Module no 7.1

General characteristics of solid state

Amorphous and crystalline solids

General characteristics of solid state:

Matter can exist in three states namely, solid, liquid and gas. Under a given set of conditions of temperature and pressure. Which of these would be the most stable state of a given substance depends upon the net effect of two opposing factors. Intermolecular forces tend to keep the molecules (or atoms or ions) closer, whereas thermal energy tends to keep them apart by making them move faster. At sufficiently low temperature, the thermal energy is low and intermolecular forces bring them so close that they cling to one another and occupy fixed positions. These can still oscillate about their mean positions and the substance exists in solid state. The following are the characteristic properties of the solid state:

i. They have definite mass, volume and shape.
ii. Intermolecular distance are short
iii. Intermolecular forces are strong.
iv. Their constituent particles (atoms, molecules or ions) have fixed positions and can only oscillate about their mean positions.
v. They are incompressible and rigid.

Amorphous and crystalline solids:

Crystalline solids:

Solids can be classified as *crystalline or amorphous* on the basis of the nature of order present in the arrangement of their constituent particles. A crystalline solid usually consists of a large number of small crystals, each of them having a definite characteristic geometrical shape. In a crystal, the arrangement of constituent particles (atoms, molecules or ions) is ordered. It has long range order which means that there is a regular pattern of arrangement of particles which repeats itself periodically over the entire crystal. Sodium chloride and quartz are typical examples of crystalline solids.

Amorphous solids:

Solids are most stable in crystalline form. However, if a solid is formed rapidly (for example, when a liquid is cooled quickly), its atoms or molecules do not have time to align themselves and many become locked in positions other than those in a regular crystal. The resulting solid is said to be amorphous. Amorphous solids, such as glass, lack a regular three-dimensional arrangement of atoms or molecules.

Glass is a valuable and versatile material. We discuss the properties of glass now.

Glass commonly refers to an optically transparent fusion product of inorganic materials that has cooled to a rigid state without crystallizing. By fusion product we mean that the glass is formed by mixing molten silicon dioxide (SiO_2), its chief component, with compounds such as sodium oxide (Na_2O), boron oxide (B_2O_3), and certain transition metal oxides for color and other properties. In some respects glass behaves more like a liquid than a solid. X-ray diffraction studies show that glass lacks long-range periodic order.

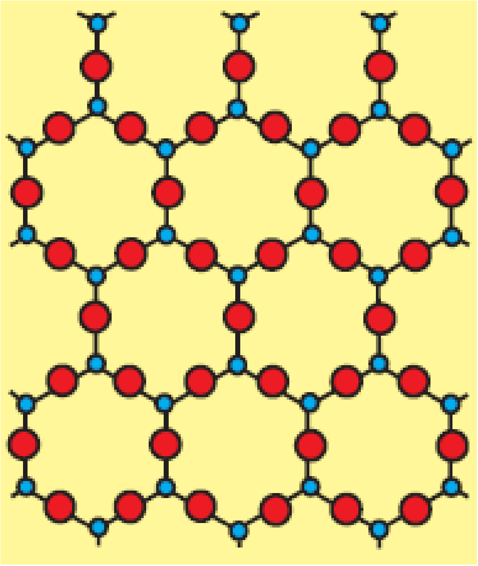
Self check question:

Amorphous solids are

a. Solids substances in real sense
b. Super cooled liquids
c. Having long range orderof attractions.
d. Substances with definite melting points

Solution: b

There are about 800 different types of glass in common use today. Figure below shows two-dimensional schematic representations of crystalline quartz and amorphous quartz glass.(see the symmetrical structure.)



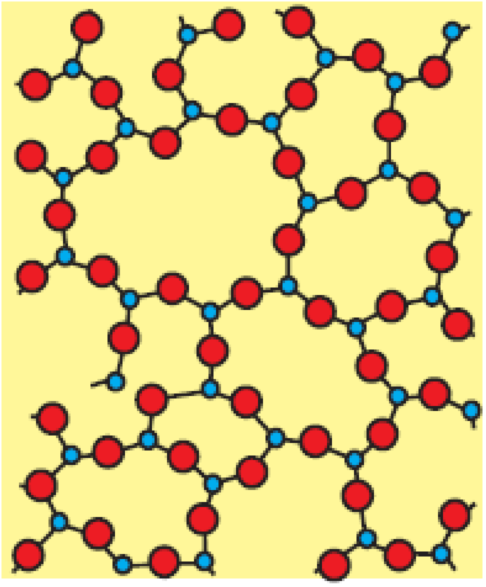


Table below shows the composition and properties of quartz, Pyrex, and soda-lime glass.

Composition and Properties of Three Types of Glass

Name	**Composition**	**Properties and Uses**
Pure quartz glass	100% SiO_2	Low thermal expansion, transparent to wide range of wavelengths. Used in optical research.
Pyrex glass	SiO_2. 60-80% B_2O_3, 10-25% Al_2O_3, small amount	Low thermal expansion; transparent to visible and infrared, but not to UV, radiation. Used mainly in laboratory and household cooking glassware.
Soda-lime glass	SiO_2, 75% Na_2O, 15% CaO, 10%	Easily attacked by chemicals and sensitive to thermal shocks. Transmits visible light, but absorbs UV radiation. Used mainly in windows and bottles.

The color of glass is due largely to the presence of metal ions (as oxides). For example, green glass contains iron (III) oxide, Fe_2O_3, or copper (II) oxide, CuO; yellow glass contains uranium (IV) oxide, UO_2; blue glass contains cobalt (II) or copper (II) oxides, CoO and CuO; and red glass contains small particles of gold or copper. We note that most of the ions mentioned here are derived from the transition metals oxides.

Self check question:

The characteristic features of solids are

a. Definite shape
b. Definite size
c. Definite shape and size
d. Definite shape, size and rigidity

Solution: d

Self check question:

Crystalline solids are

a. Short range order
b. Long range order
c. Isotropic in nature
d. Irregular in shape

Solution: b

The green colour of glass is due to the presence of _________

a. Fe_2O_3
b. CuO
c. UO_2
d. Both a) and b)

Solution: d

Review question:

1. Discuss the characteristic properties of the sold state?

Solution:

The following are the characteristic properties of the solid state:

- i. They have definite mass, volume and shape.
- ii. Intermolecular distances are short
- iii. Intermolecular forces are strong.
- iv. Their constituent particles (atoms, molecules or ions) have fixed positions and can only oscillate about their mean positions.
- v. They are incompressible and rigid.

2. Define the term “crystalline”state. Give a few examples of crystalline solids.

Solution:

Solids can be classified as *crystalline or amorphous* on the basis of the nature of order present in the arrangement of their constituent particles. A crystalline solid usually consists of a large number of small crystals, each of them having a definite characteristic geometrical shape. In a crystal, the arrangement of constituent particles (atoms, molecules or ions) is ordered. It has long range order which means that there is a regular pattern of arrangement of particles which repeats itself periodically over the entire crystal. Sodium chloride and quartz are typical examples of crystalline solids.

3. Define the term amorphous. Give examples.

Solution:

Solids are most stable in crystalline form. However, if a solid is formed rapidly (for example, when a liquid is cooled quickly), its atoms or molecules do not have time to align themselves and many become locked in positions other than those in a regular crystal. The resulting solid is said to be amorphous.

Amorphous solids, such as glass lack a regular three-dimensional arrangement of atoms or molecules.

4. Amorphous solids are
   a. Having short and long range order
   b. Having short range order
   c. Having long range order
   d. Having sharp melting points

Solution: b

Exercise questions:

1. Why are solids rigid?
2. Why glass is considered a super cooled liquid?
3. Distinguish between crystalline and amorphous solids.

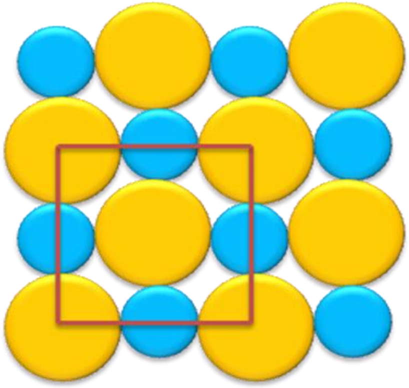
Module – 7.2
Types of Crystals

The structure and properties of crystals, such as melting point, density, and hardness, are determined by the kinds of forces that hold the particles together. Crystals may be classified into one of four types: ionic, covalent, molecular, or metallic.

Ionic Crystals:

Ionic crystals have two important characteristics: They are composed of charged species and anions and cations are generally quite different in size. There is no way to measure the radius of an individual ion, but sometimes it is possible to make a reasonable estimate. For example, if we know the radius of I^- in KI which is about 216 pm, we can determine the radius of K^+ ion in KI, and from that, the radius of Cl^- in KCl, and so on.

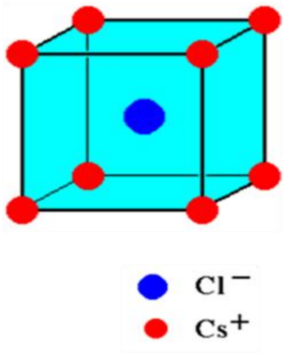
Let us consider the NaCl crystal, which has a face-centered cubic lattice. Figure below shows that the edge length of the unit cell of NaCl is twice the sum of the ionic radii of Na^+ and Cl^-.

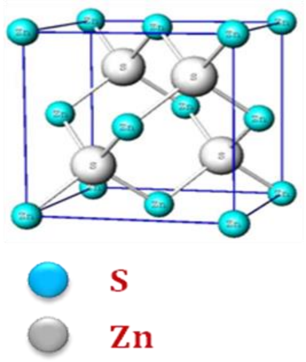


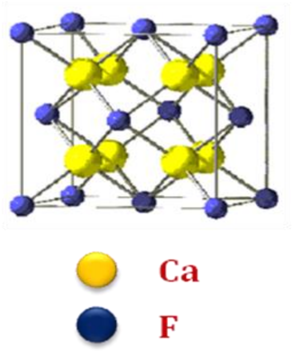
NaCl crystal - 564 pm

Therefore, we calculate the edge length to be 2 (95 + 181) pm, i.e. 552 pm. The edge length shown in the figure above was determined by X-ray diffraction to be 564 pm. The discrepancy between these two values tells us that the radius of an ion actually varies slightly from one compound to another.

Figure below shows the crystal structures of three ionic compounds: CsCl, ZnS, and CaF_2.







Because Cs^+ is considerably larger than Na^+, CsCl has the simple cubic lattice.

ZnS has the zincblende structure, which is based on the face-centered cubic lattice. If the S^{2-} ions occupy the lattice points, the Zn^{2+} ions are located one-fourth of the distance along each body diagonal. Other ionic compounds that have the zincblende structure include CuCl, BeS, CdS, and HgS.

CaF_2 has the fluorite structure. The Ca^{2+} ions occupy the lattice points, and each F^- ion is tetrahedrally surrounded by four Ca^{2+} ions. The compounds SrF_2, BaF_2, $BaCl_2$, and PbF_2 also have the fluorite structure.

The following examples show how to calculate the number of ions in a unit cell and the density of a unit cell.

Most ionic crystals have high melting points, an indication of the strong cohesive forces holding the ions together. A measure of the stability of ionic crystals is the lattice energy; the higher the lattice energy, the more stable the compound is. These solids do not conduct electricity because the ions are fixed in position. However, in the molten state or dissolved in water, the ions are free to move and the resulting liquid is electrically conducting.

