SOLID STATE

In Solids the particles (molecules, atoms or ions) are arranged in a close packed manner and Intermolecular forces are Very Strong. These are the responsible for the characteristics of the solids.

Characteristics of Solid:

➢ Fixed Mass
➢ Fixed Volume
➢ Fixed Shape
➢ Intermolecular distance are short
➢ Intermolecular forces are strong
➢ Particles have fixed positions
➢ Incompressibility
➢ Rigidity
➢ Very low entropy

Solids are Broadly Classified into two types. They are 1. Amorphous Solids

2. Crystalline solids

	Amorphous Solids	Crystalline Solids
1.	In these solids particles are arranged randomly.	In these solids particles are arranged in a regular manner.
2.	In these solids intermolecular forces are not identical throughout the solid.	In these solids intermolecular force are identical throughout the solid.
3.	They do not have fixed melting point	They have fixed melting point
4.	These are also called "Pseudo solids" or "Super cooled liquids".	These are also called "True solids"
5.	These are having short range order.	These are having long range order.
	Examples: glass, rubber, plastic, etc.,	Examples: Diamond, Graphite, NaCl, Ice, Metals, etc.,

crystalline quartz   amorphous quartz glass
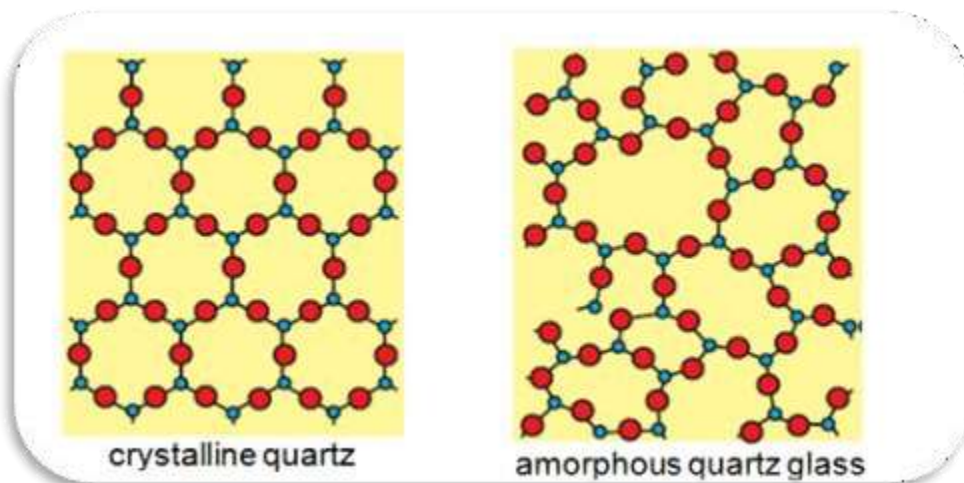
Amorphous solids:

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 molecule 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.

Ex: glass, rubber, plastic

Glass:

Glass is prepared by inorganic materials. In Glass SiO_2 is the chief component. There are 800 types of glasses.

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 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.

Types of Crystals: Based on the nature of forces existing between the particles, crystals can be classified into four types. They are

1. Ionic crystals
2. Covalent crystals
3. Molecular crystals
4. Metallic crystals

1. Ionic Crystals:

- In the ionic crystals the particles are ions.
- These particles are held together by ionic bonds.
- These crystals hardness is high.
- They have High Melting point.
- They are bad conductors of heat and electricity in solids, but in molten state these crystals exhibits electrical conductivity

  Ex: NaCl, KCl, CsCl, $MgCl_2$, CaF_2, etc .,

2. Covalent Crystals:

- In the Covalent Crystals the particles are atoms.
- These atoms are held together by covalent bonds.
- These crystals hardness is very high.
- They have very high melting point.
- They are bad conductors of electricity. (except graphite, graphite exhibits electrical conductivity)

  Ex: Graphite, Diamond, Silicon Carbide, Boran Carbide, Quartz (SiO_2)

3. Molecular Crystals:

- In the molecular crystals the particles are molecules.
- These molecules are held together by Vander wall forces.
- These Crystals hardness is low. i.e, soft.
- They have very low melting point.
- They are bad conductors of heat and electricity.

