd will remain vacant. Hence,

no. of vacancies in 1 mole of NaCl = $\frac{2}{3} \times 4.517 \times 10^{23} = 3.01 \times 10^{23}$

Calculation of percentage of metal ions with variable valency from the formula of a non-stoichiometric compound. These calculations can be done keeping in mind that the total positive charge on cations must be equal to total negative charge on anions.

Sample Problem The composition of a sample of wustite is $\text{Fe}_{0.93}\text{O}_{1.00}$. What percentage of the iron is present in the form of Fe (III) ?

Solution. The composition is $\text{Fe}_{0.93}\text{O}_{1.00}$ instead of FeO because some Fe^{2+} ions have been replaced by Fe^{3+} ions. Let us first calculate the number of Fe^{2+} and Fe^{3+} ions present. The formula $\text{Fe}_{0.93}\text{O}_{1.00}$ implies that 93 Fe atoms are combined with 100 O-atoms. Out of 93 Fe atoms, suppose Fe atoms present as $\text{Fe}^{3+} = x$. Then $\text{Fe}^{2+} = 93 - x$. As the compound is neutral, total charge on Fe^{2+} and Fe^{3+} ions = total charge on O^{2-} ions. Thus,

$$3 \times x + 2(93 - x) = 2 \times 100 \quad \text{or} \quad 3x + 186 - 2x = 200 \quad \text{or} \quad x = 14$$

i.e.,

$$\text{Fe}^{3+} = 14.$$

Hence,

$$\text{Fe}^{2+} = 93 - 14 = 79.$$

Thus, the given formula, in fact, implies $\text{Fe}_{0.79}^{2+}\text{Fe}_{0.14}^{3+}\text{O}_{1.0}^{2-}$

Total molar mass = $0.93 \times 56 + 1 \times 16 = 68.08 \text{ g}$

Fe^{3+} present = $0.14 \times 56 = 7.84 \text{ g}$

$$\therefore \% \text{ age of Fe present as Fe (III)} = \frac{7.84}{68.08} \times 100 = 11.5\%$$



PROBLEM FOR PRACTICE

Analysis shows that a metal oxide has the empirical formula of $M_{0.96}O_{1.00}$. Calculate the percentage of M^{2+} and M^{3+} ions in this crystal. (Pb. Board 2011)

ANSWER

8.3%

1.18. Electrical Properties of Solids

Different types of solids show electrical conductivity which varies from as low as 10^{-20} $\text{ohm}^{-1} \text{m}^{-1}$ to 10^7 $\text{ohm}^{-1} \text{m}^{-1}$, i.e., it extends over 27 orders of magnitude. Depending upon the difference in electrical conductivities, the solids are classified into the following three types :

(i) **Conductors.** The solids which have conductivities in the range 10^4 to 10^7 $\text{ohm}^{-1} \text{m}^{-1}$ are called conductors. Metals have conductivities of the order of 10^7 $\text{ohm}^{-1} \text{m}^{-1}$ and hence are the best conductors of electricity.

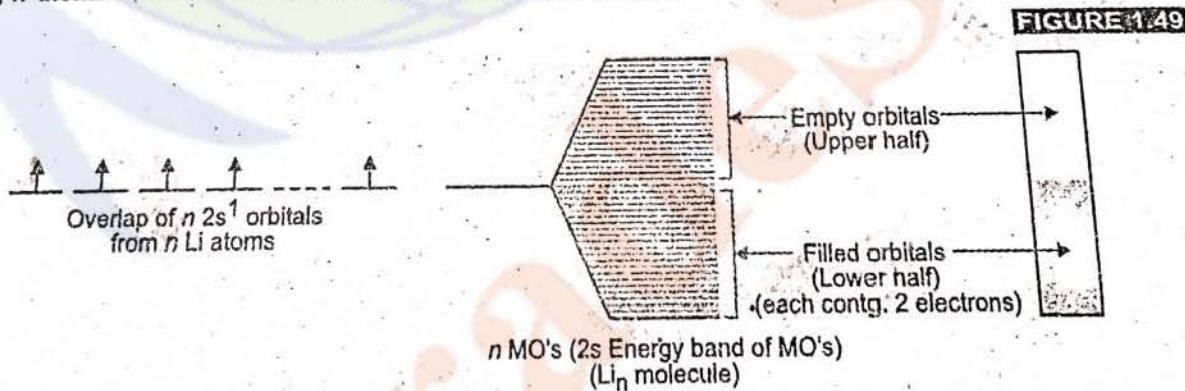
They are further classified as metallic conductors and electrolytic conductors. In the metallic conductors, the flow of electricity is due to flow of electrons (electronic conductors) without any chemical change occurring in the metal. The conductivity of metals depends upon the number of valence electrons available per atom. In case of electrolytic conductors like NaCl, KCl, etc., the flow of electricity takes place to a good extent only when they are taken in the molten state or in aqueous solution. The flow of electricity is due to flow of ions. However, in the solid state, they conduct electricity only to a small extent which is due to the presence of defects (holes, electrons, etc.).

