THE SOLID STATE

TOPIC-1

Classification of solids with structures

VERY SHORT ANSWER QUESTIONS

1. What are solids?

Ans: Solids are characterized by their high density and low compressibility as compared to those of the gas phase. The properties of solids indicate that the molecule (or ions) in them are relatively close together

2. What are different types of solid?

Ans: There two types of solids. They are crystalline solids and amorphous solids.

3. What are different types of crystalline solids?

Ans: There are fou different types of crystalline solids. They are a) Ionic solids, b) covalent solids c) molecular solids and d) metallic solids.

4. What are crystallites?

Ans: Due to short range order,, amorphous solids may have small parts in crystalline and the rest non-crystalline form. Crystalline parts of an otherwise amophous substance are called crystallites.

SHORT ANSWER QUESTIONS

1. **What are the properties of solids?**

Ans:

- Solids have a definite shape, mass and volume.
- Solids are almost incompressible, rigid and have mechanical strength.
- Solids have high density but very slow diffusion rate.
- Solids can have only vibrational motions the constituents have fixed positions.
- In solids constituents have strong force of attraction as intermolecular distances are short.

2. What are the properties of crystalline solids?

Ans:

- In these solids, the constituents are arranged in a definite or orderly manner which repeats itself over long distances.
- They have a definite geometry with flat and sharp edges.
- Such solids have sharp edges and undergo clean cleavage.
- They are considered as true solids.
- They show anisotropy i.e. different physical properties in different directions.
- They are normally incompressible.

3. **What are the properties of amophous solids?**

Ans:

- In these solids the constituents are not arranged in a regular or orderly manner over a long range.
- Such solids do not have sharp melting points and clean cleavage that is, have no irregular cut.
- These are considered as pseudo solids.
- These show isotropy, i.e. same physical properties in all directions.
- They do not show clean cleavage.

4. What are the properties of ionic solids?

Ans:

- The constituent particles are ions.
- They are bound by strong electrostatic forces of attraction.
- They are hard but brittle.
- They have high melting points
- Their bond energy lies between 400 – 4000 kJ/mole.
- They are good conductors in molten and dissolved state.

5. What are the properties of covalent solids or network solids?

Ans:

- These solids contain atoms.
- These possess covalent bonds
- These are very hard.
- Melting points of these solids is very high, i.e. > 3900 C,.
- The bond energy is 150 – 500 kJ/mole.
- These are generally insulators.

6. What are the properties of molecular solids?

Ans:

- These solids generally contain molecules.
- These are bound by weak Vander Waal's forces of attraction.
- These are soft solids.
- They posses low melting points , 300C
- Bond energy is < 40 kJ/mole.
- These are generally insulators.

7. What are the properties of molecular solids?

Ans:

- These solids contain atoms.
- These are bound by metallic bond.
- These are very hard, malleable and ductile.
- Possess high melting points.
- Bond energy is 80 – 1000 kJ/mole.
- These are all conductors.

LONG ANSWER QUESTIONS

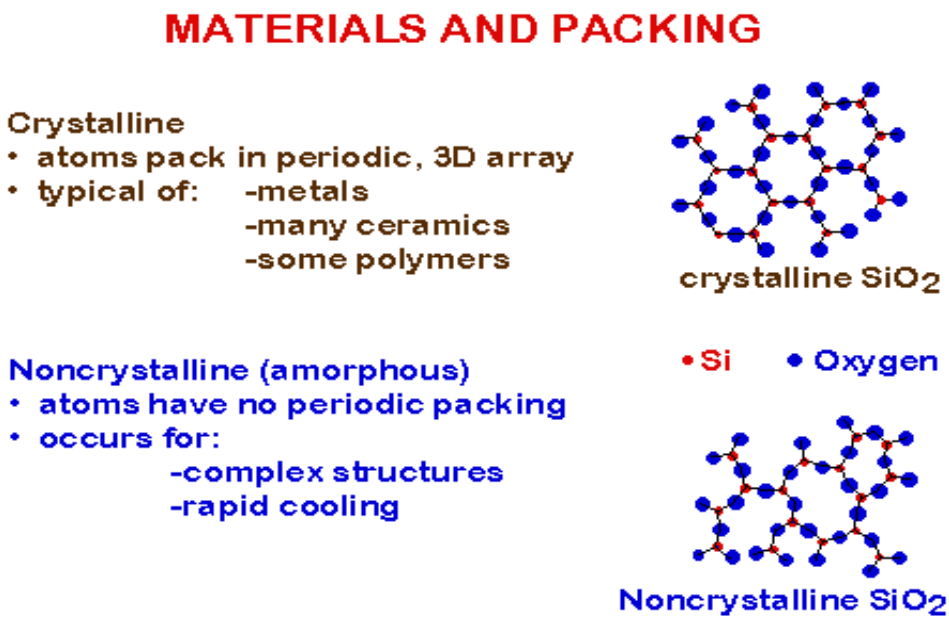
1. Explain the classification of solids.