Self check question:

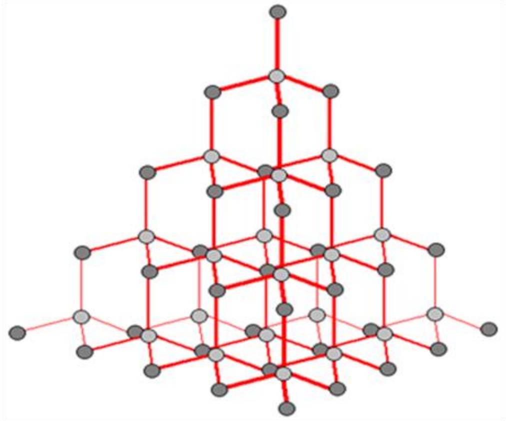
The crystals which are poor conductors of heat and electricity are ……. substances.

a. Ionic
b. Covalent
c. Molecular
d. Metallic

Solution: a)

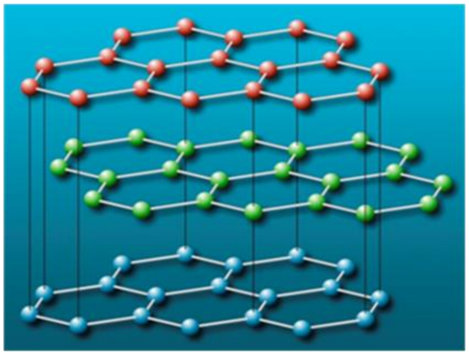
Covalent Crystals:

In covalent crystals, atoms are held together in an extensive three-dimensional network entirely by covalent bonds. The two allotropes of carbon, diamond and graphite, are two well-known examples. In diamond, each carbon atom is sp^3-hybridized; it is bonded to four other atoms.



Diamond

1.54 A^0 between the layers



Graphite

3.35 A^0 between the layers

The strong covalent bonds in three dimensions contribute to diamond's unusual hardness (it is the hardest material known) and very high melting point (3550°C).

In graphite, carbon atoms are arranged in six-membered rings. The atoms are all sp^2-hybridized; each atom is covalently bonded to three other atoms. The remaining unhybridised $2p$ orbital is used in pi bonding. In fact, each layer of graphite has the kind of delocalized molecular orbital that is present in benzene. Because electrons are free to move around in this extensively delocalized molecular orbital, graphite is a good conductor of electricity in directions along the planes of carbon atoms. The layers are held together by weak van der Waals forces. The covalent bonds in graphite account for its hardness; however, because the layers can slide over one another, graphite is slippery to touch and is effective as a lubricant. It is used in pencils and in ribbons made for computer printers and typewriters.

Another covalent crystal is quartz (SiO_2). The arrangement of silicon atoms in quartz is similar to that of carbon in diamond, but in quartz there is an oxygen atom between each pair of Si atoms. Because Si and O have different electronegativities, the Si –O bond is polar. Nevertheless, SiO_2 is similar to diamond in many respects, such as hardness and high melting point (1610°C).

Self check question:

Which of the following is a covalent crystalline solid?

a. Lime stone
b. Quartz
c. Sucrose
d. Copper

Solution: b)

Molecular Crystals:

In a molecular crystal, the lattice points are occupied by molecules, and the attractive forces between them are van der Waals forces and/or hydrogen bonding. An example of a molecular crystal is solid sulfur dioxide (SO_2), in which the predominant attractive force is a dipole-dipole interaction. Intermolecular hydrogen bonding is mainly responsible for maintaining the three-dimensional lattice of ice. Other examples of molecular crystals are I_2, P_4, and S_8.

In general, except in ice, molecules in molecular crystals are packed together as closely as their size and shape allow. Because van der Waals forces and hydrogen bonding are generally quite weak compared with covalent and ionic bonds, molecular crystals are more easily broken apart than ionic and covalent crystals. Indeed, most molecular crystals melt at temperatures below 100°C.

Self check question:

Ice is an example of ________ types of crystal lime solid.

a. Ionic
b. Covalent

c. Molecular
d. Metallic

Solution: c)

Metallic Crystals:

The structure of metallic crystals is the simplest because every lattice point in a crystal is occupied by an atom of the same metal. Metallic crystals are generally body-centered cubic, face-centered cubic, or hexagonal close-packed. Consequently, metallic elements are usually very dense.

The bonding in metals is quite different from that in other types of crystals. In a metal, the bonding electrons are delocalized over the entire crystal. In fact, metal atoms in a crystal can be imagined as an array of positive ions immersed in a sea of delocalized valence electrons.

The great cohesive force resulting from delocalization is responsible for a metal's strength. The mobility of the delocalized electrons makes metals good conductors of heat and electricity.

Self check question:

A metallic crystalline sold is

a. a poor conductor of heat
b. a good conductor of electricity
c. a volatile
d. brittle in nature

Solution: b)

Table below summarizes the properties of the four different types of crystals discussed

Type of Crystal	Force(s) holding the units together	General properties	Examples
Ionic	Electrostatic	Hard, brittle, high	NaCl, LiF, MgO,

	attraction	melting point, poor conductor of heat and electricity	$CaCO_3$
Covalent	Covalent bond	Hard, high melting point, poor conductor of heat and electricity	C (diamond),[‡] SiO_2 (quartz)
Molecular [*]	Dispersion forces, dipole – dipole force, hydrogen bonds	Soft, low melting point, poor conductor of heat and electricity	Ar, CO_2, I_2, H_2O $C_{12}H_{22}O_{11}$ (sucrose)
Metallic	Metallic bond	Soft to hard, low to high melting point, good conductor of heat and electricity	All metallic elements; for example, Na, Mg, Fe, Cu

Note: * Included in this category are crystals made up of individual atoms.

[‡] Diamond is a bad thermal conductor.

Self check question:

Which of the following sets of solids are all molecular crystals in solid state?

a. LiF, CO_2, diamond
b. ZnS, I_2 NaCl
c. CO_2, I_2, Ice
d. Graphite, CsCl, Fe

Solution: c)

Review questions:

1. Solid A is a very hard electrical insulator in solid state as well as in molten state. It melts at extremely high temperature. What type of crystalline solid it forms? Explain.

Solution:

Covalent crystal.

2. Graphite crystallizes in hexagonal solid form. Give its characteristics.

Solution:

In graphite, carbon atoms are arranged in six-membered rings. The atoms are all sp^2-hybridized; each atom is covalently bonded to three other atoms. The remaining unhybridised $2p$ orbital is used in pi bonding. In fact, each layer of graphite has the kind of delocalized molecular orbital that is present in benzene. Because electrons are free to move around in this extensively delocalized molecular orbital, graphite is a good conductor of electricity in directions along the planes of carbon atoms. The layers are held together by weak van der Waals forces. The covalent bonds in graphite account for its hardness; however, because the layers can slide over one another, graphite is slippery to the touch and is effective as a lubricant. It is used in pencils and in ribbons made for computer printers and typewriters.

3. What do you know about molecular crystals? Discuss.

Solution:

Molecular Crystals:

In a molecular crystal, the lattice points are occupied by molecules, and the attractive forces between them are van der Waals forces and/or hydrogen bonding. An example of a molecular crystal is solid sulfur dioxide (SO_2), in which the predominant attractive force is a dipole-dipole interaction. Intermolecular hydrogen bonding is mainly responsible for maintaining the three-dimensional lattice of ice. Other examples of molecular crystals are I_2, P_4, and S_8.

In general, except in ice, molecules in molecular crystals are packed together as closely as their size and shape allow. Because van der Waals forces and hydrogen bonding are generally quite weak compared with covalent and ionic bonds, molecular crystals are more easily broken apart than ionic and covalent crystals. Indeed, most molecular crystals melt at temperatures below 100°C.

4. Which type of solids are electrical conductors, mellable and ductile?

   a. Ionic
   b. Covalent
   c. Molecular
   d. Metallic

Solution: d)

5. Which of the following forms an ionic crystal?
   a. H_2O
   b. $CaCO_3$
   c. SiO_2
   d. I_2

Solution: b)

Exercise questions:

1. Write short notes on the following giving suitable examples
   a. Ionic crystals
   b. Metallic crystals
2. How many types of crystals are known? What are they? Give an example for each of them.
3. Write a brief account on covalent crystals
4. Write a note on molecular crystals.

Module – 7.3

Crystal structure system and Bravais lattices

Solids can be divided into two categories: crystalline and amorphous. Ice is a **crystalline solid**, which possesses rigid and long-range order; its atoms, molecules, or ions occupy specific positions. The arrangement of such particles in a crystalline solid is such that the net attractive intermolecular forces are at their maximum. The forces responsible for the stability of a crystal can be ionic forces, covalent bonds, van der Waals forces, hydrogen bonds, or a combination of these forces. *Amorphous solids* such as glass lack a well-defined arrangement and long-range molecular order. In this module, we will study the structure of crystalline solids.

Space Lattice:

The regular arrangement of an infinite set of points (atoms, molecule, or ions) in space is called space lattice.

An array of points showing the arrangement of constituents in 3- Dimensional space.

Unit cell:

The smallest repeating unit from which the lattice is built is known as unit cell.

Self check question:

The three dimensional graph of lattice points which sets pattern for the whole lattice is called

a. Space lattice
b. Simple lattice
c. Unit cell
d. Crystal lattice

Solution: a)

Unit cells can be broadly divided into two categories. They are **primitive** and **centered** unit cells.

1. Primitive Unit Cells:

When constituent particles are present only on the corner positions of a unit cell, it is called as primitive unit cell.

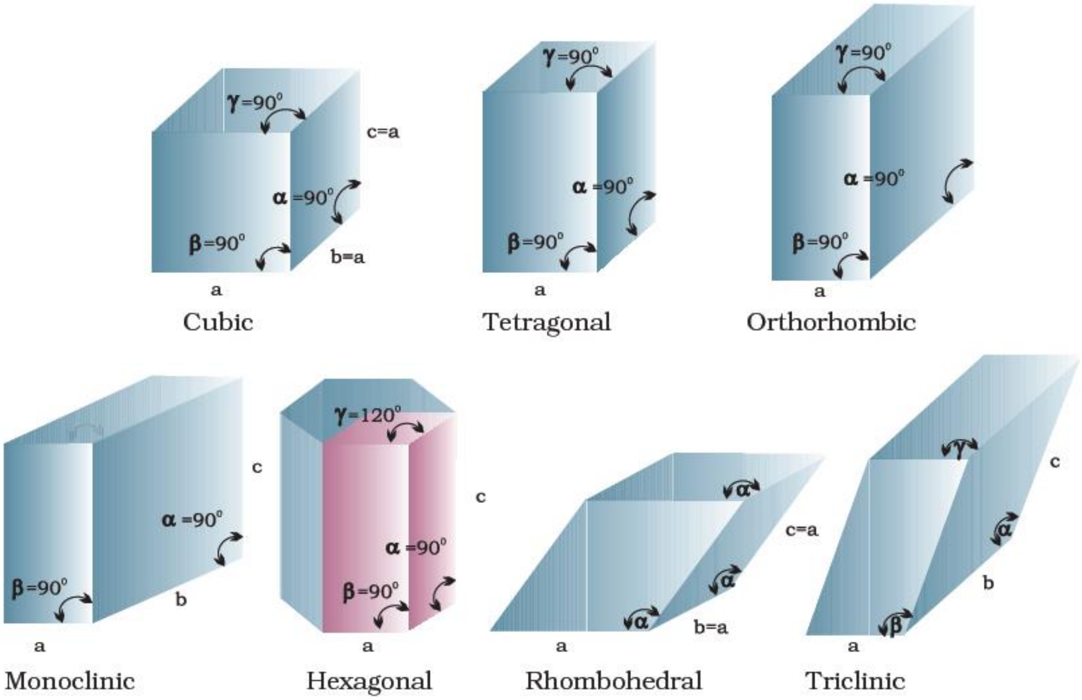
2. Body centered unit cells:

Such a unit cell contains one constituent particle (atom, molecule or ion) at its body centre besides the ones that are at its corners.

3. Face centered unit cells:

Such a unit cell contains one constituent particle present at the centre of each face, besides the ones that are at its corners.

In all, there are seven types of primitive unit cells.