Thus, whereas metals conduct electricity in the solid as well as molten state, electrolytes conduct electricity only in aqueous solution or molten state.

(ii) **Insulators.** The solids which have extremely low conductivity, i.e., ranging between 10^{-20} to 10^{-10} $\text{ohm}^{-1} \text{m}^{-1}$ are called insulators, e.g., plastics, wood, rubber, sulphur, phosphorus etc.

(iii) **Semiconductors.** The solids which have conductivity in between those of conductors and insulators, i.e., ranging from 10^{-5} to 10^4 $\text{ohm}^{-1} \text{m}^{-1}$ are called semiconductors.

Band theory of metals. In case of a metal, the atomic orbitals of the metal atoms are so close in energy that they overlap to form a large number of molecular orbitals very close in energy. This set of molecular orbitals is called a band. For example, the formation of a band by overlap of $n 2s^1$ orbitals of n Li atoms is shown in Fig. 1.49. Remember that just as two atomic orbitals combine to form two molecular orbitals, n atomic orbitals combine to form n molecular orbitals.

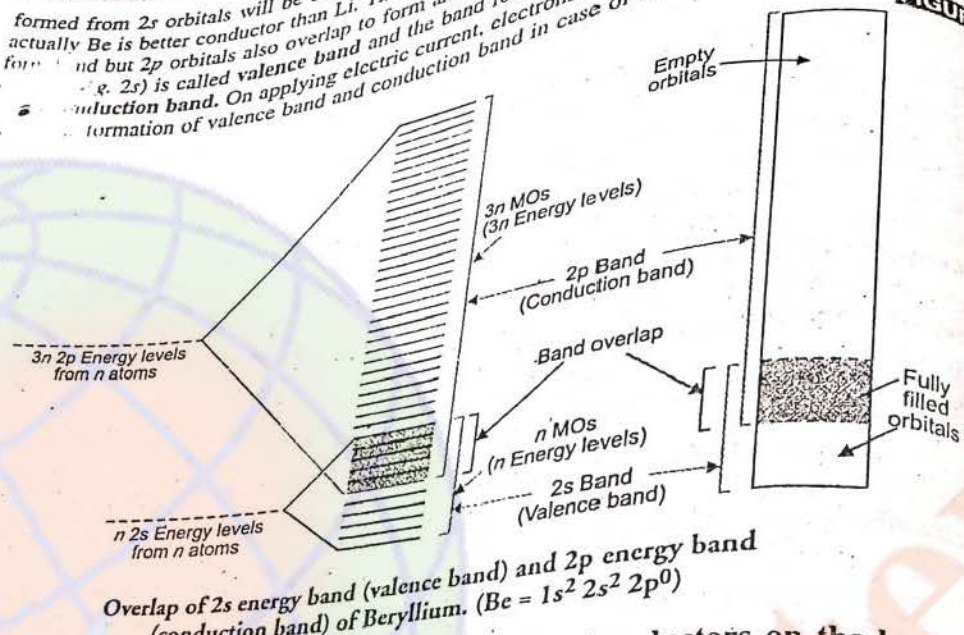


2s orbitals of Li atoms combining to form molecular orbitals equal to the number of Li atoms (2s orbitals) combining together. ($\text{Li} = 1s^2, 2s^1$)

In case of lithium, the lower half of molecular orbitals are completely filled while the upper half is empty. On applying electric current, electrons can move into the vacant levels. Hence, electric current can flow. However, in case of next metal, beryllium (${}_{4}\text{Be} = 1s^2 2s^2 2p^0$), as 2s orbitals are filled, the band