Ans:

Solids are characterized by their high density and low compressibility as compared to those of the gas phase. The properties of solids indicate that the molecule (or ions) in them are relatively close together.

Solids can be broadly classified into two categories, namely, crystalline and amorphous solids. The main characteristics of these are described in the following.

1. <u>Crystalline Solids</u>: The outstanding characteristics of a crystal are its sharp melting point, its flat faces and sharp edges. These properties are due to a high degree of internal order which extends throughout the crystal (a definite pattern constantly repeating in space). This is know as long-range order.



2. <u>Amorphous Solids</u>: Amorphous solids do not have the long-range order but have a short-range order. These characteristics may not be found around a similar atom placed at a distance from the other atom.

Examples of amorphous solids are glass, used silica, rubber and polymers.

Amorphous solids do not have the characteristics as possessed by crystalline solids. In many ways, they are more closely related to liquids than to the crystalline solids and are, therefore, regarded as super cooled liquids with high viscosity. A given material may be converted into the amorphous or glassy form by rapidly cooling the melt or freezing the vapour.

CLASSIFICATION OF CRYSTALS BASED ON BOND TYPE

The properties of most of the crystals are found to conform to one of the four general types of chemical bonds, in terms of which it is possible to classify them into four categories as described in the following.

a) Molecular Crystals (or Vander Waals Crystals):

Molecular crystals are those in which the crystalline state is composed of an aggregate of discrete molecules held together by Van der Waals forces.

Because of these weaker forces, molecular crystals are soft and posses comparatively low melting points.

Examples are CO_2, CCl_4, Ar and most of the organic compounds.

b) **Ionic Crystals**: Ionic crystals involve electrostatic forces amongst their structural units.

Because of stronger forces, ionic crystals are strong and likely to be brittle. The melting points are high, which decease with increasing size of the ions. In ionic crystals, some of the atoms may be held together by covalent bonds to form ions having definite positions and orientations in crystal lattice.

c) Covalent Crystals: Covalent crystals involve forces of chemical nature (covalent bonds) extended in three dimensions. These forces are strong, and consequently the crystals are strong and hard, with high melting points. Examples are diamond, silicon, etc.

d) Metallic crystals: Electrons are held loosely in these type of crystals. They are god conductors or electricity. Metallic crystals are strong and can be bent..

THE SOLID STATE

TYPES OF SOLIDS AND CRYSTAL SYSTEMS

VERY SHORT ANSWER QUESTIONS

1. **Name an element that forms monoclinic crystals**?
   ANS: Monoclinic sulphur (S).

2. **What is the crystalline structure of orange coloured oxidising agent used in lab?**
   Ans: The orange coloured oxidising agent used in lab is $K_2Cr_2O_7$. The crystal structure of $K_2Cr_2O_7$ is Triclinic.

3. **Graphite crystallizes in hexagonal solid form. Give its characteristics. ?**
   Ans: The Axial and angular characteristics of Graphite is

   → **a = b ≠ c**

   → **α = β = 90**

   → **γ = 120**

4. **Explain ferromagnetic soli materials?**
   Ans: Ferromagnetic materials show permanent magnetism even after the applied magnetic field is removed, i.e. once such materials are magnetised they retain their mangnetism.