  Ex: Ice, dry ice, CO_2, I_2, S_8, P_4, glucose ($C_6H_{12}O_6$), sucrose ($C_{12}H_{22}O_{11}$)

4. Metallic Crystals:

- In the metallic crystals the particles are metals.
- These metals are held together by metallic bonds.
- These crystals hardness is low as well as high.
- They have melting point low as well as high.
- They are good conductors of heat and electricity.

  Ex: All metals, examples are Na, Mg, Fe, Cu.

Crystal Lattice (or) Space Lattice:

The regular arrangement of particles in a crystal is called its **Crystal lattice** or **Space lattice**. There are only 14 possible 3-D lattices. These are called Bravais lattices.

Unit Cell:

The smallest repeating unit which gives the total crystal structure is called **Unit cell**.

Lattice Points:

➢ Each point in crystal lattice is called **lattice point**.
➢ Each point in a crystal lattice represents one constituent particle which may be an atom, molecule or an ion.
➢ Lattice points are joined by straight lines to bring out the geometry of the lattice.

Unit cell is characterized by

1) Its dimensions along three edges a, b and c.

2) Angles between the edges α (between b and c)

B (between a and

c) Ɣ (between a

and b)
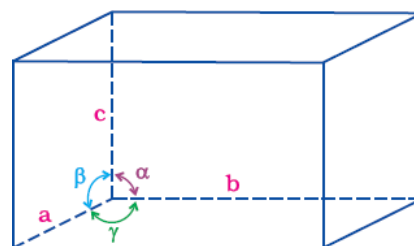
Illustration of parameters of a unit cell

Unit cells are broadly divided into two categories. They are 1. Primitive unit cell

2. Centered unit cell

1) Primitive unit cell:

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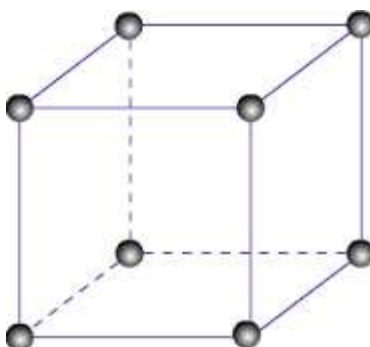
2) Centered unit cell:

Centered unit cell is further classified into three types. They are

a) Body centered unit cell

b) Face centered unit cell

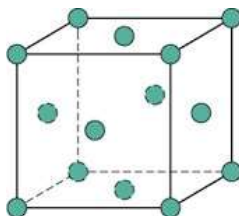c) End face centered unit cell

a) Body Centered unit cell:

A **Body centered unit cell** contains one constituent particle (atom, molecule or ion) at its body centre besides the ones that are at its corners.
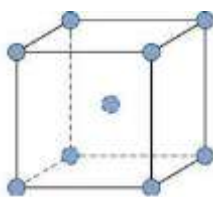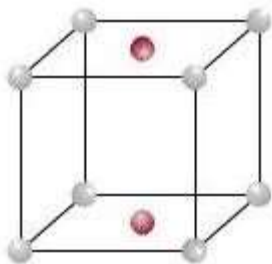
b) Face centered unit cell:

A **Face centered unit cell** contains one constituent particle present at the center of each face, besides the ones that are its corners.

c) End Face centered unit cell:

In **End Face centered Unit cell**, the constituent particles are present at the centre of any two opposite faces besides the ones present at its corners.