1/50

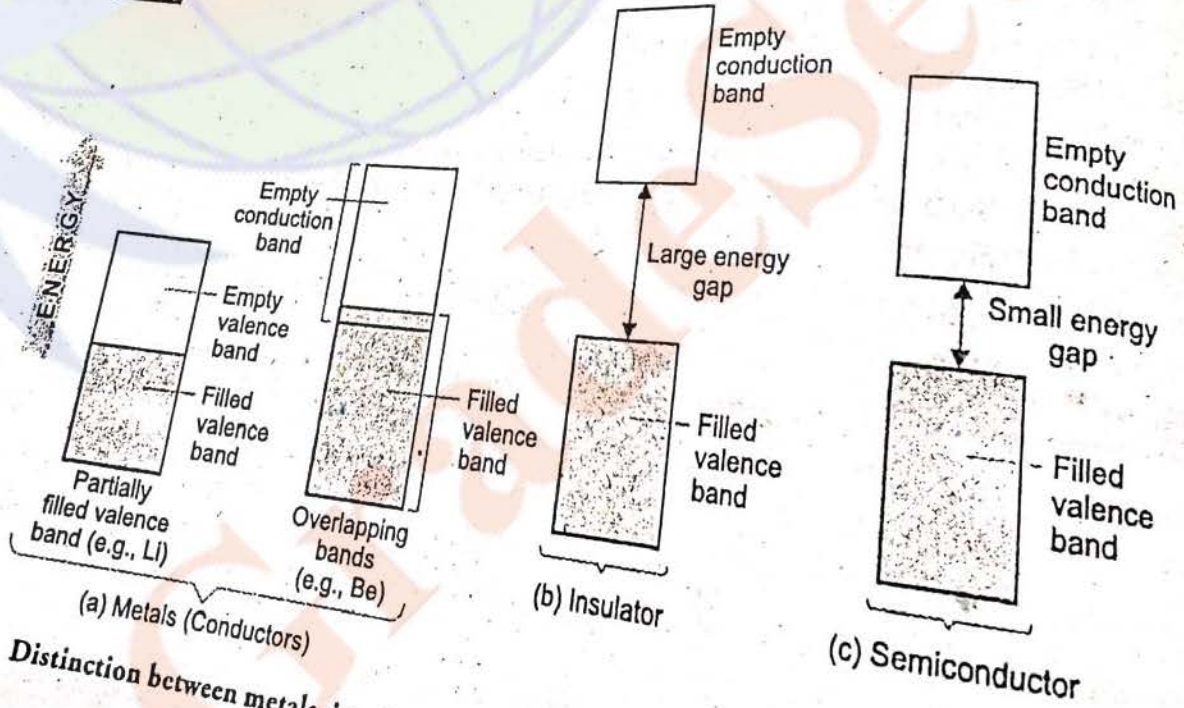
formed from 2s orbitals will be completely filled. Hence, no conduction of electricity should occur. Actually Be is a better conductor than Li. This is explained by suggesting that not only 2s orbitals overlap to form a band but 2p orbitals also overlap to form an empty band. The band formed by lower energy valence orbitals (e.g. 2s) is called valence band and the band formed by slightly higher energy valence orbitals (e.g. 2p) is called conduction band. On applying electric current, electrons can flow from valence band to conduction band. Formation of valence band and conduction band in case of Be is shown below in Fig. 1.51



Overlap of 2s energy band (valence band) and 2p energy band (conduction band) of Beryllium. ($Be = 1s^2 2s^2 2p^0$)

Explanation of behaviour of conductors, insulators and semiconductors on the basis of band theory. If the valence band is partially filled (e.g., in case of lithium) or it overlaps with the higher energy or unoccupied conduction band (as in case of beryllium) then electrons can easily flow under the influence of an applied electric field. Hence, the metal conducts electricity (Fig. 1.51 a).

FIGURE 1.51



Distinction between metals, insulators and semiconductors in terms of band theory

If the gap between the filled valence band and the unoccupied conduction band is large, electrons cannot jump from valence band to conduction band. Hence, the substance has extremely low conductivity and it behaves as an insulator (Fig. 1.51 b).