   Ex: Fe, Co, Ni are only three elements which show ferromagnetism at room temperatue.

5. **What is meant by space lattice?**

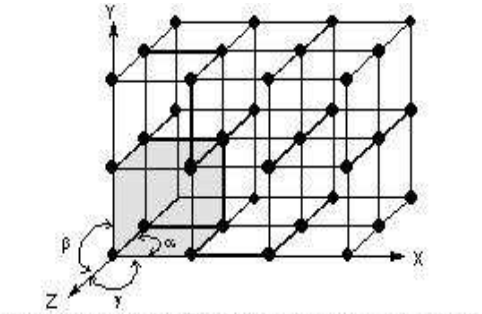
Ans: All crystals consist of regularly repeating array of atoms, molecules or ions which are the structural units (or basic units). It is much more convenient to represent each unit of pattern by a point, called lattice point, rather than drawing the entire unit of pattern. This results in a three dimensional orderly arrangement of points called a space lattice or a crystal lattice

Thus, a space lattice may be defined as a regular three dimensional arrangement of identical points in space or it can be defined as an array of points showing how molecules, atoms or ions are arranged at different sites in three dimensional space.

It must be noted that:

(a) Each lattice point has the same environment as that of any other point in the lattice

(b) The constituent particles have always to be represented by a lattice point, irrespective of whether it contains a single atom or more than one atom



A crystal or space lattice - The shaded portion represents the unit cell

Space lattice

6. **Name the crystal systems?**

   Ans: There are Seven Crystal Systems**.** To describe a unit cell, six parameters are required. These are the three basis vectors along the three crystallographic axes (represented by the symbols a, b and c and the three angles between the crystallographic axes (represented by the symbols α, β and γ).

   The seven types of crystal systems are; a) Cubic, b) Tetragonal, c) Orthorhombic d) Hexagonal e) Trigonal or Rhombohedral f) Monoclinic and g)Triclinic.

7. **How many unit cells share each of the lattice points in a cubic lattice?**

   The no of atom in a unit cell can be calculated by keeping in view following points

   1. An atom at the corners is shared by eight unit cells. Hence the contribution of an atom at the corner to a particular cell = 1/8.

   2. An atom at the face is shared by two unit cells. Hence the contribution of an atom at the face to a particular cell = 1/2

   3. An atom at the edge centre is shared by four unit cells in the lattice and hence contributes only 1/4 to a particular unit cell.

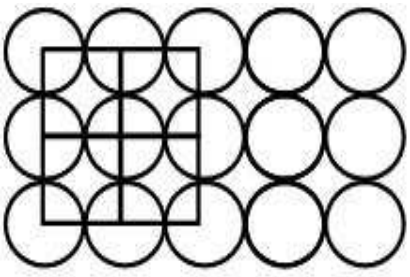
   4. An atom at the body centre of a unit cell belongs entirely to it, so its contribution = 1

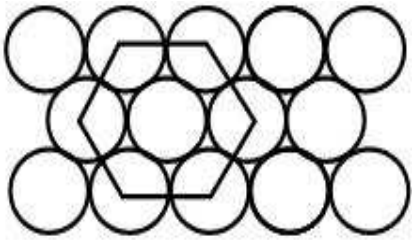
8. **Explain two dimensional close packing in crystals**?

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

(i) 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

(ii) 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





Square close packing **Hexagonal close packing (coordination no 4)** **(coordination no 6)**

9. Explain three dimensional close packing in crystals?

Ans: In two dimensional packing, a more efficient packing is given by hexagonal close packing. In order to develop three dimensional close packing let us retain the hexagonal close packing in the first layer. If the spheres in the second layer are just placed over the spheres in the first layer so that the spheres in the two layers are vertically aligned, its voids will come above the voids in the first layer. This is an inefficient way of filling the space.