In all, there are seven types of primitive unit cells

Seven primitive unit cells in crystals
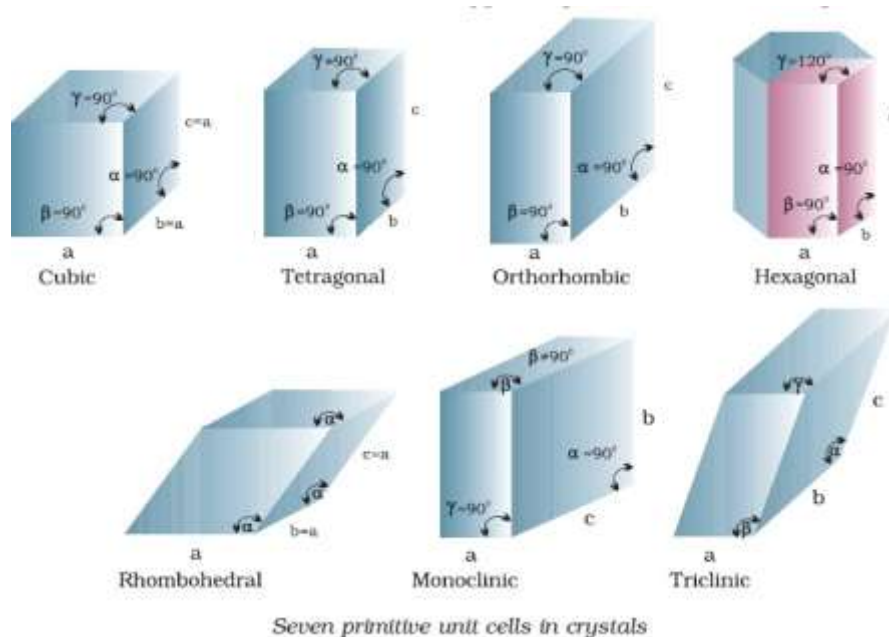
Table: Seven Primitive unit cells and their possible variations as centered unit cells

| Crystal system	Possible variations	Axial distances or edge lengths	Axial angles	Examples
Cubic	Primitive, Body-centred, Face-centred	$a = b = c$	$\alpha = \beta = \gamma = 90°$	NaCl, Zinc blende, Cu
Tetragonal	Primitive, Body-centred	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	White tin, SnO_2, TiO_2, $CaSO_4$
Orthorhombic	Primitive, Body-centred, Face-centred, End-centred	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	Rhombic sulphur, KNO_3, $BaSO_4$
Hexagonal	Primitive	$a = b \neq c$	$\alpha = \beta = 90°$ $\gamma = 120°$	Graphite, ZnO,CdS,
Rhombohedral or Trigonal	Primitive	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	Calcite ($CaCO_3$), HgS (cinnabar)
Monoclinic	Primitive, End-centred	$a \neq b \neq c$	$\alpha = \gamma = 90°$ $\beta \neq 90°$	Monoclinic sulphur, $Na_2SO_4.10H_2O$
Triclinic	Primitive	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	$K_2Cr_2O_7$, $CuSO_4.5H_2O$, H_3BO_3

Bravaiss Lattices: There are 14 different possible kinds of three dimensional lattices. These 14 lattices are called **Bravais lattices**. These **14 bravais lattices** are grouped into **seven crystals**.
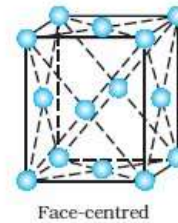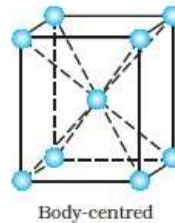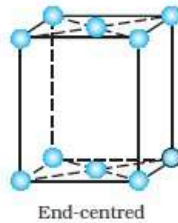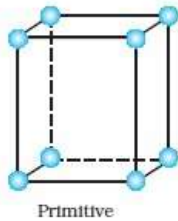
Unit Cells of 14 Types of Bravais Lattices