If the gap between the valence band and conduction band is small, some electrons may jump from valence band to conduction band. Hence, the substance shows some conductivity and it acts as a semiconductor (Fig. 1.51 c)

Effect of temperature on electrical conductivity. Electrical conductivity of metals decreases with increase of temperature because on heating, the positive ions of the metal atoms start vibrating and produce hinderance in the flow of electrons. The electrical conductivity of semiconductors increases with increase in temperature because more electrons can jump to the conduction band. Substances like silicon and germanium which show this type of behaviour are called **intrinsic semiconductors**. In fact, all pure substances that show conductivity similar to that of silicon and germanium are called *intrinsic semiconductors*.

Increasing the conductivity of intrinsic semiconductors. The conductivity of intrinsic semiconductors is so low that as such they have no practical use. The conductivity can be increased by **doping**, as already discussed, either by adding **electron rich impurities** or **electron deficit impurities**. The semiconductors thus obtained are called *n-type* and *p-type* semiconductors, as already discussed.

For example, electrical conductivity of silicon and germanium is very low at room temperature. It can be increased by doping with elements of Group 15 or Group 13 (as already discussed).

Similar to combination of Group 14 elements with those of Group 15 or Group 13, semiconductors have been prepared by combination of elements of Group 13 and 15 (e.g., InSb, AlP and GaAs) or Group 12 and 16 (e.g., ZnS, CdS, CdSe and HgTe).

Applications of n-type and p-type semiconductors. *n-* and *p-*type semiconductors are combined suitably to form a number of electronic components, e.g.,

- (i) A *diode* is a combination of *p-* and *n-*type semiconductors which is used as a *rectifier*.
- (ii) The solar cell is an efficient photo-diode used for conversion of light energy into electrical energy.
- (iii) *Transistors* are sandwich semiconductors of the type *pnp* or *nnp* which are used to detect or amplify radio or audio signals.
- (iv) Gallium arsenide (GaAs) semiconductors have very fast response and have revolutionised the designs of semiconductor devices.

Conductivity of transition metal oxides. It is interesting to point out that the variation in conductivity is very large even among similar compounds, e.g., monoxides of transition metals, all of which possess NaCl structure, show such large variations in electrical properties. Similar variations are observed among other similar oxides. For example,

- (i) TiO is metallic, MnO, FeO, CuO etc. are insulators whereas VO is metallic or insulating depending upon temperature.
- (ii) CrO₂ is metallic, MnO₂ is insulator whereas VO₂ is metallic or insulating depending upon temperature.
- (iii) ReO₃ is metallic whereas VO₃ and TiO₃ are metallic or insulating depending upon temperature.

To sum up : (i) TiO, CrO₂ and ReO₃ are metallic. (ii) MnO, FeO and CuO are insulators.

(iii) VO, VO₂, VO₃ and TiO₃ change from metallic to insulator at a certain temperature.

It is interesting to mention that Rhenium oxide, ReO₃, has the conductivity as well as appearance like that of copper.

Similar variation is observed among the sulphides of transition elements.

CURIOSITY QUESTION

Q What are diodes and transistors? For what purpose are they generally used?
Ans. A diode is a combination of p- and n-type semiconductors which is used as a rectifier. Transistors are sandwich semiconductors of the type pnp or npn which are used to detect or amplify radio audio signals.

1.19. Magnetic Properties of Solids

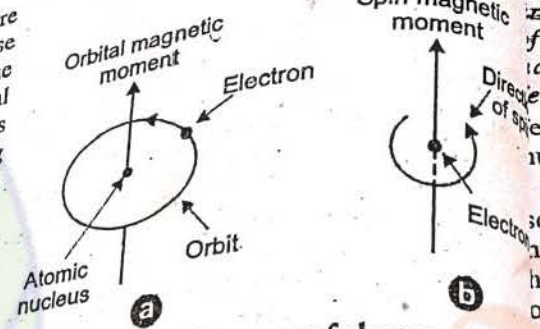
The magnetic properties of different materials are studied in terms of their *magnetic moments* which arise due to the orbital motion and spinning motion of the electrons. As electron is a charged particle, its orbital motion produces a small magnetic field along the axis of rotation, as shown in Fig. 1.52 and its spinning motion produces a small magnetic field along the spin axis.* Thus, each electron may be considered as a small magnet having a resultant permanent magnetic moment. As magnetic moment is a vector quantity, the net magnetic moment of an electron may be represented by an arrow. Thus, a material may be considered to contain a number of *magnetic dipoles* (similar to a bar magnet with north and south poles). Based on the behaviour in the external magnetic field, the substances are divided into different categories as explained below :

(i) **Diamagnetic substances.** Substances which are weakly repelled by the external magnetic field are called *diamagnetic substances*, e.g., TiO_2 , H_2O , $NaCl$, benzene, etc. The property thus exhibited is called *diamagnetism*. This property is shown only by those substances which contain fully-filled orbitals, i.e., no unpaired electron is present. The magnetic moment possessed by an electron with spin in one direction is cancelled by that with spin in the opposite direction.