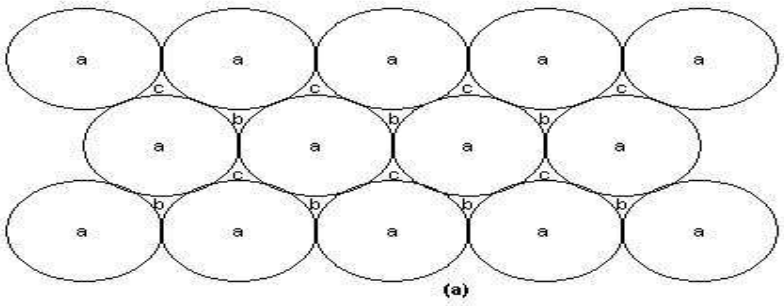
When the second layer is placed in such a way that its spheres find place in the 'b' voids of the first layer, the 'c' voids will be left unoccupied. Since under this arrangement no sphere can be placed in them, (c voids), i.e. only half the triangular voids in the first layer are occupied by spheres in the second layer (i.e. either b or c)

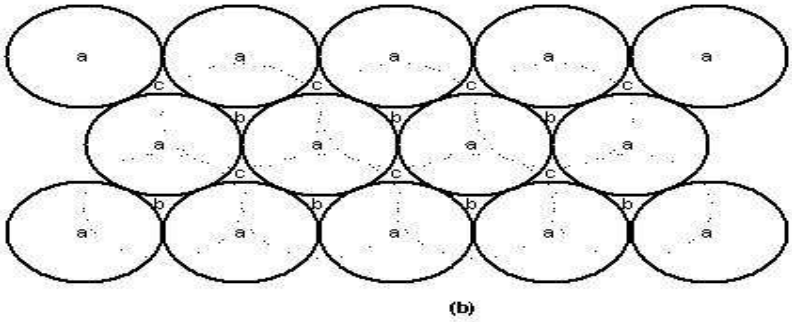
There are two alternative ways in which spheres in the third layer can be arranged over the second layer

(1) When a third layer is placed over the second layer in such a way that the spheres cover the tetrahedral or 'a' voids; a three dimensional closest packing is obtained where the spheres in every third or alternate layers are vertically aligned (i.e. the third layer is directly above the first, the fourth above the second layer and so on) calling the first

layer A and second layer as layer B, the arrangement is called ABAB ……. pattern or hexagonal close packing (HCP) as it has hexagonal symmetry.

(2) When a third layer is placed over the second layer in such a way that spheres cover the octahedral or 'c' voids, a layer different from layers A and B is produced. Let it be layer 'C'. Continuing further a packing is obtained where the spheres in every fourth layer will be vertically aligned to the spheres present in the first layer. This pattern of stacking spheres is called ABCABC ……. pattern or cubic close packing (ccp). It is similar to face centred cubic (fcc) packing as it has cubic symmetry





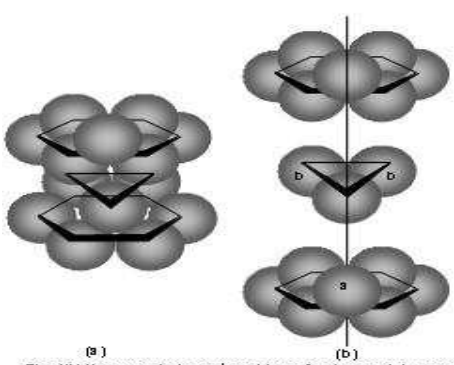


Fig. (X) Hexagonal closest packing of spheres: (a) normal and (b) exploded view

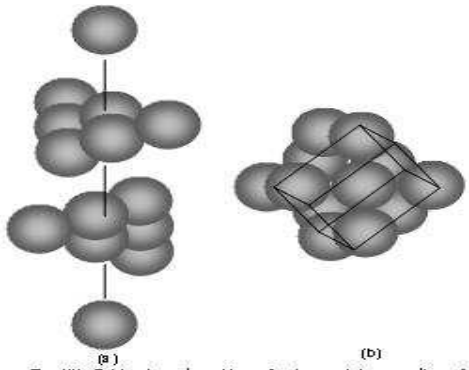


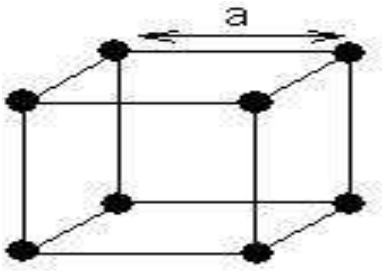
Fig. (X): Cubic closest packing of spheres: (a) generation of unit from closest-packed layers, and (b) rotation to show cubic symmetry