Cubic Tetragonal Orthorhombic

Monoclinic Hexagonal Rhombohedral Triclinic

Seven primitive unit cells in crystals

Self check question:

How many basic crystal systems known?

a. 7

b. 8

c. 6

d. 4

Solution: a

Crystal system	Possible variations	Axial distance or edge lengths	Axial angles	Examples
Cubic	Primitive, body – centred, face – centred	$a = b = c$	$\alpha = \beta = \surd = 90^0$	NaCl, Zinc blende, Cu
Tetragonal	Primitive, body – centred	$a = b \neq c$	$\alpha = \beta = \surd = 90^0$	White tin, SnO_2, TiO_2, $CaSO_4$
Orthorhombic	Primitive, body – centred, face – centred, end – centred	$a \neq b \neq c$	$\alpha = \beta = \surd = 90^0$	Rhombic sulphur, KNO_3, $BaSO_4$
Hexagonal	Primitive	$a = b \neq c$	$\alpha = \beta = 90^0$ $\surd = 120^0$	Graphite, ZnO, CdS
Rhombohedral	Primitive	$a = b = c$	$\alpha = \beta = \surd \neq 90^0$	Calcite ($CaCO_3$), Hgs (cinnabar)
Monoclinic	Primitive, end – centred	$a \neq b \neq c$	$\alpha = \surd = 90^0$ $\beta \neq 90^0$	Monoclinic sulphur, Na_2SO_4, $10H_2O$
Triclinic	Primitive	$a \neq b \neq c$	$\alpha \neq \beta \neq \surd \neq 90^0$	$K_2Cr_2O_7$, $CuSO_4.5H_2O$. H_3BO_3

Self check question:

In a crystal; a ≠ b ≠ c and α = γ = 90^0, β ≠ 120^0. Is it?

a. Monoclinic

b. Rhombic

c. Trigonal

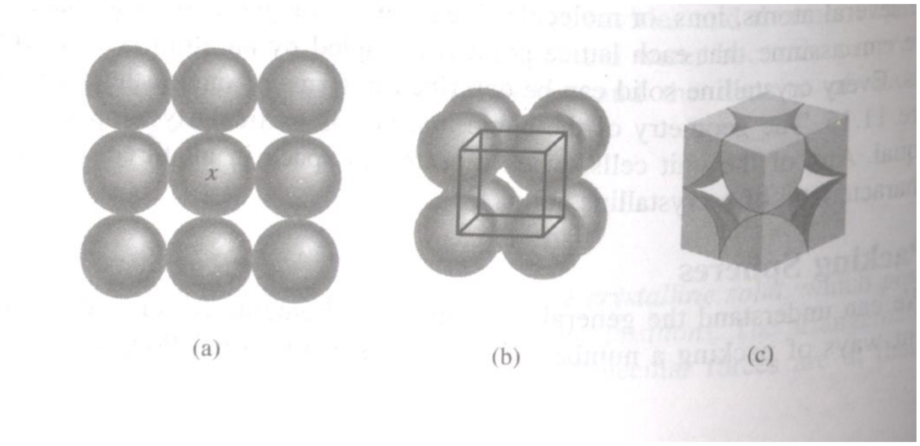
d. Tetragonal

Solution: a)

Packing Spheres:

We can understand the general geometric requirements for crystal formation by considering the different ways of packing a number of identical spheres to form an ordered three-dimensional structure. The way the spheres are arranged in layers determines what type of unit cell we have.

In the simplest case, a layer of spheres can be arranged as shown in figure (a) below.



(a) (b) (c)

The three-dimensional structure can be generated by placing a layer above and below this layer in such a way that spheres in one layer are directly over the spheres in the layer below it. This procedure can be extended to generate many, many layers, as in the case of a crystal. Focusing on the sphere labeled with an "*x*," we see that it is in contact with four spheres in its own layer, one sphere in the layer above, and one sphere in the layer below. Each sphere in this arrangement is said to have a coordination number of 6 because it has six immediate neighbors. The **coordination number** is defined as the number of atoms (or ions) surrounding an atom (or ion) in a crystal lattice. Its value gives us a measure of how tightly the spheres are packed together – the larger the coordination number, the closer the spheres are to each other. The basic, repeating unit in the array of spheres is called a *simple cubic cell* (figure b).

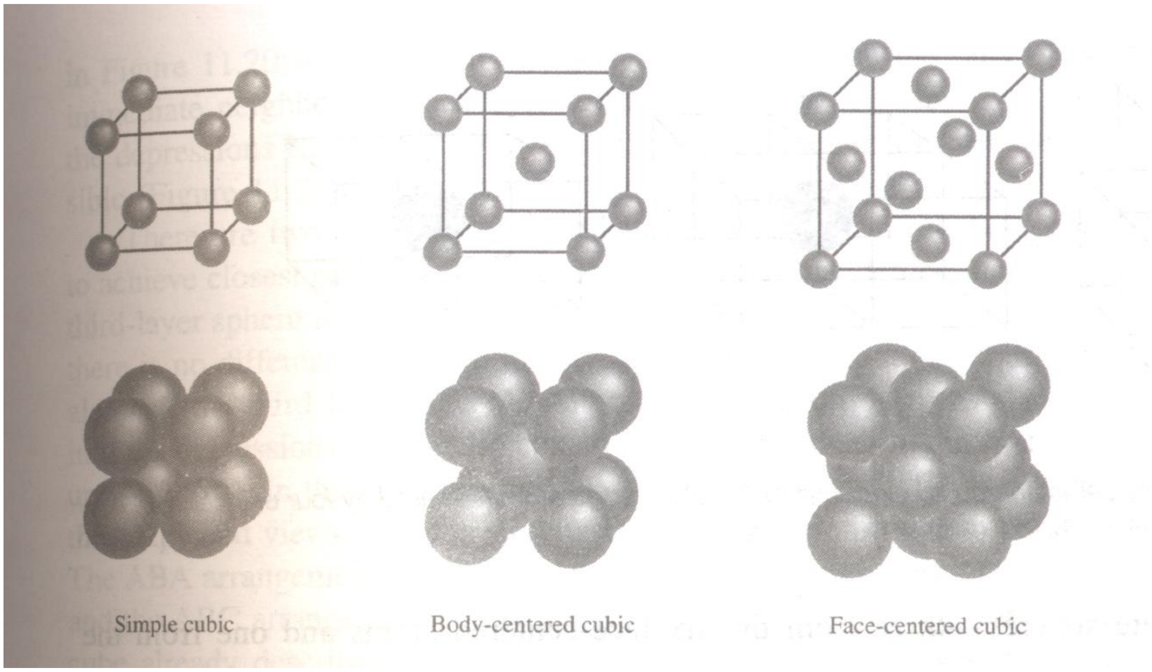
Self Check Question:

The number of atoms (or ions) surrounding an atom (or ion) in a crystal lattice is known as ______

A. Coordination number
B. Oxidation number
C. Atomic number
D. Valency

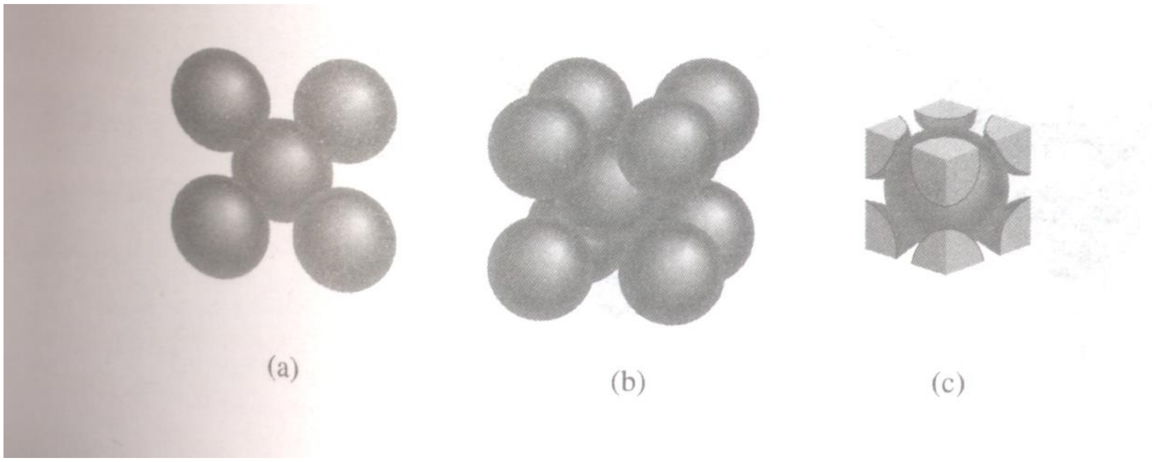
Solution: a)

The other types of cubic cells are the body-centered cubic cell (bcc) and the face-centered cubic cell (fcc).



Simple cubic Body-centered cubic Face-centered cubic

A body-centered cubic arrangement differs from a simple cube in that the second layer of spheres fits into the depressions of the first layer and the third layer into the depressions of the second layer.



(a) (b) (c)

The coordination number of each sphere in this structure is 8 (each sphere is in contact with four spheres in the layer above and four spheres in the layer below).

Self check Question:

The coordination of each sphere in Body centered cubic structure is _____

A. 6

B. 12

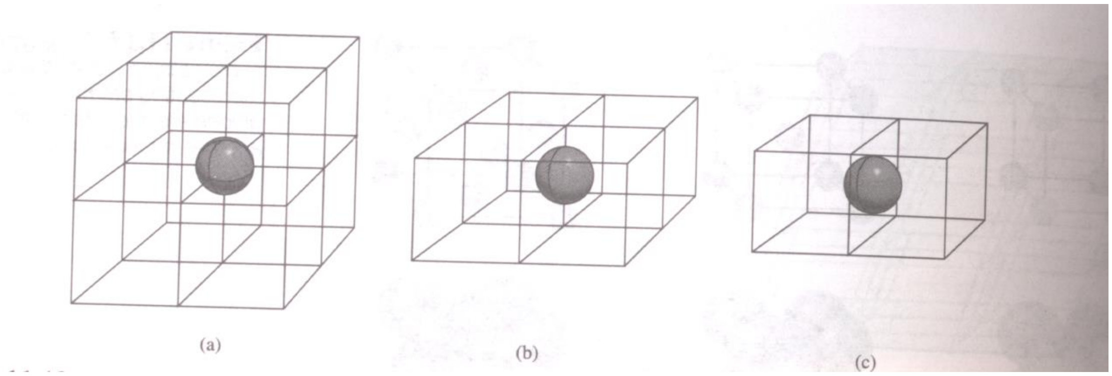
C. 8

D. 4

Solution: C

In the face-centered cubic cell, there are spheres at the center of each of the six faces of the cube, in addition to the eight corner spheres.

Because every unit cell in a crystalline solid is adjacent to other unit cells, most of cell's atoms are shared by neighboring cells. For example, in all types of cubic cells, each corner atom belongs to eight unit cells (figure a below); an edge atom is shared by four unit cells (figure b), and a face-centered atom is shared by two unit cells (figure c).



Because each corner sphere is shared by eight unit cells and there are eight corners in a cube, there will be the equivalent of only one complete sphere inside a simple cubic unit cell. A body-centered cubic cell contains the equivalent of two complete spheres, one in the center and eight shared corner spheres. A face-centered cubic cell contains four complete spheres – three from the six face-centered atoms and one from the eight shared corner spheres.

Self check question:

In a face centered cubic lattice, the number of nearest neighbours for a given lattice point is

a. 6

b. 8

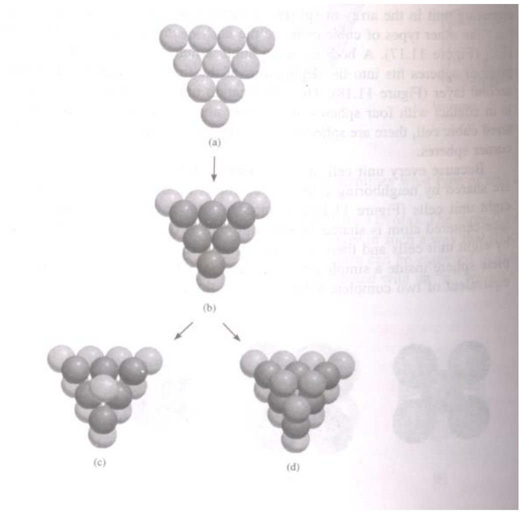
c. 12

d. 14

Solution: c)

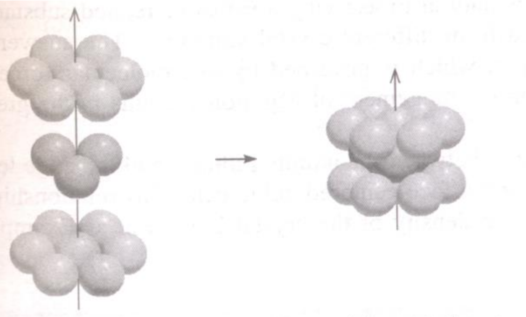
Closest Packing:

Clearly there is more empty space in the simple cubic and body-centered cubic cells than in the face-centered cubic cell. **Closest packing**, the most efficient arrangement of spheres, starts with the structure shown in figure (a) below, which we call layer A.