(ii) **Paramagnetic substances.** Substances which are attracted by the external magnetic field are called *paramagnetic substances*. The property thus exhibited is called *paramagnetism*. This property is shown by those substances whose atoms, ions or molecules contain unpaired electrons, e.g., O_2 , Cu^{2+} , Fe^{3+} and Cr^{3+} . These substances, however, lose their magnetism in the absence of the magnetic field.

(iii) **Ferromagnetic substances.** Substances which show permanent magnetism even in the absence of the magnetic field are called *ferromagnetic substances*, e.g., Fe, Ni, Co, gadolinium (Gd) and Cr . These substances remain permanently magnetised, once they have been magnetised. The reason for such a magnetic behaviour by these substances is that in the solid state, the metal ions of these substances are grouped together in small regions called **domains**. Each domain acts as a tiny magnet having a definite magnetic moment. In an unmagnetised piece of any ferromagnetic substance, the domains are randomly oriented such that the magnetic moments cancel each other. However, when the substance is placed in a magnetic field, all the domains get oriented in the direction of the magnetic field, as shown in Fig. 1.53 (a). As a result, the substance has a very high magnetic moment. This ordering of domains persists even when the external magnetic field is removed. Hence, the substance remains permanently magnetised. In fact, ferromagnetic material, CrO_2 , is used to make magnetic tapes used for audio recording.

*Magnetic moment is expressed in terms of Bohr Magnetron ($\mu_B = 9.27 \times 10^{-24} \text{ A m}^2$). Spin magnetic moment of each electron = $\pm \mu_B$ and orbital magnetic moment = $m_l \mu_B$ where m_l is the magnetic quantum number of the electron.



(a) Magnetic moment of electron due to orbital motion (b) Magnetic moment of electron due to spin motion

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 (iv) Antiferromagnetism
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SU YOUR

1. Some non-organic compounds in...
2. Some elements...
3. I...

(iv) **Anti-ferromagnetic substances.** Substances which are expected to possess paramagnetism or ferromagnetism on the basis of magnetic moments of the domains but actually they possess zero net magnetic moment are called anti-ferromagnetic substances, e.g., MnO. Anti-ferromagnetism is due to the presence of equal number of domains in the opposite directions as shown in Fig. 1.53 (b).

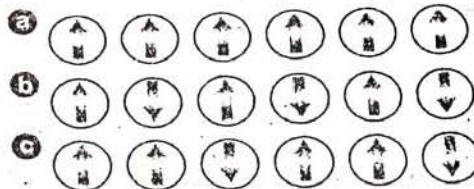
(v) **Ferrimagnetic substances.** Substances which are expected to possess large magnetism on the basis of the magnetic moments of the domains but actually have small net magnetic moment are called ferrimagnetic substances, e.g., magnetite (Fe_3O_4), ferrites of the formula $M^{2+}Fe_2O_4$ where $M = Mg, Cu, Zn$, etc. Ferrimagnetism arises due to the unequal number of domains in opposite direction resulting in some net magnetic moment, as shown in Fig. 1.53 (c).

It may be noted that all magnetically ordered solids, i.e., ferromagnetic and anti-ferromagnetic solids change into paramagnetic at high temperature. This is due to randomisation of domains (spins) on heating. Ferrimagnetic substance, Fe_3O_4 , becomes paramagnetic at 850 K. It may be further pointed out here that each ferromagnetic substance has a characteristic temperature above which no ferromagnetism is observed. This is known as **Curie temperature**.

Like electrical conductivity, the magnetic behaviour of the compounds of transition elements with similar structure may not be same. For example,

- (i) TiO, VO and CuO are paramagnetic whereas MnO, FeO, CoO and NiO are antiferromagnetic.
- (ii) TiO_2 is diamagnetic, VO_2 is paramagnetic, CrO_2 is ferromagnetic whereas MnO_2 is antiferromagnetic.