10. What is unit cell and how many different types of unit cells are possible?

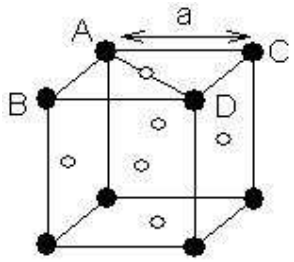
Ans: A unit cell is the smallest repeating unit in space lattice which when repeated over and over again results in a crystal of the given substance. Unit cell may be also defined as a three dimensional group of lattice points that generates the whole lattice on repetition.

Types of unit cells

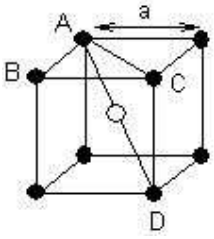
1. **Simple unit cell** having lattice points only at the corners is called simple, primitive or basic unit cell. A crystal lattice having primitive unit cell is called simple crystal lattice



2. **Face centred cubic lattice** (fcc) – A unit cell in which the lattice point is at the centre of each face as well as at the corner.



3. **Body centred cubic lattice** (bcc) A unit cell having a lattice point at the centre of the body as well as at the corners.



4. **Another type of unit cell, called end – centred unit cell** is possible for orthorhombic and monoclinic crystal types. In an end centred there are lattice points in the face centres of only one set of faces in addition to the lattice pints at the corners of the unit cell

10. Derive relations between the density of the crystalline substance and the unit cell length?

Ans: From the unit cell dimensions, it is possible to calculate the volume of the unit cell. Knowing the density of the metal, we can calculate the mass of the atoms in the unit cell. The determination of the mass of a single atom gives an accurate determination of Avogadro constant.

Suppose edge of unit cell of a cubic crystal determined by X – Ray diffraction is a, d is density of the solid substance and M is the molar mass, then in case of cubic crystal

Volume of a unit cell = a^3

Mass of the unit cell = no. of atoms in the unit cell × mass of each atom = Z × m

Here Z = no. of atoms present in one unit cell

m = mass of a single atom

Mass of an atom present in the unit cell = m/N_A

Density d = mass of unit cell / volume of unit cell = $Z.m / a^3$

$$\mathbf{d = Z.M. / a^3 \times N_A}$$

Note: Density of the unit cell is same as the density of the substance

LONG ANSWER QUESTIONS

1. How do you recognize crystal lattice and unit cell?

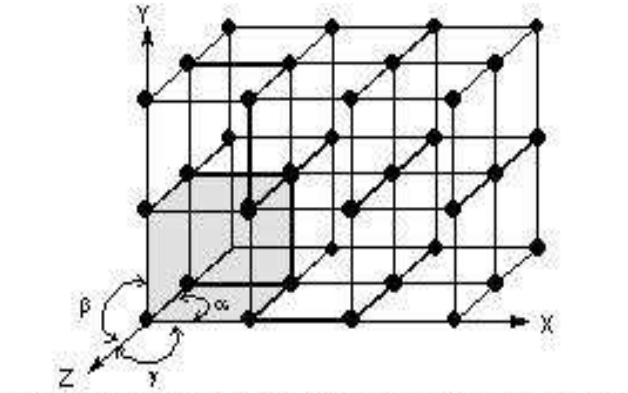
Ans: All crystals consist of regularly repeating array of atoms, molecules or ions which are the structural units (or basic units). It is much more convenient to represent each unit of pattern by a point, called lattice point, rather than drawing the entire unit of pattern. This results in a three dimensional orderly arrangement of points called a space lattice or a crystal lattice

Thus, a space lattice may be defined as a regular three dimensional arrangement of identical points in space or it can be defined as an array of points showing how molecules, atoms or ions are arranged at different sites in three dimensional space.