Focusing on the only enclosed sphere, we see that it has six immediate neighbors in that layer. In the second layer (which we call layer B), spheres are packed into the depressions between the spheres in the first layer so that all the spheres are as close together as possible.

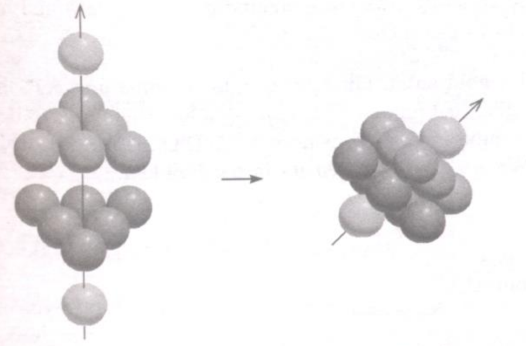
There are two ways that a third-layer sphere may cover the second layer to achieve closest packing. The spheres may fit into the depressions so that each third-layer sphere is directly over a first-layer sphere (figure c). Because there is no difference between the arrangement of the first and third layers, we also call the third layer A. Alternatively, the third-layer spheres may fit into the depressions that lie directly over the depressions in the first layer (figure d). In this case, we call the third layer C. Figure below shows the “exploded views” and the structures resulting from these two arrangements.



Exploded view

Hexagonal close-packed structure

(a)



Exploded view

Cubic close-packed structure

(b)

The ABA arrangement is known as the *hexagonal close-packed (hcp) structure*, and the ABC arrangement is the *cubic close-packed (ccp) structure*, which corresponds to the face-centered cube. We note that in the hcp structure, the spheres in every other layer occupy the same vertical position (ABABAB…), while in the ccp structure, the spheres in every fourth layer occupy the same vertical position (ABCABCA…). In both structures, each sphere has a coordination number of 12 (each sphere is in contact with six spheres in its own layer, three spheres in the layer above, and three spheres in the layer below). Both the hcp and ccp structures represent the most efficient way of packing identical spheres in a unit cell, and there is no way to increase the coordination number to beyond 12.

Self check Question:

In a primitive cubic cell the coordination number cannot go beyond ______

a. 12

b. 6

c. 8

d. 4

Solution: a)

Bravias lattices:

In 1848, Bravias showed that there are 14 different possible kinds of three dimensional lattices. The geometric shape of the crystal must be same as that of the solid crystal itself. For example, the crystal is a cube if the unit lattice also is having a cubic structure. The mathematical analysis of the ideas discussed earlier. (Namely the crystal is obtained by repetition of unit cell in three dimensions and that the unit cell and the crystal have identical shapes) and the fundamental laws of crystallography, when combined, give that there are only 14 basic arrangements, known as Bravais lattices. These 14 Bravais lattices are grouped into seven crystal systems, based on unit cell symmetry. The number of space lattices in a given crystal system is shown in the table.

S.No	**Crystal system**	**No. of space lattices or Bravias lattice possible**	**Common names of these lattices**
1.	Cubic	3	Simple cubic, fcc and bcc simple cubic; body centered tetragonal prisms
2.	Tetragonal	2	Rectangular; body centered rectangular prisms; rhombic prisms
3.	Rhombic	1	Hexagonal prism
4.	Trigonal	1	Rhombohedral
5.	Monoclinic	1	Primitive & edge centered
6.	Triclinic	1	Triclinic primitive

Self check question:

Bravais lattices are of

a. 10 types
b. 8 types
c. 7 types

d. 14 types

Solution: d)

Review question:

1. a. Define unit cell. 2 Marks

b. write the total number of atoms present in one unit cell of each of the following lattice? 3 Marks

a. Primitive cubic
b. Face - centered cubic
c. Body - centered cubic

Solution:

a. A **unit cell** is the basic repeating structural unit of a crystalline solid. Figure below shows a unit cell and its extension in three dimensions. Each sphere represents an atom, ion, or molecule and is called a *lattice point*. In many crystals, the lattice point does not actually contain such a particle.

b. Each cubic unit cell has 8 atoms on its corners; the total number of atoms present in unit cell is 8×1/8 =1 atom.

Body centre wholly belongs to the unit cell in which it is present. Thus in a body-centered cubic (bcc) unit cell:

i. 8 corners $\times \frac{1}{8}$ per corner atom=8×1/8=1 atom
ii. 1 body centre atom=1× 1=1 atom

∴ Total number of atoms per unit cell=2 atoms

In a face centred cubic unit cell

i. 8 corners atoms $\times \frac{1}{8}$ atom unit cell=8×1/8=1 atom
ii. $6 \text{ face centred atoms } \times \frac{1}{2} \text{ atom per unit cell} = 6 \times$

∴ Total number of atoms per unit cell=2 atoms

2. (a). What is meant by the term ‘coordination number’? 2 Marks

(b). Mention the coordination number of atoms in the following examples

3 Marks

i. NaCl

ii. CsCl

Solution:

a. The **coordination number** is defined as the number of atoms (or ions) surrounding an atom (or ion) in a crystal lattice. Its value gives us a measure of how tightly the spheres are packed together – the larger the coordination number, the closer the spheres are to each other. The basic, repeating unit in the array of spheres is called a *simple cubic cell*.

b. i. In NaCl crystal the coordination number of Na^+ ion as well as Cl^- ion is 6.i.e.each Na^+ ion has six Cl^- ions as nearest neighbours.

ii. In CsCl crystal the coordination number of Cs^+ ion as well as Cl^- ion is 8.i.e.each Na^+ ion has eight Cl^- ions as nearest neighbours.

.

3. Define primitive and centred unit cells with examples. (5 marks)

Solution:

Unit cell can be broadly divided into two categories, primitive and centred unit cells

a. primitive unit cells

When constituent particles are present only on the corner positions of a unit cell, it is called as primitive unit cell.

b. Centered unit cells: when constituent particles present at positions other than corners in addition to those at corners, it is called a centred unit cell. Centred unit cells are of three types:
   - i. Body centred unit cells: such a unit cell contains one constituent particle (atom, molecule or ion) at its body-centre besides the ones that are at its corners.
   - ii. Face centred unit cell: such a unit cell contains one constituent particle present at the corner of each face, besides the ones that are at its corners.
   - iii. End centred unit cell: In such a unit cell, one constituent particle is present at the corner of any two opposite faces besides the ones present at its corners.

4. Define hexagonal close packed (hcp) structure and cubic close packed (ccp), what is the coordination number of both, give examples. (5 marks)

Solution:

The ABA arrangement is known as the *hexagonal close-packed (hcp) structure*, and the ABC arrangement is the *cubic close-packed (ccp) structure*, which corresponds to the face-centered cube. We note that in the hcp structure, the spheres in every other layer occupy the same vertical position (ABABAB…), while in the ccp structure, the spheres in every fourth layer occupy the same vertical position (ABCABCA…). In both structures, each sphere has a coordination number of 12 (each sphere is in contact with six spheres in its own layer, three spheres in the layer above, and three spheres in the layer below). Both the hcp and ccp structures represent the most efficient way of packing identical spheres in a unit cell, and there is no way to increase the coordination number to beyond 12.

For example, magnesium, titanium, and zinc crystallize with their atoms in a hcp array, while aluminum, nickel, and silver crystallize in the ccp arrangement. All solid noble gases have the ccp structure except helium, which crystallizes in the hcp structure.

5. The cubic unit cell has _____ corners and _____ faces.
   a. 8,6
   b. 6,8
   c. 8,1
   d. 1,8

Solution:

6. The arrangement of layers of spheres in hcp is in the order
   a. ABC ABC…..
   b. AB AB…..
   c. ACB ACB….
   d. All the above

Solution: b

7. The basic repeating unit in a crystalline solid is
   a. Lattice point
   b. Point group
   c. Unit cell
   d. All the above

   Solution: c)

Exercise question:

1. Explain the term space lattice and unit cell.
2. What is mean by Bravais lattices?
3. Write about seven crystal systems.

Module - 7.4

Bragg’s equation

Introduction:

X-ray diffraction refers to the scattering of X rays by the units of a crystalline solids. The scattering or diffraction patterns produced are used to deduce the arrangement of particles in the solid lattice. We have learned the interference phenomenon associated with waves in the previous classes. Because X -rays are also electromagnetic waves, we would expect them to exhibit interference phenomenon under suitable conditions. The wavelength of X -rays is comparable in magnitude to the distances between lattice points in a crystal. Therefore, the crystal lattice should be able to diffract X-rays. An X-ray diffraction pattern is the result of interference in the waves associated with X rays.

Self Check Question:

X – Rays are one form of

a. Magnetic radiations
b. Electric field
c. Electromagnetic radiations
d. Visible radiations

Solution: c)

Types of interference waves:

The X- rays are originated from two separate points. The two waves from the sources interfere with one another. If a wave reinforces the second, then they are said to have constructive interference. On the other hand if they mutually nullify, it is called destructive interference. The waves, if present in the same phase, they undergo constructive interference. If waves are not present in same phase, they undergo destructive interference.

Self Check Question:

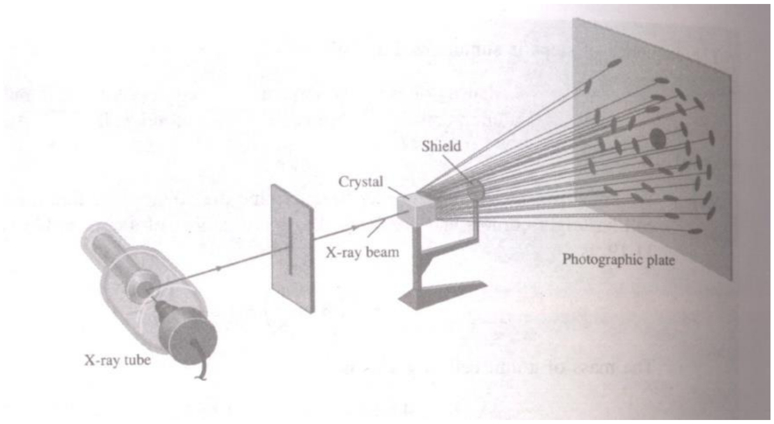
Constructive interference of waves takes place when they are in ________

a. Same phase
b. Different phases
c. Both a) and b)
d. neither a) nor b)

Solution: a)

X – Ray diffraction of scattering:

Figure below shows a typical X-ray diffraction set up.



X- rays are generated from the source X- ray tube. These rays are allowed to pass through a slit and it is made to fall on a crystal. The crystal absorbs some rays and it is scattered. This scattered rays fall on the photographic plate forming black bands.

A beam of X rays is directed at a mounted crystal. Atoms in the crystal absorb some of the incoming radiation and then remit it; the process is called the *scattering of X rays*.

To understand how a diffraction pattern may be generated, we consider the scattering of X rays by atoms in two parallel planes.