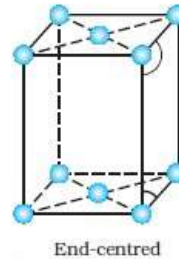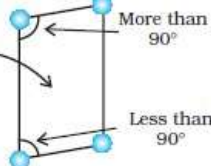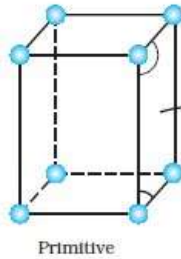**Primitive (or simple)**   **Body-centred**   **Face-centred**
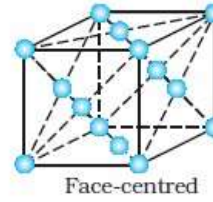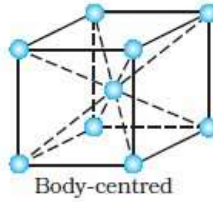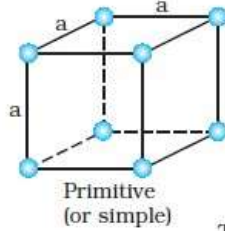
The three cubic lattices: all sides of same length, angles between faces all 90°
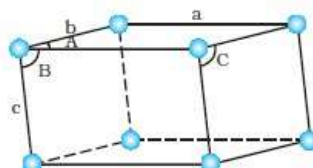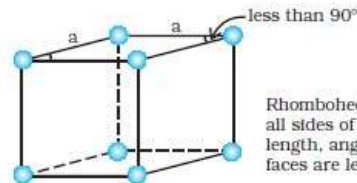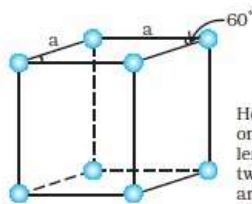
Primitive   **Body-centred**
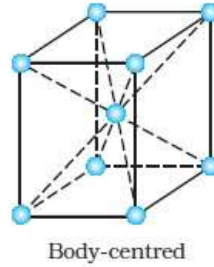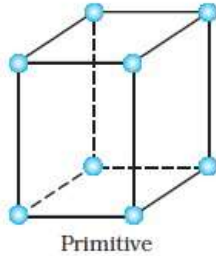
The two tetragonal: one side different in length to the other, two angles between faces all 90°

Primitive   **End-centred**   **Body-centred**   **Face-centred**

The four orthorhombic lattices: unequal sides, angles between faces all 90°

More than 90°

Less than 90°

Primitive   **End-centred**

The two monoclinic lattices: unequal sides, two faces have angles different from 90°

60°

Hexagonal lattice– one side different in length to the other two, the marked angles on two faces are 60°

less than 90°

Rhombohedral lattice– all sides of equal length, angles on two faces are less than 90°

Triclinic lattice– unequal sides a, b, c, A, B, C are unequal angles with none equal to 90°
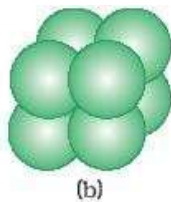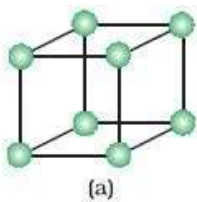
Number of atoms in a unit cell:

1) Primitive cubic unit cell:
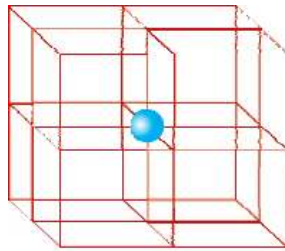
In a simple cubic unit cell, each corner atom is shared between 8 unit cells.

(a)   (b)   (c)

A primitive cubic unit cell (a) open structure (b) space-filling structure (c) actual portions of atoms belonging to one unit cell.

Eight unit cells share each corner atom.

At each corner we have = 1/8 atom
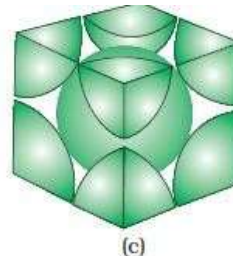
At 8 corners we have = (1/8) X 8 **= 1 atom**

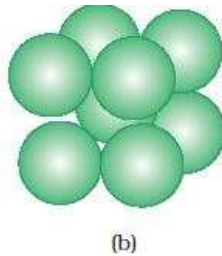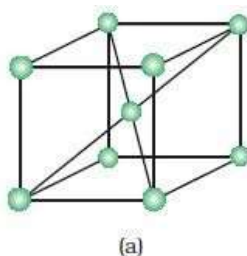**2) Body centered cubic unit cell:**

8 corners X (1/8) per corner atom = 1

atom 1 body centre atom = 1X 1 = 1

atom

Total number of **atoms**.

(a)   (b)   (c)

A body-centred cubic unit cell (a) open structure (b) space-filling structure (c) actual portions of atoms belonging to one unit cell.