It must be noted that

(a) Each lattice point has the same environment as that of any other point in the lattice

(b) The constituent particles have always to be represented by a lattice point, irrespective of whether it contains a single atom or more than one atoms



A crystal or space lattice - The shaded portion represents the unit cell

UNIT CELL

A unit cell is the smallest repeating unit in space lattice which when repeated over and over again results in a crystal of the given substance. Unit cell may be also defined as a three dimensional group of lattice points that generates the whole lattice on repetition.

Types of unit cells

1. **Simple unit cell** having lattice points only at the corners is called simple, primitive or basic unit cell. A crystal lattice having primitive unit cell is called simple crystal lattice

2. **Face centred cubic lattice** (fcc) – A unit cell in which the lattice point is at the centre of each face as well as at the corner.

3. **Body centred cubic lattice** (bcc) A unit cell having a lattice point at the centre of the body as well as at the corners.

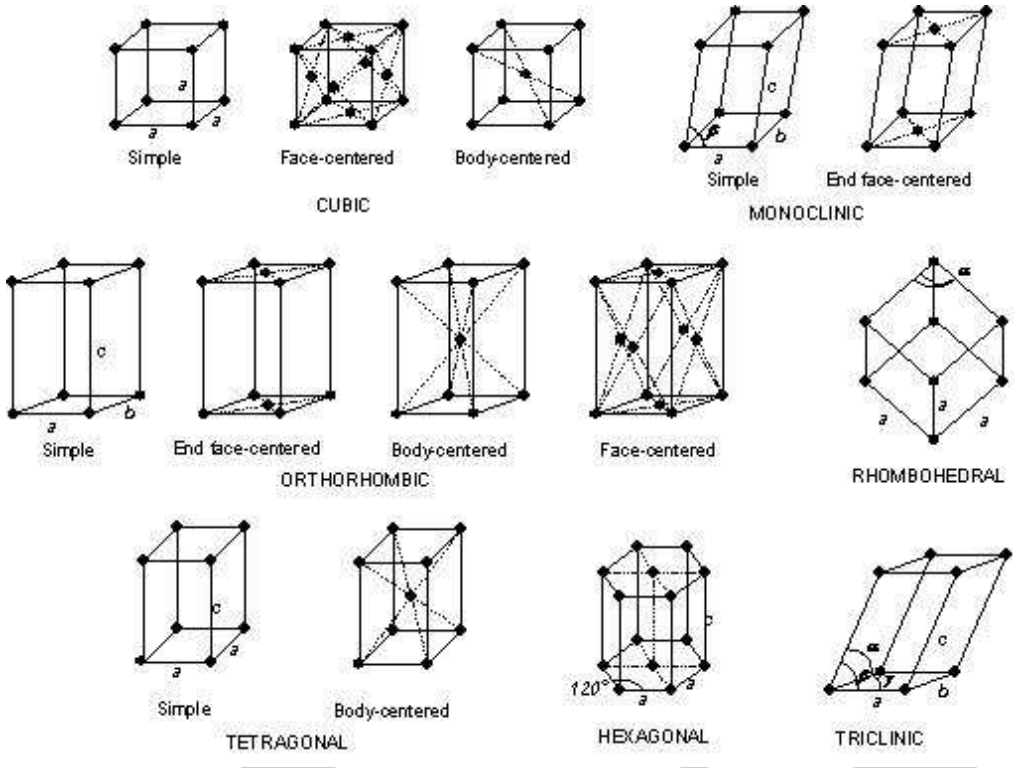
Another type of unit cell, called end – centred unit cell is possible for orthorhombic and monoclinic crystal types.