Self Check Question:

Atoms in the crystal absorb some of the incoming radiation and then remit it. This is called ________

A. Diffraction

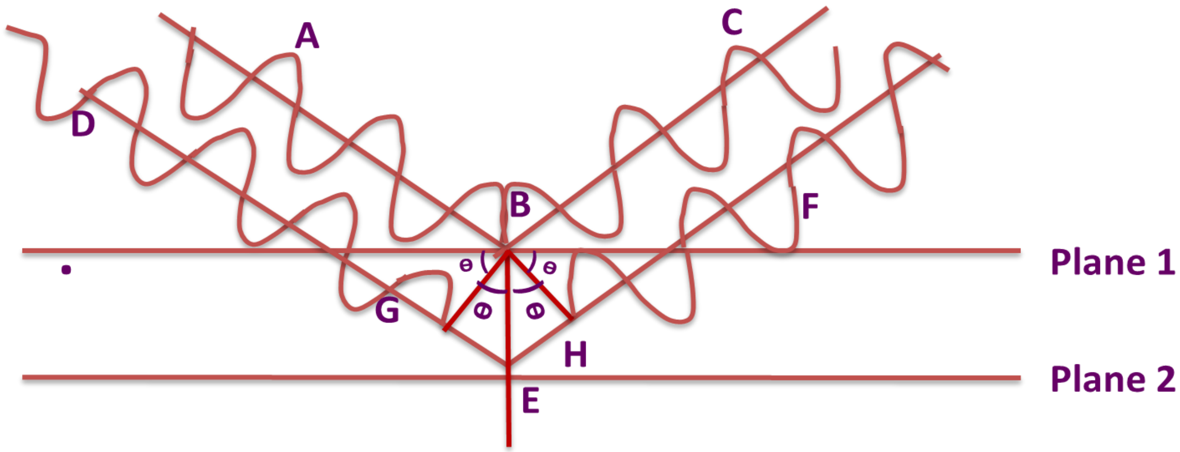
B. Scattering

C. Reflection

D. Refractive

Solution: b)

Bragg's equation



Initially, the two incident rays are in phase with each other (their maxima and minima occur at the same positions). The upper wave is scattered, or reflected, by an atom in the first layer, while the lower wave is scattered by an atom in the second layer. In order for these two scattered waves to be in phase again, the extra distance traveled by the lower wave must be an integral multiple of the wave length (λ) of the X ray; that is,

$$GE + HE = 2d\, sin\theta = n\lambda \quad \text{Where n = 1, 2, 3,…}$$

$$2d\ sin\theta = n\lambda \qquad (1)$$

Where θ is the angle between the X- rays and the plane of the crystal and d is the distance between adjacent planes. Equation (1) is known as the Bragg equation. The reinforced wave produces a dark spot on a photographic film for each value of θ that satisfies the Bragg equation.

Self Check Question:

What is Bragg's equation?

A. $2d\ sin\theta = n\lambda$
B. $2d\ cos\theta = n\lambda$
C. $2d\ sin\theta = n\ \lambda/2$
D. $2dcos\theta = n\ \lambda/2$

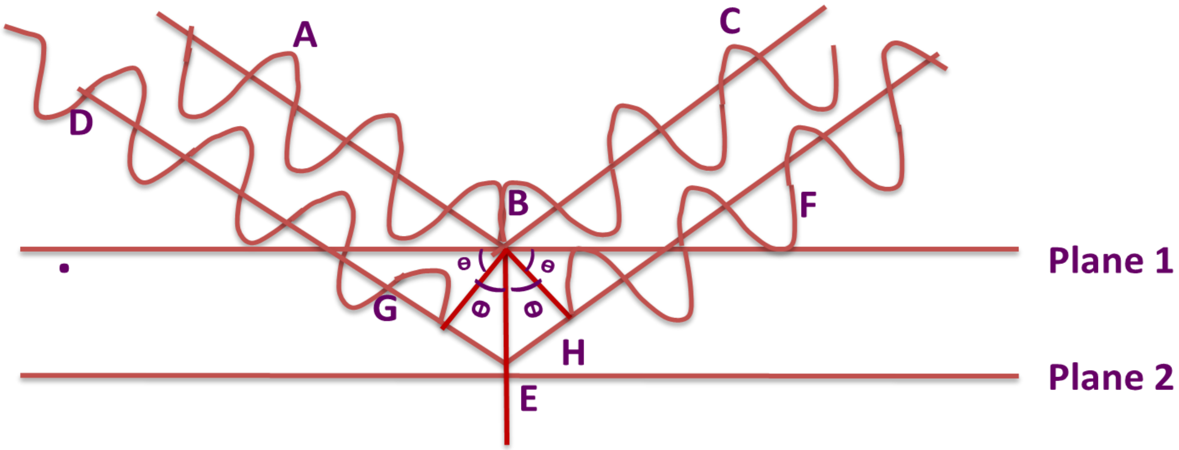
Solution: a)

Review questions:

1. Derive Bragg's equation?

Solution:

Bragg's equation:



X – ray diffraction at the atoms in crystal plane

Initially, the two incident rays are in phase with each other (their maxima and minima occur at the same positions). The upper wave is scattered, or reflected, by an atom in the first layer, while the lower wave is scattered by an atom in the second layer. In order for these two scattered waves to be in phase again, the extra distance traveled by the lower wave must be an integral multiple of the wave length (λ) of the X ray; that is,

$$GE + HE = 2d\ sin\theta = n\lambda$$ Where n = 1, 2, 3,…

$$2d\ sin\theta = n\lambda \qquad (1)$$

Where θ is the angle between the X- rays and the plane of the crystal and d is the distance between adjacent planes. Equation (1) is known as the Bragg equation. The reinforced wave produces a dark spot on a photographic film for each value of θ that satisfies the Bragg equation.

2. X rays of wavelength 0.164 nm strike a magnesium crystal; the rays are reflected at an angle of 30°. Assuming that n = 1, calculate the spacing between the planes of magnesium atoms (in pm) that is responsible for this angle of reflection.

Solution:

Step1: Given,

Wave length of the magnesium = 0.164 nm (10^{-12} pm)

Angle of the magnesium atom = 30^0

n = 1

Step2: Bragg's equation is,

$$2d\ sin\theta = n\lambda$$

Step3: substituted this values in equation,

$$d = \frac{n\lambda}{2\,sin\theta}$$

If n =1 then,

$$d = \frac{\lambda}{2\,sin\theta}$$

$$d = \frac{0.164\,nm \times \frac{1000\,pm}{1nm}}{2\,sin30^0} \qquad (\sin 30^0 = \frac{1}{2})$$

$$d = 164pm$$

Distance between two magnesium plates is **164 pm**

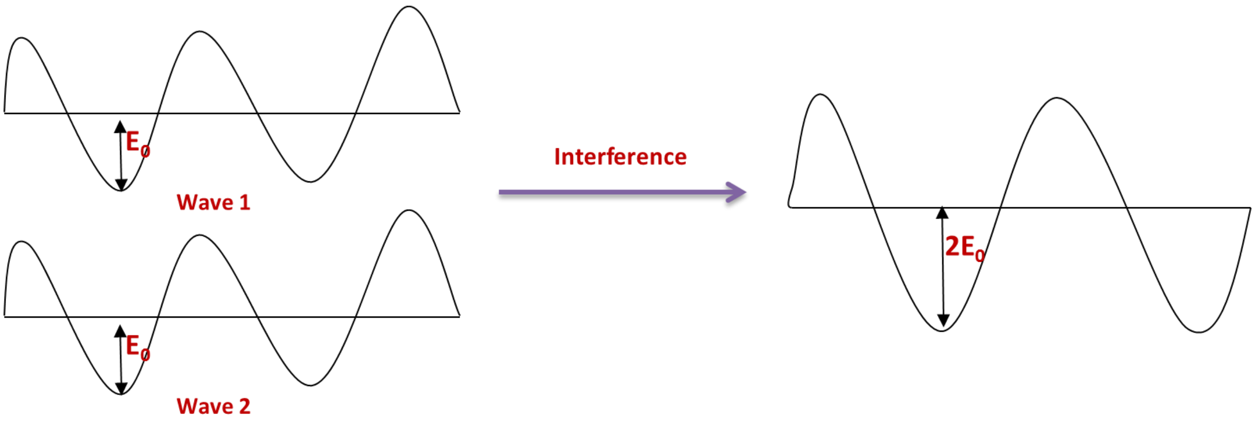
3. Explain types of interference waves?

Solution:

Types of interference waves:

The X- rays are originated from two separate points. The two waves from the sources interfere with one another. If a wave reinforces the second then they are said to have constructive interference. They are mutually nullified, it is called destructive interference.

Constructive interference:

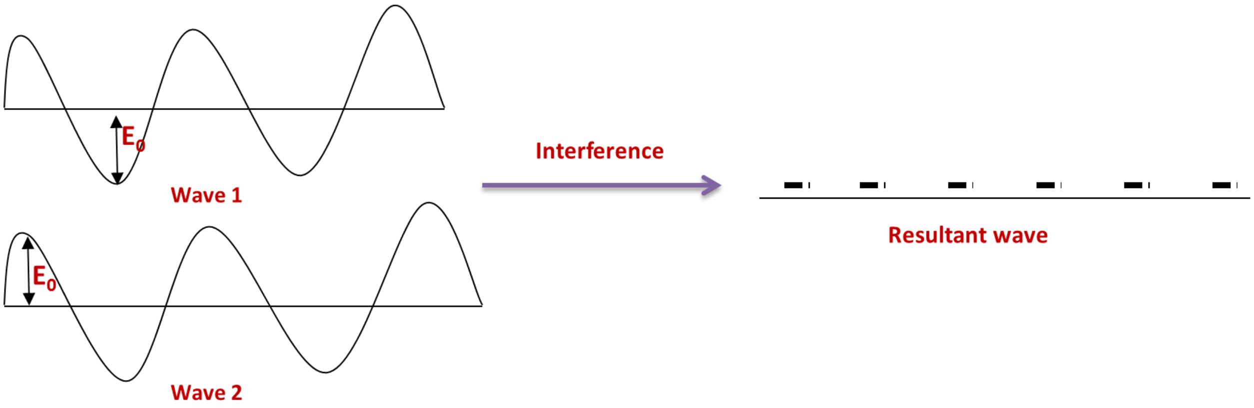


Amplitude = E_0 Resultant wave

Constructive interference amplitude = $2E_0$

If waves are present in same phase, they undergo constructive interference

Destructive interference:



Amplitude = $(+E_0 - E_0) = 0$

Amplitude = $\pm E_0$, Destructive interference

If waves are not present in same phase, they undergo destructive interference.

4. What is X- ray scattering effect?

Solution:

A beam of X rays is directed at a mounted crystal. Atoms in the crystal absorb some of the incoming radiation and then remit it; the process is called the *scattering of X rays*.

5. X-ray diffraction studies used to know
   a. The crystal structure
   b. Density
   c. Mass
   d. Volume

Solution: a)

6. If the two waves reinforce in different phases then the interference is
   a. Constructive
   b. Destructive

c. Alternative
d. Different

Solution: b)

Exercise questions:

1. X-rays of wavelength 0.154nm are diffracted from a crystal at an angle of 14.17^0. Assuming that n is first order, calculate the distance (in pm) between layers in the crystal.
2. The distance between layers in NaCl crystal is 282 pm. X rays are diffracted from these layers at an angle of 23.0°. Assuming that n= 1, calculate the wavelength of the X-rays in nm?
3. X-rays of wavelength 0.154 nm strike an aluminum crystal, the rays are reflected at an angle of 19.3°. The spacing between the planes of aluminum atoms is 0.233nm. Calculate the order of reflection?
4. X-rays of wavelength 0.254nm are diffracted from a crystal at an angle of 24.17^0. Assuming that n is second order, calculate the distance (in pm) between layers in the crystal. (Up to two decimals)
5. The distance between layers in NaCl crystal is 182 pm. X-rays are diffracted from these layers at an angle of 13.0°. Assuming that n=3, calculate the wavelength of the X-rays in nm? (Up to four decimals)
6. X-rays of wavelength 0.2107 nm strike an aluminum crystal, the rays are reflected at an angle of 39.3°. The spacing between the planes of aluminum atoms is 0.333nm. Calculate the order of reflection? (Enter only integer only)

7.5 Calculation of density of unit cell, number of atoms per unit cell in solids

Calculation of the contribution of lattice points per unit cell of a substance

A three dimensional crystal lattice is built up by the unit cells arranged in three directions. The unit cells have different shapes depending on the arrangement of the component atoms or ions in space lattice. Each lattice point and the component particle contribute fraction to the unit cell because they are shared by the vicinal unit cells. For calculating the different parameters like the wave length (λ) of the X – rays used, theoretical density of a solid (or unit cell); the dimensions of the unit cell etc these contributions of the lattice points towards an unit cell must be known. The following discussion will make it clear about the contributions of lattice points to the unit cell.

The atoms, molecules or ions that are making up the crystal are present at the lattice points and are represented by points. In various unit cells, the lattice points can be categorized into three types:

i. Lattice points located at the corners of the unit cell
ii. Lattice points in the face centers of the unit cell and
iii. Points lie entirely within the unit cell.

A point that is located at the **corner of a unit cell** is shared together by **eight** such unit cells, that is each unit cell has a share of $^{1}/_{8^{\mathrm{th}}}$ of such a point.