FIGURE 1.53



Alignment of the magnetic moments of domains in (a) ferromagnetic substance (b) antiferromagnetic substance (c) ferrimagnetic substance

SUPPLEMENT YOUR KNOWLEDGE

1. **Some Organic Polymers as Newly Discovered Conductors.** Conductors are metals or their alloys or some non-metals like carbon black and graphite or aqueous solutions or melts of electrolytes. Recently, some organic polymers have been synthesized which are electronic conductors, e.g., polyacetylene exposed to iodine vapours gives a product with metallic lustre and conductivity. Similarly, we have polyaniline, polypyrrole and polythiophene. As they are lighter and have better mechanical properties, they can be used in making light weight batteries and electronic devices like transistors which can be bent like plastic sheet.
2. **Superconductivity.** A substance is said to be superconducting when it offers no resistance to the flow of electricity. The phenomenon was discovered by Kammerlingh Onnes in 1913 when it was found that mercury becomes superconducting at 4 K. Most of the metals become superconducting at very low temperatures (2 K – 5 K). Certain organic compounds also become superconducting below 5 K. Such low temperatures can be attained only with liquid helium which is very expensive. Certain alloys of niobium have been found to be superconducting at temperatures as high as 23 K. Further researches since 1987 have revealed that many metal oxides become superconducting even at fairly high temperatures. For example, the oxide $Tl_2Ca_2Ba_2Cu_3O_{10}$ has been found to be superconducting at 125 K. Efforts are on to find out the materials which are superconducting at room temperature. Once this is done, it will revolutionize the fields of electronics, power transmission and levitation transportation, i.e., running of trains in air without the rails.

3. **Examples of some common magnetic substances**

Type of Substance	Examples
(i) Paramagnetic	Molecules (NO and O_2), transition metals (Cr, Mn, Ni, Co, Fe), metal ions (Cu^{2+} , Ni^{2+} , Fe^{3+} , Cr^{3+}) metal oxides (CuO , VO_2)
(ii) Diamagnetic	N_2 , NaCl, Zn, Cd, Cu^+ , TiO_2 , H_2O
(iii) Ferromagnetic	Ni, Fe, Co, Gd, CrO_2
(iv) Anti-ferromagnetic	MnO, Mn_2O_3 , MnO_2
(v) Ferrimagnetic	Fe_3O_4 and ferrites

4. **Dielectric Properties of Solids.** Insulators do not conduct electricity because the electrons on them are held tightly by the nuclei. However, when electric field is applied, polarisation takes place. In polar crystals show the following properties:
- (i) **Piezoelectricity.** When mechanical stress is applied on such crystals, electricity is produced. This phenomenon is called piezoelectricity and the crystals are called piezoelectric crystals, e.g., titanates of barium and lead, lead zirconate (PbZrO_3), ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) and quartz.
- (ii) **Pyroelectricity.** Some piezoelectric crystals when heated produce a small electric current. This phenomenon is called pyroelectricity (pyre means heat).
- (iii) **Ferroelectricity.** In some of the piezoelectric crystals, the dipoles are permanently polarized even in the absence of the electric field. However, on applying electric field, the direction of polarization changes. This phenomenon is called ferroelectricity due to analogy with ferromagnetism. Some examples of ferroelectric solids are barium titanate (BaTiO_3), sodium potassium tartarate (Rochelle salt) and potassium dihydrogen phosphate (KH_2PO_4). It may be pointed out here that all ferroelectric solids are piezoelectric but the reverse is not true.
- (iv) **Anti-ferroelectricity.** In some crystals, the dipoles align themselves in such a way that alternately they point up and down so that the crystal does not possess any net dipole moment. Such crystals are called anti-ferroelectric. A typical example of such crystals is lead zirconate (PbZrO_3).