In an end centred there are lattice points in the face centres of only one set of faces in addition to the lattice pints at the corners of the unit cell. The various types of unit cells possible for different crystal classes (in all seven) are given below in tabular form

Crystals class	Axial distances	Angles	Possible types of unit cells	Examples
Cubic	a = b = c	$\alpha = \beta = \gamma = 90°$	Primitive, Body centred face	Copper , KCl, NaCl zinc blende,

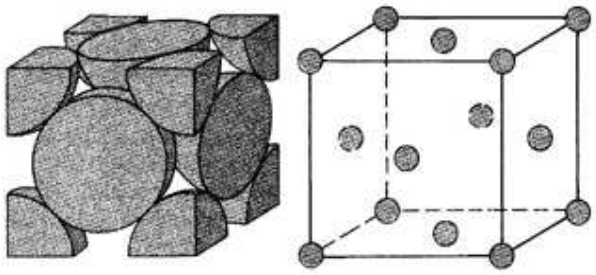
			centred	diamond
Tetragonal	a = b ≠ c	α = β = γ = 90°	Primitive, body centred	SnO_2, White tin, TiO_2
Orthorhombic	a ≠ b ≠ c	α = β = γ = 90°	Primitive body centred, face centred end centred	Rhombic sulphur, KNO_3, $CaCO_3$
Hexagonal	a = b ≠ c	α = β = 90° γ = 120°	Primitive	Graphite, Mg, ZnO
Trigonal or Rhombohedral	a = b = c	α = β = γ ≠ 90°	Primitive	($CaCO_3$) Calcite, HgS(Cinnabar)
Monoclinic	a ≠ b ≠ c	α = β = 90° γ ≠ 90°	Primitive and end centred	Monoclinic sulphur, $Na_2SO_4.10H_2O$
Triclinic	a ≠ b ≠ c	α ≠ β ≠ γ ≠ 90°	Primitive	$K_2Cr_2O_7$, $CuSO_4.5H_2O$

The Bravais space lattices associated with various crystal system are show in fig below



2. Place the atoms of an element 'A' in the lattice points of face centered cubic structure?

Ans: A face centred cubic (fcc) unit cell contains atoms at all the centers of all the faces of the cube. The following is the structure of fcc unit cell



- The characteristics of fcc structure are;
- Each atom is located at the face-center is shared between two unit cells.
- Each atom located at the corner is shared between eight adjacent unit cells
- The structure has a cubic close packing symmetry.

3. What do you know about amorphous substances? Discuss?

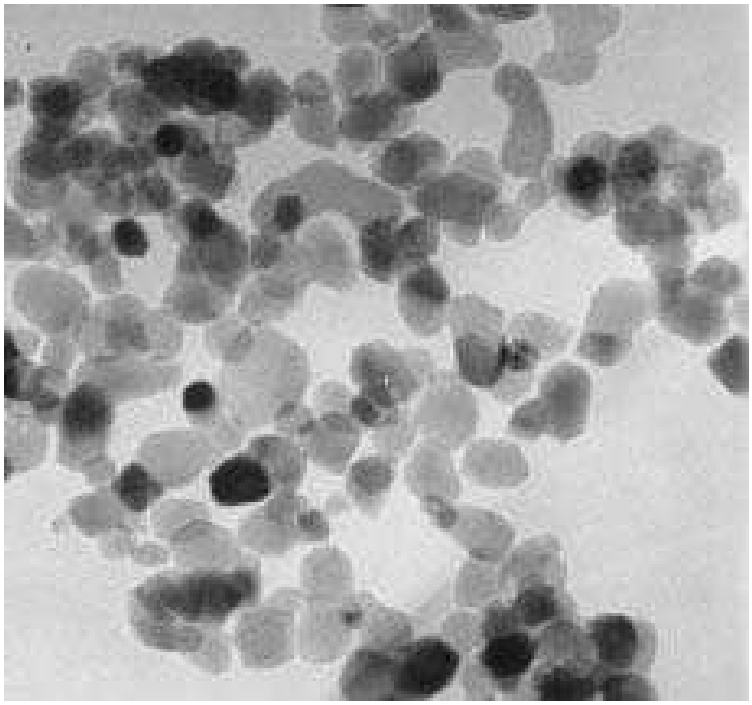
Ans: An amorphous solid is a substance whose constituent particles do not possess a regular orderly arrangement e.g. glass, plastics, rubber, starch, and proteins. Though amorphous solids do not possess long range regularity, in some cases they may possess small regions of orderly arrangement. These crystalline parts of an otherwise amorphous solid are known as **crystallites.**

An amorphous solid does not posses a sharp melting point. It undergoes liquefication over a broad range of temperature. The amorphous solid do not posses any characteristic heat of fusion. When an amorphous solid is cut with the help of sharp edged knife it results in an irregular cut.