A face-centered point is shared between two unit cells and therefore, only half of each such point lies within any one cell.

A body-centered point lying entirely within a unit cell belongs completely to this unit cell.

Now one can calculate the total number of points per unit cell.

Total number of lattice points or lattice sites in a simple cubic structure = contributions by 8 corner sites in the cube. Each point contributes $\frac{1}{8}^{th}$ of a point (because 8 unit cell share it).

Total contribution from 8 points = 8 x $1/8$ = 1.0. If each point represents an atom, then the unit cell has 1 atom.

Contributions of lattice points in body centered cubic lattice arrangement.

Contributions from 8 corners = 8 x $1/8$ = 1 atom

Contributions form body centered point = 1 atom

Total contribution per unit cell = 2 atoms or points.

Contribution of lattice points in a fcc lattice.

Total points contributed from eight corner atoms

= 8 x $1/8$ = 1 atom or point.

Total points contributed by face-centered points i.e. 6 faces of a cube

= 6 x $1/2$ = 3 atoms or points.

Total contribution of points per unit cell in fcc arrangement = 4 atoms.

Self check question

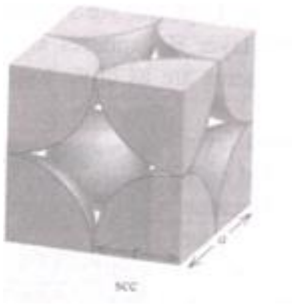
The numbers of atoms in FCC unit cell are

a. 2
b. 4
c. 1
d. 3

Solution: **b**

Figure below summarizes the relationship between the atomic radius ‘r’ and the edge length ‘a’ of a simple cubic cell, a body-centered cubic cell, and a face-centered cubic cell. This relationship can be used to determine the atomic radius of a sphere if the density of the crystal is known.

Simple cubic cell:



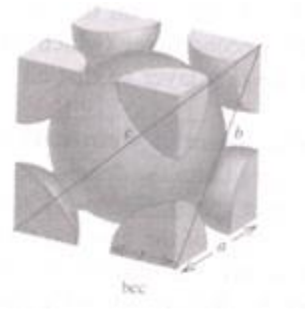
$a = 2r$

Body centered cubic:

$b^2 = a^2 + a^2$

$c^2 = a^2 + b^2$

$= a^2 + a^2 + a^2$



$= 3a^2$

$c = \sqrt{3}\ a = 4r$

$a = \frac{4}{\sqrt{3}} r$

Face centered cubic:

$b = 4r$

$b^2 = a^2 + a^2$

$16r^2 = 2a^2$

$a = \sqrt{8}\, r = 2\sqrt{2}$

Self check question

Suppose **a** is the axial length of the body centred cubic unit cell, then the distance between nearest neighbours is

a. $\frac{a}{2}$
b. $\frac{a}{\sqrt{2}}$
c. $\frac{\sqrt{2}}{4}a$
d. $\sqrt{3}a$

Solution: **d**

Calculation of density of unit cell

Knowing the unit cell dimensions, the density of a crystalline substance can be calculated as follows:

Let the molecular weight of a crystalline substance be ‘M’. Let the Avogadro’s number be ‘N_0’. ‘Z’ is the number of atoms present per unit cell and ‘p’ is the density of the unit cell or of the substance. The unit cell length is ‘a’, so that the volume of the unit cell is ‘a^3’ (=V). Then the mass corresponding to each lattice point = M/N_0 .

$\therefore$ The mass of ‘Z’ lattice points = $\frac{ZM}{N_0}$.

i.e. density of the unit cell = $\frac{\text{mass}}{\text{volume}} = \frac{\frac{Z.M}{N_0}}{a^3} = \frac{Z.M}{N_0 a^3}$

$$\rho = \frac{ZM}{N_0 V}$$

Where

ρ = density

Z = no. of atoms per unit cell

M = mol. Wt. of the lattice particle

a = unit cell length.

Self check question

The density of a crystalline solid can be calculated from the formula ρ =

a. $\frac{ZM}{N_0 V}$

b. $\frac{ZV}{N_0 M}$

c. $\frac{ZN_0}{VN}$

d. $\frac{ZN_0}{V^2 M}$

Solution: **a**

Review questions

1. Gold (Au) crystallizes in a cubic close-packed structure (the face-centered cubic unit cell) and has a density of 19.3 g/cm^3. Calculate the atomic radius of gold in picometers.

Solution

We want to calculate the radius of a gold atom. For a face-centered cubic unit cell, the relationship between radius (r) and edge length (a) is $a = \sqrt{8}\ r$. Therefore, to determine r of an Au atom, we need to find a . The volume of a cube is $V = a^3$ or $a = \sqrt[3]{V}$. Thus, if we can determine the volume of the unit cell, we can calculate a .

Step1: calculating the number of atoms

Each unit cell has eight corners and six faces. The total number of atoms within such a cell is

$$8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

Step2: calculating the mass of a unit cell in grams is

$$m = \frac{4\ \text{atoms}}{1\ \text{unit cell}} \times \frac{1\ \text{mol}}{6.022 \times 10^{23}\ \text{atoms}} \times \frac{197.0\ \text{g Au}}{1\ \text{mol Au}} = 1.31 \times 10^{-21}\ \text{g/unit cell}$$

Step3: calculating the volume of the unit cell:

From the relation $d = m/V$, we calculate the volume of the unit cell:

$$V = \frac{m}{d} = \frac{1.31 \times 10^{-21}\ \text{g}}{19.3\ \text{g/cm}^3} = 6.79 \times 10^{-23}\ \text{cm}^3$$

Step4: calculating the edge length (a) of the unit cell:

The edge length (a) of the cell is

$$a = \sqrt[3]{V}$$

$$= \sqrt[3]{6.79 \times 10^{-23}}$$

$$= 4.08 \times 10^{-8} \text{ cm}$$

Step4: calculating the radius

The radius of an Au sphere is given by

$$r = \frac{a}{\sqrt{8}}$$

$$= \frac{4.08 \times 10^{-8}}{\sqrt{8}}$$

$$= 1.44 \times 10^{-8} \text{ cm}$$

$$= 1.44 \times 10^{-8} \text{ cm} \times \frac{1 \times 10^{-2} \text{ m}}{1 \text{ cm}} \times \frac{1 \text{ pm}}{1 \times 10^{-2} \text{ m}}$$

$$= 1.44 \text{ pm}$$

2. When silver crystallizes, it forms face-centered cubic cells. The unit cell edge length is 408.7 pm. Calculate the density of silver. (silver at.wt = 107.8 g)

Solution:

Step1: Calculation of density

Given data

Z = In FCC the number of atoms is 4

M = Atomic weight of silver is 107.8 g

N = Avogadro number (6.022×10^{23})

V = volume of unit cell ($V = a^3$); a = 408.7pm or 4.087 A^0 or 4.087×10^{-8} cm

Step 2: Substituting the data

Density = $\frac{ZM}{NV}$

$$d = \frac{4 \times 107.8}{6.022 \times 10^{23} \times (4.087 \times 10^{-8})^3}$$

$d = 11.22$ gm/cm³

3. Density of a crystal is 13.6gm/cm^3 which is crystallizing in BCC with atomic weight 84gm/mol. Calculate length of unit cell.

Step1: Given data

Density of crystal = 13.6gm/cm^3

Its atomic weight = 84gm/mol

Avogadro number N = 6.022×10^{23}

Step2: Substituting the data in the formula

$$d = \frac{ZM}{NV}$$

$$d = \frac{ZM}{Na^3}$$

$$a = \sqrt[3]{\frac{ZM}{Nd}}$$

$$a = \sqrt[3]{\frac{2 \times 84}{6 \times 10^{23} \times 13.6}}$$

$= 2.72 \times 10^{-8}$ cm

$= 2.72$ A^0

4. The density of iron crystal is 7.86gm/c.c. The volume of unit cell is 24 × 10^{-24} cm^3. To what type of crystal does iron belongs, find it. (At. Wt=56)

Solution:

Step1: Given data

Volume of unit cell = 24 × 10^{-24} cm^3

Density of the crystal = 7.86gm/c.c

Avogadro number N = 6.022 × 10^{23}

Atomic weight = 56

Step 2: Substituting the data

$$d = \frac{ZM}{NV}$$

$$Z = \frac{dNV}{M}$$

$$= \frac{7.86 \times 6 \times 10^{23} \times 24 \times 10^{-24}}{56}$$

= 2

So the crystal belongs to BCC since the structure has two spheres per unit cell.

5. The length of a unit cell which is crystallizing in an FCC crystal is 9 A^0. Calculate the radius of atom.

For a face-centered cubic unit cell, the relationship between radius (r) and edge length (a) is $a = \sqrt{8}\ r$ or r = $\frac{a}{2\sqrt{2}}$

Step1: Given data

a = 9 A^0

Step 2: Substituting the data

$$r = \frac{9}{\sqrt[2]{2}}$$

$= 3.2\ A^0$

6. The length of a unit cell of Li crystal is crystallizing in BCC crystal is $3.5\ A^0$. Calculate the radius of atom.

Solution:

For a Body-centered cubic unit cell, the relationship between radius (r) and edge length (a) is $r = \frac{\sqrt{3}\, a}{4}$

Step1: Given data

$a = 3.5A^0$

Step 2: Substituting the data

$$r = \frac{\sqrt{3}\, a}{4}$$

$$= \frac{\sqrt{3} \times 3.5}{4}$$

$= 1.52\ A^0$

7. Calcium crystallizes in an fcc lattice. The edge length of one unit cell is 556 pm. Calculate the radius of a calcium atom

a. 278 pm

b. 241 pm

c. 481 pm

d. 197 pm

Solution: **d**

8. Lithium crystallizes in a body centred cubic lattice of unit cell length 352 pm. The distance between nearest neighbours is

    a. 150 pm

    b. 75 pm

    c. 304 pm

    d. 122 pm

Solution: **c**

Exercise questions

1. Calculate the density of a crystal whose at.wt is 197 gm/mol. Which is crystallizing like Rock salt(NaCl) structure FCC, whose length of the unit cell is 4 A^0?

2. Calculate length of unit cell of NaCl if its Density is 2.17kg/m^3 which is crystallizing in FCC with molecular weight 58.6 gm/mol.

3. The density of silver crystal is 11.22g/cm^3. The volume of unit cell is 64×10^{-24}cm^3.To what type of crystal does NaCl belongs, find it. (Mol. Wt=107.8)

4. The length of a unit cell which is crystallizing in an FCC crystal is 10 A^0. Calculate the radius of atom.

5. The length of a unit cell of Li crystal is crystallizing in BCC crystal is 4.5 A^0. Calculate the radius of atom.

Intext Questions

1.10 Give the significance of a 'lattice point'.

1.11 Name the parameters that characterise a unit cell.

1.12 Distinguish between

(i) Hexagonal and monoclinic unit cells

(ii) Face-centred and end-centred unit cells.

1.13 Explain how much portion of an atom located at (i) corner and (ii) body-centre of a cubic unit cell is part of its neighbouring unit cell.

1.6 Close Packed Structures

In solids, the constituent particles are close-packed, leaving the minimum vacant space. Let us consider the constituent particles as identical hard spheres and build up the three dimensional structure in three steps.

(a) Close Packing in One Dimension

There is only one way of arranging spheres in a one dimensional close packed structure, that is to arrange them in a row and touching each other (Fig. 1.13).

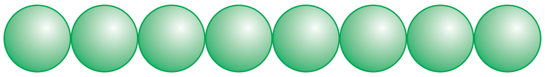


Fig. 1.13: *Close packing of spheres in one dimension*

In this arrangement, each sphere is in contact with two of its neighbours. The number of nearest neighbours of a particle is called its **coordination number**. Thus, in one dimensional close packed arrangement, the coordination number is 2.

(b) Close Packing in Two Dimensions

Two dimensional close packed structure can be generated by stacking (placing) the rows of close packed spheres. This can be done in two different ways.

(i) The second row may be placed in contact with the first one such that the spheres of the second row are exactly above those of the first row. The spheres of the two rows are aligned horizontally as well as vertically. If we call the first row as 'A' type row, the second row being exactly the same as the first one, is also of 'A' type. Similarly, we may place more rows to obtain AAA type of arrangement as shown in Fig. 1.14 (a).