3) Face centered cubic unit cell:

An atom at face centre of unit cell is shared between 2 unit cells

8 corners X (1/8) per atom = 1 atom

6 faces X (1/2) per atom = 3 atoms Total number of atoms = 1 + 3

= **4 atoms**.

(a)   (b)   (b)
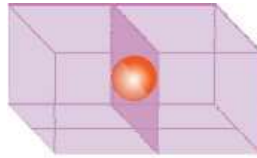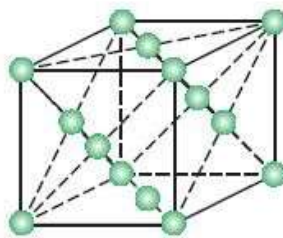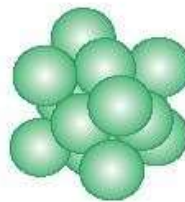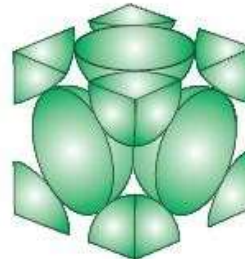
A face-centred cubic unit cell (a) open structure (b) space filling structure (c) actual portions of atoms belonging to one unit cell.

Packing in solids (or) Close packing in crystals:

In solids, the constituent particles are closely packed and leaving the minimum vacant space. Let us assume the particles are identical hard spheres.

1) Close packing in one dimension:

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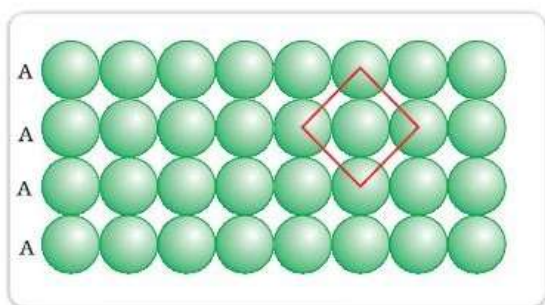

Close packing of spheres in one dimension

2) Close packing in two dimensions:

When the rows are combined touching each other. The crystal plane is obtained. The rows can be combined in two different ways.

a)The particles when placed in the adjacent rows show a horizontal as well as vertical alignment and form squares. This type of packing is called **square close packing**. In square close packing the coordination number is **4**.

b)The particles in every next row are placed in the depressions between the particles of the first row. The particles in the third row will be vertically aligned with those in the first row. This type of packing gives a hexagonal pattern and is called **hexagonal close packing**. In hexagonal close packing the coordination number is **6**.
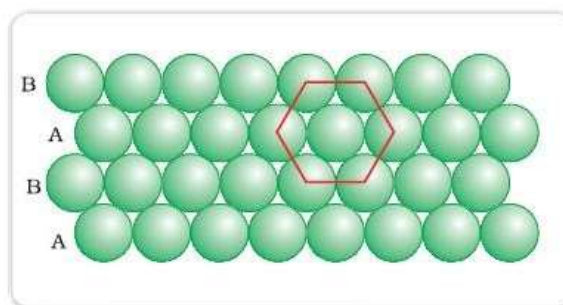
(a) Square close packing (b) hexagonal close packing of spheres in two dimensions
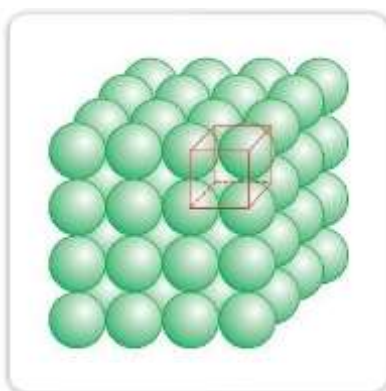
3) <u>Close packing in three dimensions:</u>

All real structures are three dimensional structures. They can be obtained by stacking two dimensional layers one above the other.

A) <u>Three dimensional close packing from two dimensional square close packed layers:</u>

*Simple cubic lattice formed*
by A A A .... arrangement

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 upper layer are 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 of the layers are perfectly aligned horizontally as well as vertically. Similarly, we may place more layers on 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**.