REVISION AT A GLANCE

- Solid.** It is that form of matter which possesses rigidity and hence a definite shape and a definite volume.
- Cause of existence as solid.** If intermolecular forces > thermal energy, substance exists as solid.
- Classification of solids.** (i) **Crystalline solids**, when the constituent particles are arranged in a definite geometric pattern in three dimensional space so that there is short range as well as long range order of particles, e.g., all elements and compounds.
(ii) **Amorphous solids**, when there is no regular arrangement of particles or at the most there is only short range order, e.g., rubber, glass etc.
- Characteristics of crystalline and amorphous solids.**
(i) **Crystalline solids**: Regular arrangement of particles, definite geometric shapes, sharp melting point, definite heats of fusion, anisotropic, undergo clean cleavage.
(ii) **Amorphous solids**: No regular arrangement of particles, irregular shapes, melt over a range, no definite heats of fusion, isotropic, undergo irregular cleavage.
- Uses of amorphous solids.** Glass in household wares, laboratory wares and construction, rubber in tyres and shoe-soles, plastics in everyday life and amorphous silica in making photovoltaic cell.
- Classification of crystalline solids.**
(i) **Ionic solids**, e.g. NaCl, MgO etc.
(ii) **Molecular solids**, polar, e.g., HCl, SO_2 etc. and non-polar, e.g., Ar, H_2 , I_2 etc.
(iii) **Covalent/Network solids**, e.g., diamond, quartz (SiO_2) etc.
(iv) **Metallic solids**, e.g., all metals and alloys.
- Crystal lattice/Space lattice.** It is a regular arrangement of the constituent particles of a crystal in a three dimensional space.
- Unit cell.** It is the smallest three dimensional portion of the complete space lattice which when repeated in different directions produces the complete space lattice.

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COURSE CHEMISTRY (XII)
 because the electrons present in the crystal are polarised. Thus, dipoles are formed. This electricity is produced due to the polarisation of the crystal and the crystals are called piezoelectric crystals. Some examples of piezoelectric crystals are ammonium dihydrogen phosphate, quartz, Rochelle salt and potassium dihydrogen phosphate. Such crystals are said to be permanently polarized even in the absence of polarization change. Some examples of piezoelectric solids are piezoelectric materials. Such crystals are said to be permanently polarized even in the absence of polarization change. Some examples of piezoelectric solids are piezoelectric materials. Such crystals are said to be permanently polarized even in the absence of polarization change.

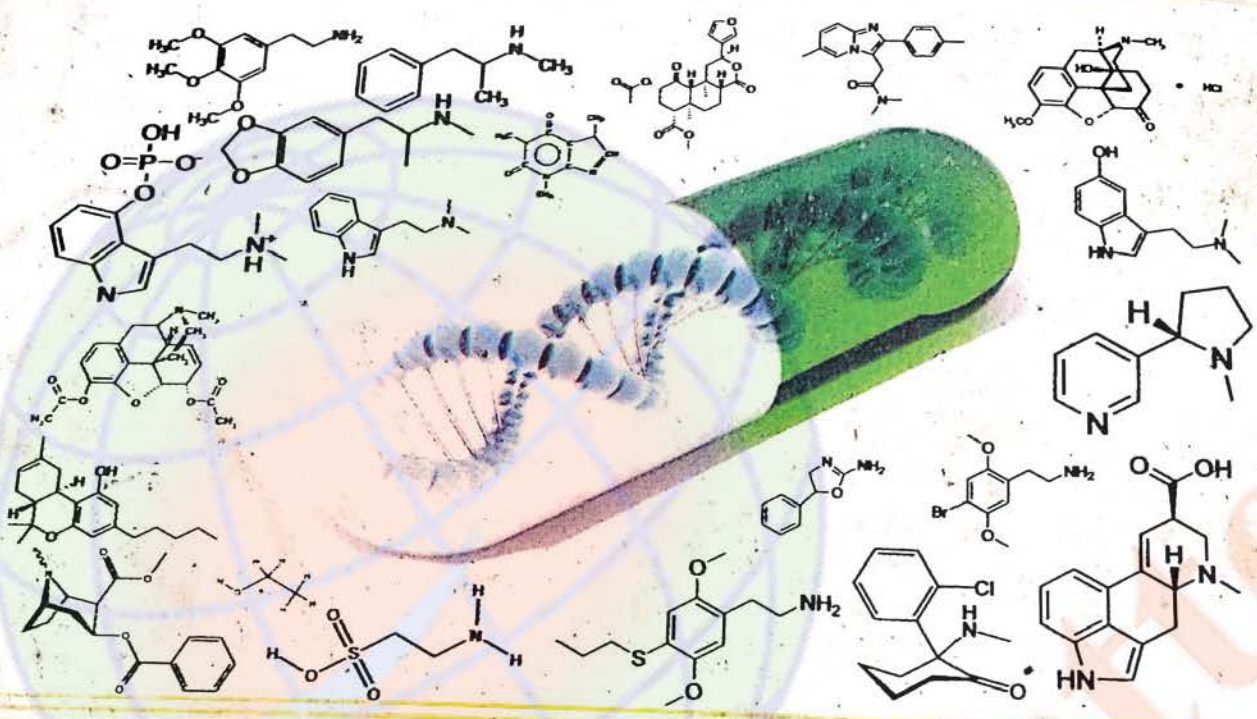
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SOLID STATE