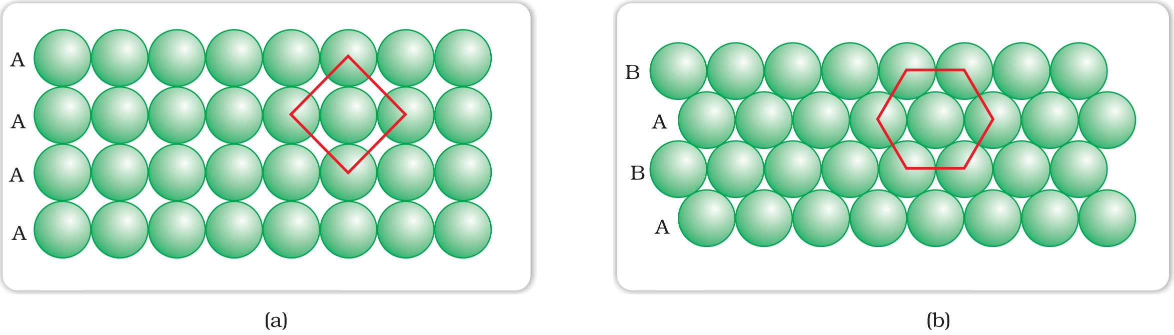


Fig. 1.14: *(a) Square close packing (b) hexagonal close packing of spheres in two dimensions*

In this arrangement, each sphere is in contact with four of its neighbours. Thus, the two dimensional coordination number is 4. Also, if the centres of these 4 immediate neighbouring spheres are joined, a square is formed. Hence this packing is called **square close packing in two dimensions**.

(ii) The second row may be placed above the first one in a staggered manner such that its spheres fit in the depressions of the first row. If the arrangement of spheres in the first row is called 'A' type, the one in the second row is different and may be called 'B' type. When the third row is placed adjacent to the second in staggered manner, its spheres are aligned with those of the first layer. Hence this layer is also of 'A' type. The spheres of similarly placed fourth row will be aligned with those of the second row ('B' type). Hence this arrangement is of ABAB type. In this arrangement there is less free space and this packing is more efficient than the square close packing. Each sphere is in contact with six of its neighbours and the two dimensional coordination number is 6. The centres of these six spheres are at the corners of a regular hexagon (Fig. 1.14b) hence this packing is called **two dimensional hexagonal close-packing.** It can be seen in Figure 1.14 (b) that in this layer there are some voids (empty spaces). These are triangular in shape. The triangular voids are of two different types. In one row, the apex of the triangles are pointing upwards and in the next layer downwards.

(c) Close Packing in Three Dimensions

All real structures are three dimensional structures. They can be obtained by stacking two dimensional layers one above the other. In the last Section, we discussed close packing in two dimensions which can be of two types; square close-packed and hexagonal close-packed. Let us see what types of three dimensional close packing can be obtained from these.

(i) *Three dimensional close packing from two dimensional square close-packed layers:* While placing the second square close-packed layer above the first we follow the same rule that was followed when one row was placed adjacent to the other. The second layer is placed over the first layer such that the spheres of the upper layer are exactly above those of the first layer. In this arrangement spheres of both the layers are perfectly aligned horizontally as well as vertically as shown in Fig. 1.15. Similarly, we may place more layers one above the other. If the arrangement of spheres in the first layer is called 'A' type, all the layers have the same arrangement. Thus this lattice has AAA.... type pattern. The lattice thus generated is the simple cubic lattice, and its unit cell is the primitive cubic unit cell (See Fig. 1.9).

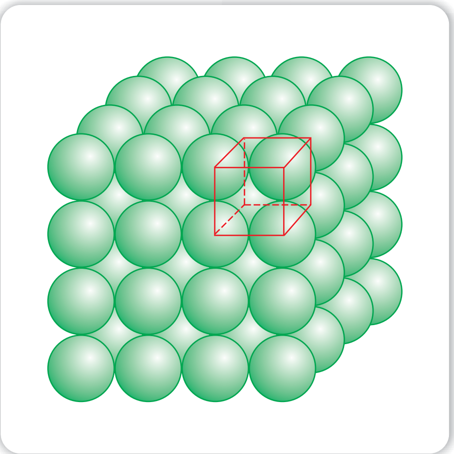


Fig. 1.15: *Simple cubic lattice formed by A A A .... arrangement*

(ii) *Three dimensional close packing from two dimensional hexagonal close packed layers:* Three dimensional close packed structure can be generated by placing layers one over the other.

(a) Placing second layer over the first layer

Let us take a two dimensional hexagonal close packed layer 'A' and place a similar layer above it such that the spheres of the second layer are placed in the depressions of the first layer. Since the spheres of the two layers are aligned differently, let us call the second layer as B. It can be observed from Fig. 1.16 that not all the triangular voids of the first layer are covered by the spheres of the second layer. This gives rise to different arrangements. Wherever a sphere of the second layer is above the void of the first layer (or vice versa) a tetrahedral void is formed. These voids are called **tetrahedral voids** because a *tetrahedron* is formed when the centres of these four spheres are joined. They have been marked as 'T' in Fig. 1.16. One such void has been shown separately in Fig. 1.17.

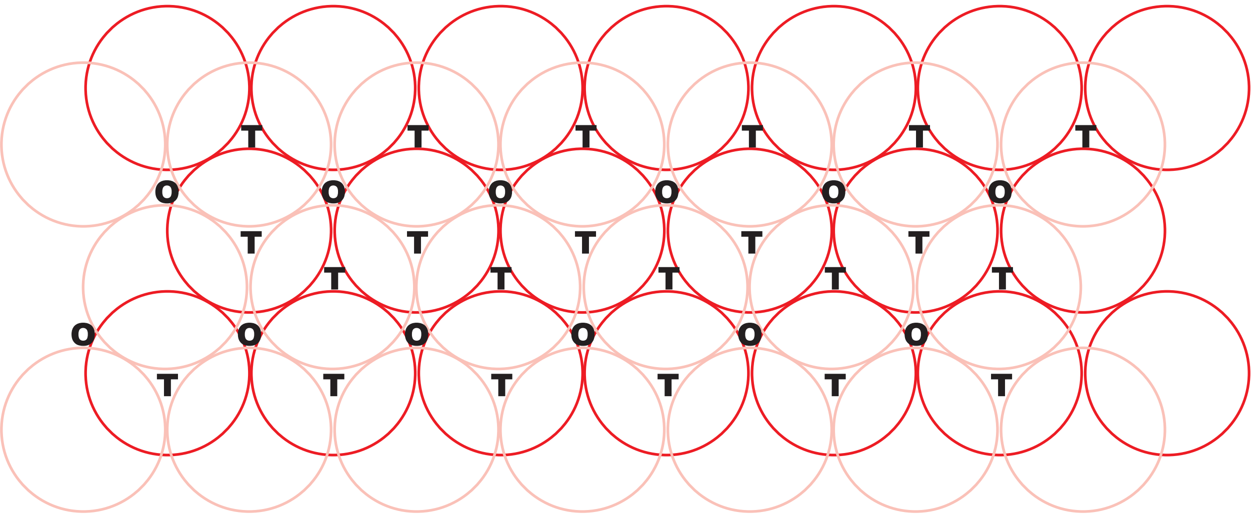


Fig. 1.16: *A stack of two layers of close packed spheres and voids generated in them. T = Tetrahedral void; O = Octahedral void*

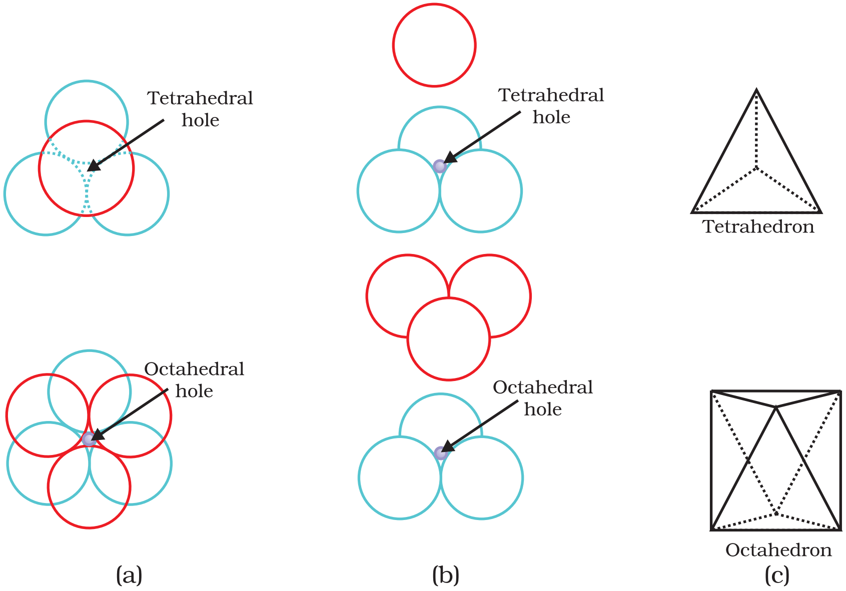


Fig 1.17
Tetrahedral and octahedral voids
(a) top view
(b) exploded side view and
(c) geometrical shape of the void.

At other places, the triangular voids in the second layer are above the triangular voids in the first layer, and the triangular shapes of these do not overlap. One of them has the apex of the triangle pointing upwards and the other downwards. These voids have been marked as 'O' in Fig. 1.16. Such voids are surrounded by six spheres and are called **octahedral voids.** One such void has been shown separately in Fig. 1.17. The number of these two types of voids depend upon the number of close packed spheres.

Let the number of close packed spheres be N, then:

The number of octahedral voids generated = N

The number of tetrahedral voids generated = $2N$

(b) Placing third layer over the second layer

When third layer is placed over the second, there are two possibilities.

(i) *Covering Tetrahedral Voids*: Tetrahedral voids of the second layer may be covered by the spheres of the third layer. In this case, the spheres of the third layer are exactly aligned with those of the first layer. Thus, the pattern of spheres is repeated in alternate layers. This pattern is often written as ABAB .... pattern. This structure is called hexagonal close packed (*hcp*) structure (Fig. 1.18). This sort of arrangement of atoms is found in many metals like magnesium and zinc.

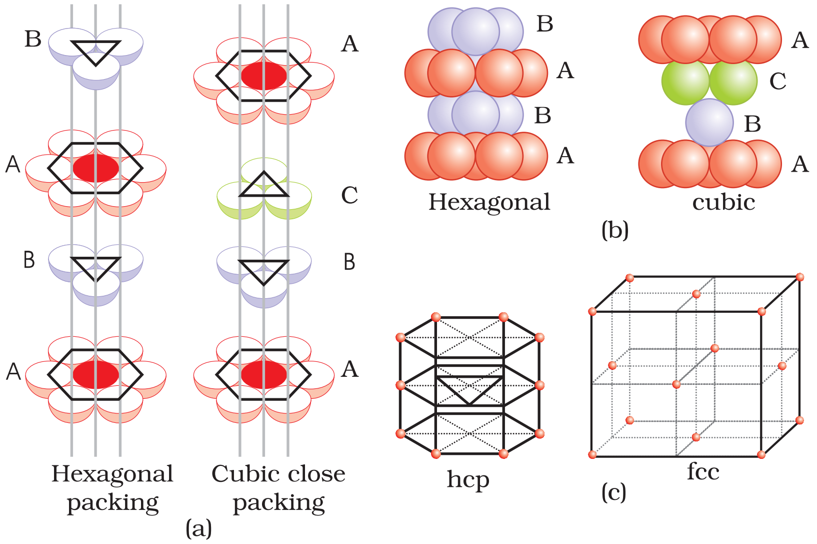


Fig. 1.18
(a) Hexagonal cubic close-packing exploded view showing stacking of layers of spheres (b) four layers stacked in each case and (c) geometry of packing.