B) <u>Three dimensional close packing from two dimensional hexagonal close packed layers:</u>

Three dimensional close packed structures can be generated by placing layers on over the other.

<u>i) Placing second layer over to the first layer:</u>

When second layer is placed in such a way that its spheres of the second layer are placed in the depressions of the first layer,
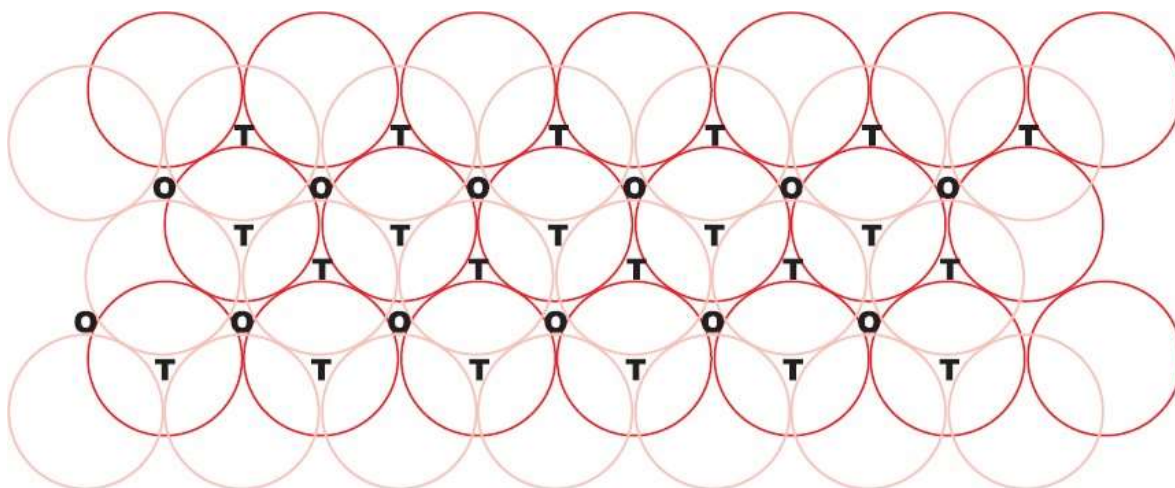
A stack of two layers of close packed spheres and voids generated in them. T = Tetrahedral void; O = Octahedral void

Let us take a two dimensional hexagonal close packed layers A and B. It can be observed from the figure 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 a tetrahedral void is formed. These voids are called **tetrahedral voids** because a tetrahedron is formed when the centers of these four spheres are joined. They have been marked as ' **T**' in the figure. The remaining voids are called **octahedral voids** because an octahedron is formed when the centers of these six spheres are joined. They have been marked as '**O**' in the figure.

(a)   (b)   (c)
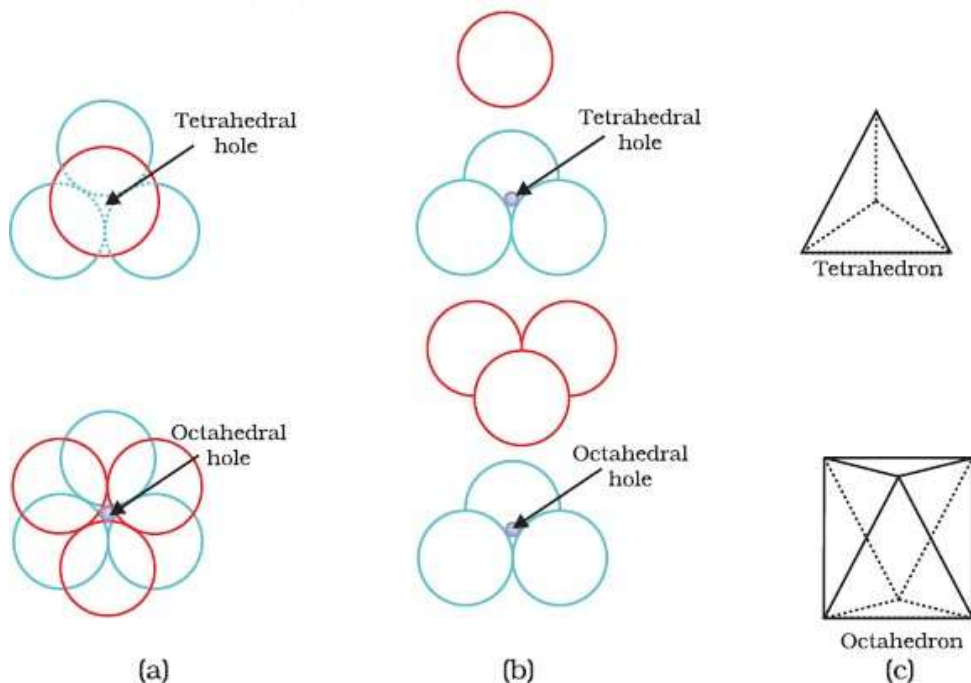
Let the number of close packed sphere be **N**, then