9. **Parameters of a unit cell.** Lengths a , b and c of the three edges and angles α , β and γ between the edges (α between b and c and so on).
10. **Types of crystal systems.** (i) Cubic ($a = b = c$, $\alpha = \beta = \gamma = 90^\circ$) (ii) Tetragonal ($a = b \neq c$, $\alpha = \beta = \gamma = 90^\circ$) (iii) Orthorhombic/Rhombic ($a \neq b \neq c$, $\alpha = \beta = \gamma = 90^\circ$) (iv) Monoclinic ($a \neq b \neq c$, $\alpha = \gamma = 90^\circ \neq \beta$) (v) Triclinic ($a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90^\circ$) (vi) Rhombohedral/Trigonal ($a = b = c$, $\alpha = \beta = \gamma \neq 90^\circ$) (vii) Hexagonal ($a = b \neq c$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$).
11. **Types of lattices/unit cells.** (a) **Primitive/Simple** - having particles only at the corners (b) **Non-primitive**: (i) **Face-centred** - having particles at corners as well as face centres (ii) **End-centred** - having particles at corners and any two opposite faces (iii) **Body-centred** - having particles at corners and one at the body centre.
12. **Contribution by particles present at different positions**
 Corner = $\frac{1}{8}$, Face-centre = $\frac{1}{2}$, Body-centre = 1, Edge-centre = $\frac{1}{4}$.
13. **Number of particles per unit cell of a cubic crystal**
 Simple = $8 \times \frac{1}{8} = 1$, Body-centred = $8 \times \frac{1}{8} + 1 = 2$, Face-centred = $8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$
14. **Close packing in crystals** (i) Hexagonal close packing (HCP) viz ABAB... type, space occupied = 74%, empty space = 26% (ii) Cubic close packing (CCP) viz ABCABC...type, space occupied = 74%, empty space = 26% (iii) Body-centred cubic (BCC), space occupied = 68%, empty space = 32% (not a close packing). Also remember that in simple cubic unit cell, space occupied = 52.4%.
15. **Tetrahedral and Octahedral voids.** A simple triangular void surrounded by four spheres is a tetrahedral void. A double triangular void surrounded by six spheres is an octahedral void.
16. **Coordination number.** It is the number of closest particles or nearest neighbours of any constituent particle (anions present around a cation or vice versa in ionic compounds). Coordination number in HCP and CCP is 12 whereas for BCC, it is 8.
17. **Sizes of tetrahedral and octahedral voids.** (i) Radius (r) of tetrahedral void = $0.225 \times R$ where R is the radius of the spheres in close packing (ii) Radius (r) of octahedral void = $0.414 R$. For cations in the voids and anions in the packing, for tetrahedral, $r_+ = 0.225 r_-$ and for octahedral, $r_+ = 0.414 r_-$.
18. **Number of voids filled and formula of a compound**
 No. of octahedral voids = No. of particles present in close packing
 No. of tetrahedral voids = $2 \times$ No. of octahedral voids
 Assuming n particles of B are present in the packing and $\frac{1}{3}$ rd of octahedral voids are occupied by particles A, then ratio of A : B = $\frac{n}{3} : n = \frac{1}{3} : 1 = 3 : 1$. Hence, formula is A_3B .
 In ccp, total no. of voids per unit cell = 4 (octahedral) + 8 (tetrahedral) = 12
 In hcp, total no. of voids per unit cell = 6 (octahedral) + 12 (tetrahedral) = 18

19. **Radius ratio rules.** Radius ratio = $\frac{\text{Radius of cation } (r_+)}{\text{Radius of anion } (r_-)}$

Radius Ratio	Coord No.	Structural arrangement	Structure type
(i) 0.155 - 0.225	3	Planar triangular	—
(ii) 0.225 - 0.414	4	Tetrahedral	Sphalerite (ZnS)
(iii) 0.414 - 0.732	6	Octahedral	Rock salt (NaCl)
(iv) 0.732 - 1	8	Body-centred cubic	Caesium chloride (CsCl)



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