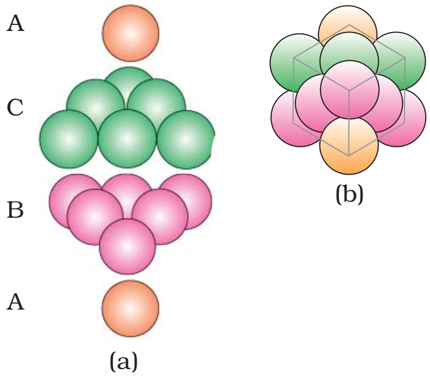


Fig. 1.19
(a) ABCABC... arrangement of layers when octahedral void is covered (b) fragment of structure formed by this arrangement resulting in cubic closed packed (ccp) or face centred cubic (fcc) structure.

(ii) *Covering Octahedral Voids*: The third layer may be placed above the second layer in a manner such that its spheres cover the octahedral voids. When placed in this manner, the spheres of the third layer are not aligned with those of either the first or the second layer. This arrangement is called 'C' type. Only when fourth layer is placed, its spheres are aligned with those of the first layer as shown in Figs. 1.18 and 1.19. This pattern of layers is often written as ABCABC .... This structure is called cubic close packed (*ccp*) or face-centred cubic (*fcc*) structure. Metals such as copper and silver crystallise in this structure.

Both these types of close packing are highly efficient and 74% space in the crystal is filled. In either of them, each sphere is in contact with twelve spheres. Thus, the coordination number is 12 in either of these two structures.

1.6.1 Formula of a Compound and Number of Voids Filled

Earlier in the section, we have learnt that when particles are close-packed resulting in either *ccp* or *hcp* structure, two types of voids are generated. While the number of octahedral voids present in a lattice is equal to the number of close packed particles, the number of tetrahedral voids generated is twice this number. In ionic solids, the bigger ions (usually anions) form the close packed structure and the smaller ions (usually cations) occupy the voids. If the latter ion is small enough then tetrahedral voids are occupied, if bigger, then octahedral voids. Not all octahedral or tetrahedral voids are occupied. In a given compound, the fraction of octahedral or tetrahedral voids that are occupied, depends upon the chemical formula of the compound, as can be seen from the following examples.

Example 1.1 A compound is formed by two elements X and Y. Atoms of the element Y (as anions) make *ccp* and those of the element X (as cations) occupy all the octahedral voids. What is the formula of the compound?

Solution The *ccp* lattice is formed by the element Y. The number of octahedral voids generated would be equal to the number of atoms of Y present in it. Since all the octahedral voids are occupied by the atoms of X, their number would also be equal to that of the element Y. Thus, the atoms of elements X and Y are present in equal numbers or 1:1 ratio. Therefore, the formula of the compound is XY.

Example 1.2 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 the elements A and B?

Solution The number of tetrahedral voids formed is equal to twice the number of atoms of element B and only 2/3rd of these are occupied by the atoms of element A. Hence the ratio of the number of atoms of A and B is 2 × (2/3):1 or 4:3 and the formula of the compound is A_4B_3.

Locating Tetrahedral and Octahedral Voids

We know that close packed structures have both tetrahedral and octahedral voids. Let us take *ccp* (or *fcc*) structure and locate these voids in it.

(a) Locating Tetrahedral Voids

Let us consider a unit cell of *ccp* or *fcc* lattice [Fig. 1(a)]. The unit cell is divided into eight small cubes.

Each small cube has atoms at alternate corners [Fig. 1(a)]. In all, each small cube has 4 atoms. When joined to each other, they make a regular tetrahedron. Thus, there is one tetrahedral void in each small cube and eight tetrahedral voids in total. Each of the eight small cubes have one void in one unit cell of *ccp* structure. We know that *ccp* structure has 4 atoms per unit cell. Thus, the number of tetrahedral voids is twice the number of atoms.

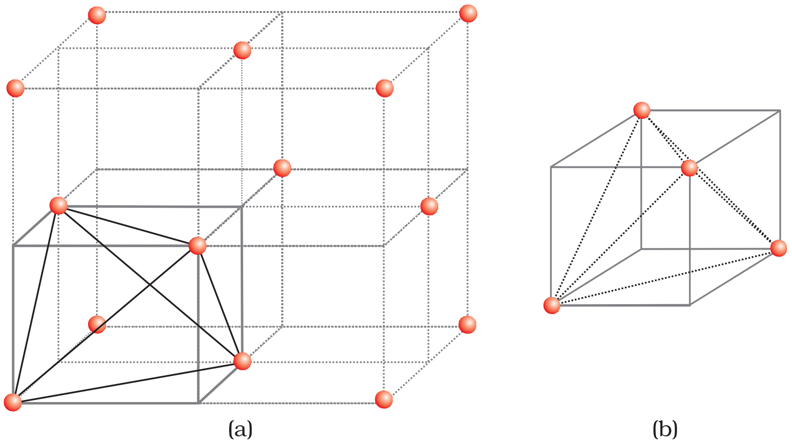

(a) (b)

Fig. 1: *(a) Eight tetrahedral voids per unit cell of ccp structure (b) one tetrahedral void showing the geometry.*

(b) Locating Octahedral Voids

Let us again consider a unit cell of *ccp* or *fcc* lattice [Fig. 2(a)]. The body centre of the cube, C is not occupied but it is surrounded by six atoms on face centres. If these face centres are joined, an octahedron is generated. Thus, this unit cell has one octahedral void at the body centre of the cube.

Besides the body centre, there is one octahedral void at the centre of each of the 12 edges. [Fig. 2(b)]. It is surrounded by six atoms, four belonging to the same unit cell (2 on the corners and 2 on face centre) and two belonging to two adjacent unit cells. Since each edge of the cube is shared between four adjacent unit cells, so is the octahedral void located on it. Only $\frac{1}{4}^{\text{th}}$ of each void belongs to a particular unit cell.

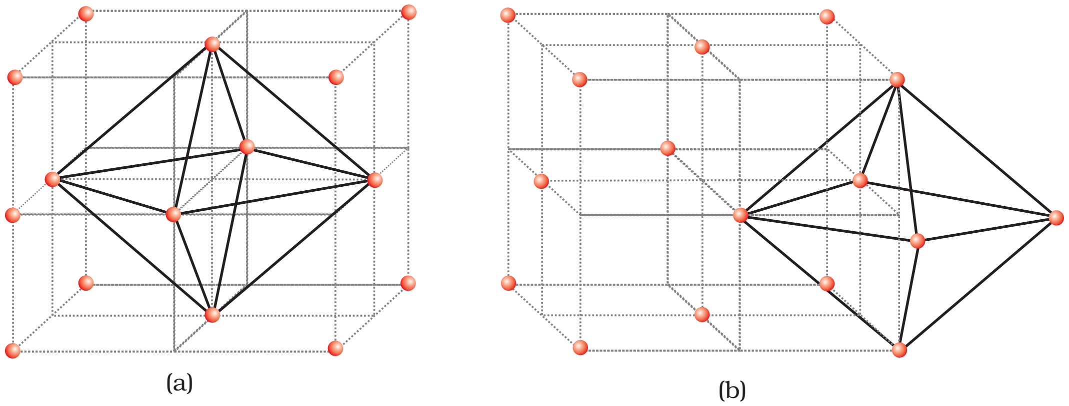

(a) (b)

Fig. 2: *Location of octahedral voids per unit cell of ccp or fcc lattice (a) at the body centre of the cube and (b) at the centre of each edge (only one such void is shown).*

Thus in *cubic close packed structure*:

Octahedral void at the body-centre of the cube = 1

12 octahedral voids located at each edge and shared between four unit cells

$$= 12 \times \frac{1}{4} = 3$$

$\therefore$ Total number of octahedral voids = 4

We know that in ccp structure, each unit cell has 4 atoms. Thus, the number of octahedral voids is equal to this number.

1.7 Packing Efficiency

In whatever way the constituent particles (atoms, molecules or ions) are packed, there is always some free space in the form of voids. **Packing efficiency** is the percentage of total space filled by the particles. Let us calculate the packing efficiency in different types of structures.

1.7.1 Packing Efficiency in *hcp* and *ccp* Structures

Both types of close packing (*hcp* and *ccp*) are equally efficient. Let us calculate the efficiency of packing in ccp structure. In Fig. 1.20 let the unit cell edge length be 'a' and face diagonal AC = b.

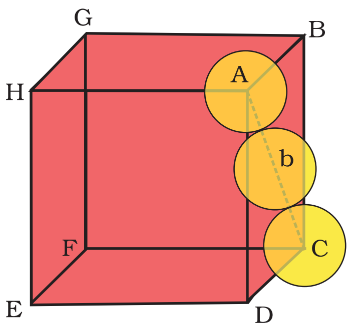


Fig. 1.20: *Cubic close packing other sides are not provided with spheres for sake of clarity.*

In Δ ABC

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

$= a^2 + a^2 = 2a^2$ or

$b = \sqrt{2}a$

If r is the radius of the sphere, we find

$b = 4r = \sqrt{2}a$

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

(we can also write, $r = \frac{a}{2\sqrt{2}}$)

We know, that each unit cell in ccp structure, has effectively 4 spheres. Total volume of four spheres is equal to $4 \times (4/3)\pi r^3$ and volume of the cube is a^3 or $\left(2\sqrt{2}r\right)^3$.

Therefore,

$$\text{Packing efficiency} = \frac{\text{Volume occupied by four spheres in the unit cell} \times 100}{\text{Total volume of the unit cell}}\,\%$$

$$= \frac{4 \times (4/3)\pi r^3 \times 100}{\left(2\sqrt{2}r\right)^3}\,\%$$

$$= \frac{(16/3)\pi r^3 \times 100}{16\sqrt{2}r^3}\,\% = 74\%$$

1.7.2 Efficiency of Packing in Body-Centred Cubic Structures

From Fig. 1.21, it is clear that the atom at the centre will be in touch with the other two atoms diagonally arranged.

In Δ EFD,

$$b^2 = a^2 + a^2 = 2a^2$$

$$b = \sqrt{2}a$$

Now in Δ AFD

$$c^2 = a^2 + b^2 = a^2 + 2a^2 = 3a^2$$

$$c = \sqrt{3}a$$

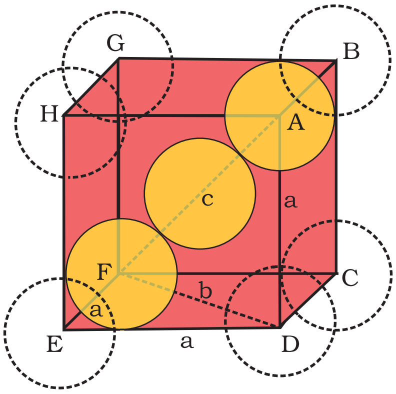


Fig. 1.21: Body-centred cubic unit cell (sphere along the body diagonal are shown with solid boundaries).

The length of the body diagonal c is equal to 4r, where r is the radius of the sphere (atom), as all the three spheres along the diagonal touch each other.

Therefore, $\sqrt{3}a = 4r$

$$a = \frac{4r}{\sqrt{3}}$$

Also we can write, $r = \frac{\sqrt{3}}{4}a$

In this type of structure, total number of atoms is 2 and their volume is $2 \times \left(\frac{4}{3}\right)\pi r^3$.

Volume of the cube, a^3 will be equal to $\left(\frac{4}{\sqrt{3}}r\right)^3$ or $a^3 = \left(\frac{4}{\sqrt{3}}r\right)^3$.

Therefore,

$$\text{Packing efficiency} = \frac{\text{Volume occupied by two spheres in the unit cell} \times 100}{\text{Total volume of the unit cell}}\%$$

$$= \frac{2 \times (4/3)\pi r^3 \times 100}{\left[\left(4/\sqrt{3}\right)r\right]^3}\%$$

$$= \frac{(8/3)\pi r^3 \times 100}{64/\left(3\sqrt{3}\right)r^3}\% = 68\%$$

1.7.3 Packing Efficiency in Simple Cubic Lattice

In a simple cubic lattice the atoms are located only on the corners of the cube. The particles touch each other along the edge (Fig. 1.22). Thus, the edge length or side of the cube 'a', and the radius of each particle, r are related as

$$a = 2r$$

The volume of the cubic unit cell = $a^3 = (2r)^3 = 8r^3$

Since a simple cubic unit cell contains only 1 atom

The volume of the occupied space = $\frac{4}{3}\pi r^3$