The number of octahedral voids generated is **N**

The number of tetrahedral voids generated is **2N**.

Voids (or) holes: Some space is not occupied by the spheres these gaps are called **voids** or **holes**.

**ii) Placing the third layer over the second layer:**

a) 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.

b) 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. This pattern of layers is often written as **ABCABC….** This structure is called **cubic close packed (ccp)** structure.

Bothe in HCP and CCP the coordination number is **12**.

A

C

B

A

(a)

(b)
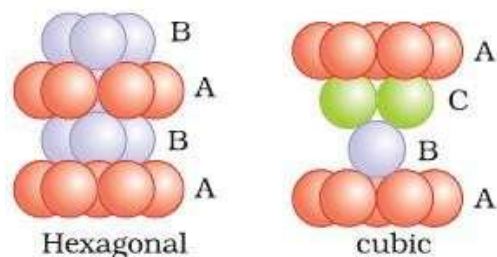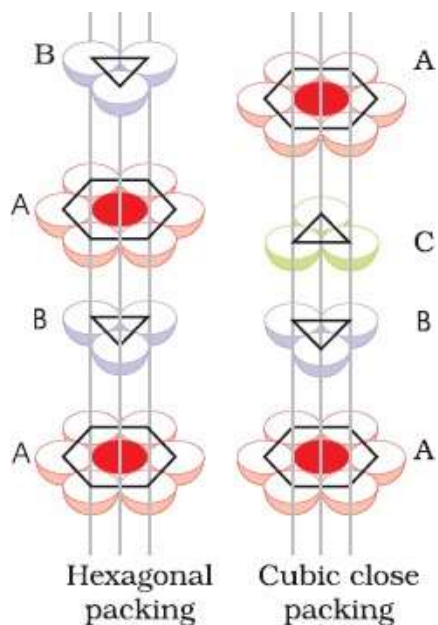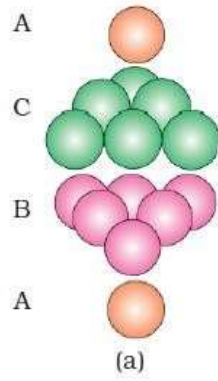
(a) ABCABC...
arrangement of
layers when
octahedral void is
covered

(b) fragment
of structure formed
by this arrangement
resulting in cubic
closed packed (ccp)

Calculation of density of unit cell:

The density of a crystal can be calculated by using the formula

$$\text{Molecular mass} = \text{Mass of avagadro particles (No)}$$

$$\text{One particle mass} = \frac{\text{Molecular weight}}{\text{Avagadro number}} = \frac{M}{No}$$

$$\text{Mass of Z particles} = \frac{ZM}{No}$$

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

$$= \frac{ZM}{No\ V}$$

$$= \frac{ZM}{No\ a^3} \quad \left[\text{since } V = a^3 \right]$$

Where ρ = density

Z = number of atoms per unit cell

M = molecular weight of the lattice

particle   a = unit cell length

Introduction:

Crystal structures are studied by **X-ray diffraction method**. X-rays are also electromagnetic waves, we would expect them to exhibit interference phenomenon under suitable conditions.

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.
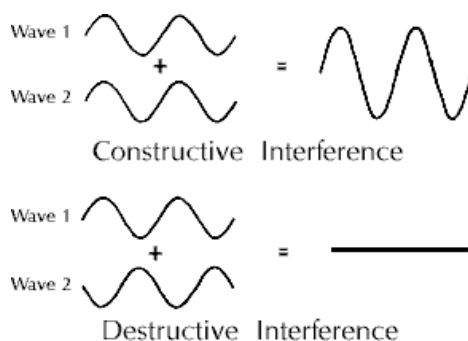

X- Ray diffraction of scattering:

X- Rays are generated from the source of X-ray tube. These rays are allowed to pass through a lead screen 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.
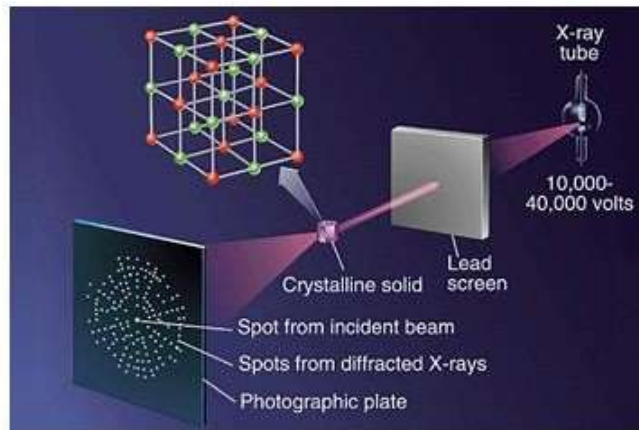
X-ray diffraction set up

Bragg's equation:

The process was based upon the principle that a crystal may be considered to be made up of a number of parallel equidistant atomic planes, as represented by lines $P_1P_1{}^1$, $P_2P_2{}^1$ and $P_3P_3{}^1$ in the following figure.
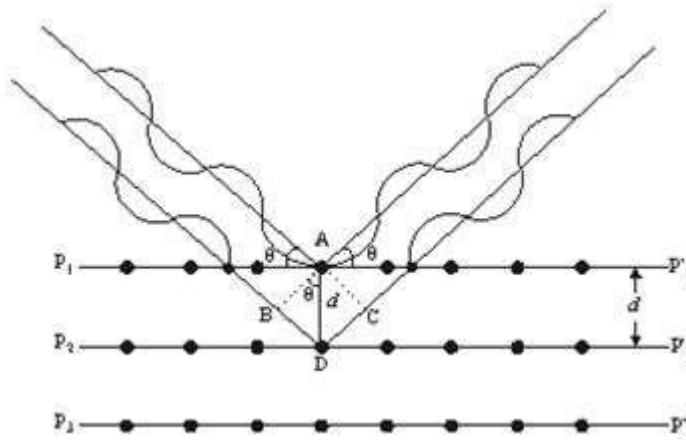
Suppose two waves of X-ray beams, which are in phase falls on the surface of the crystal. If the first ray gets reflected from the first layer i.e., $P_1P_1{}^1$ line and the second ray is reflected from the second layer of atoms i.e., $P_2P_2{}^1$ line, then it is evident that as compared to the first ray, second ray has to travel a longer distance, equal to BDC in order to emerge out of the crystal. If the waves are in phase after reflection, the difference in distance travelled by the two rays must be equal an integral number of wavelength ($n\lambda$), for constructive interference.

Thus,

Distance BDC = nλ

……………………………….. (i)   It is obvious from the figure that

BD = DC = AD sinθ

Therefore BDC = 2 AD sinθ ……………………. (ii)

If the distance between the successive atomic plane is = d   Then, AD = d

………………………………………… (iii)

So, from equations i, ii, iii

nλ = 2 d sinθ

Thus, Bragg gave a mathematical equation to establish a relationship between the layers and the angle of diffraction.

Here λ = wavelength of X-ray used

θ = incident angle or reflected angle

d = Distance between planes of the constituent particles in a crystal.

n = An integer (1,2,3,4, etc) which represents the serial order of diffracted beams.

Bragg's equation can be used to calculate the distances between repeating planes of the particles in a crystal. Similarly, if interplanar distances are given, the corresponding wavelengths of the incident beam of X-ray can be calculated.