Amorphous substances are also, sometimes, referred to as super cooled liquids because they posses disorderly arrangement like liquids. In fact many amorphous solids such as glass are capable flowing. Careful examination of the window panes of very old houses reveals that the panes are thicker at the bottom than at the top because the glass has flown under constant influence of gravity.

USES OF AMORPHOUS SOLIDS

Amorphous solids such as glass and plastics are very important materials and are widely used in construction, house ware, laboratory ware etc. Amorphous silica is likely to be the best material for converting sunlight into electricity (photovoltaic). Another well known amorphous solid is rubber which is used in making tyres shoes soles etc.



4. Draw distinction between space lattice and crystal lattice?

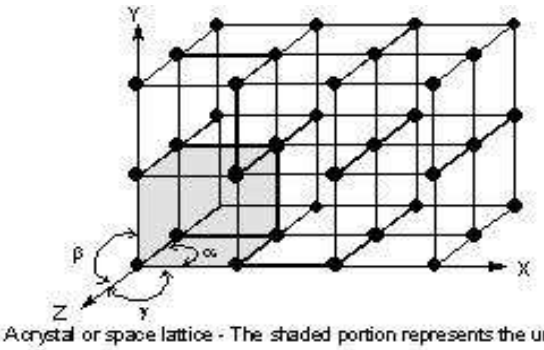
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A crystal or space lattice - The shaded portion represents the unit cell

5. Write the differences between crystalline and amorphous solids?

DISTINCTION BETWEEN CRYSTALLINE AND AMORPHOUS SOLIDS

Crystalline solids	Amorphous solids
1. The internal arrangement of particles is regular so they possess definite and regular geometry	1. The internal arrangement of particles is irregular. Thus they do not have any definite geometry.
2. They have sharp melting points	2. They do not have sharp melting points
3. There is regularity in the external form when crystals are formed	3. There is no regularity in the external form when amorphous solids are formed

4. Crystalline solids give a regular cut when cut with a sharp – edged knife	4. Amorphous solids give irregular cut.
5. They have characteristic heat of fusion.	5. They do not have characteristic heat of fusion.
6. Crystalline solids are rigid and their shape is not distorted by mild distorting forces	6. Amorphous solid are not very rigid. These can be distorted by bending or compressing forces.
7. Crystalline solids are regarded as true solids	7. Amorphous solids are regarded as super cooled liquids or pseudo solids
8. Crystalline solids are anisotropic. This implies that physical properties such as refractive index, conductivity, thermal expansion etc are different in different directions. This is due to orderly arrangement of particles	8. Amorphous solids are isotropic in nature. This implies that various physical properties are same in all the directions. This is because of random arrangement of particles.

THE SOLID STATE

TOPIC-3
BRAGG'S EQUATION AND CALCULATION OF DENSITY OF CRYSTAL

VERY SHORT ANSWER QUESTIONS

1. **Explain Bragg's equation?**

Ans: Braggg's equation is given by;

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

where,

n = order of diffraction
λ = wave length
d = distance between the planes
Θ = angle of incident beam.

2. **Which crystal structure has 12 as co-ordination number?**

Ans: Crystals having hexagonal close packing (hcp) crystal has coordination number '12'.

3. **The diffracted X-rays from copper sulphate crystal are allowed to fall on a photographic plate. What happens to the photgraphic plate?**

Ans: The photographic plate gets bright and dark patches that result from the constructive and destructive interference of the diffracted rays.

4. **How many lattice points are there in a unit cell of a) bcc lattice; b) end centered lattice**?

Ans:

a) In bcc the lattice points are 8. They are the corners of primitive unit cell.

b) The end centered unit cell has 4 nearest lattice points to the lattice **x** and **y** in primitive unit cell.

The end centered lattice has lattice point on each of the two faces bounded by edge of length **a** and **b.**

Therefore, the number of lattice points is 10.

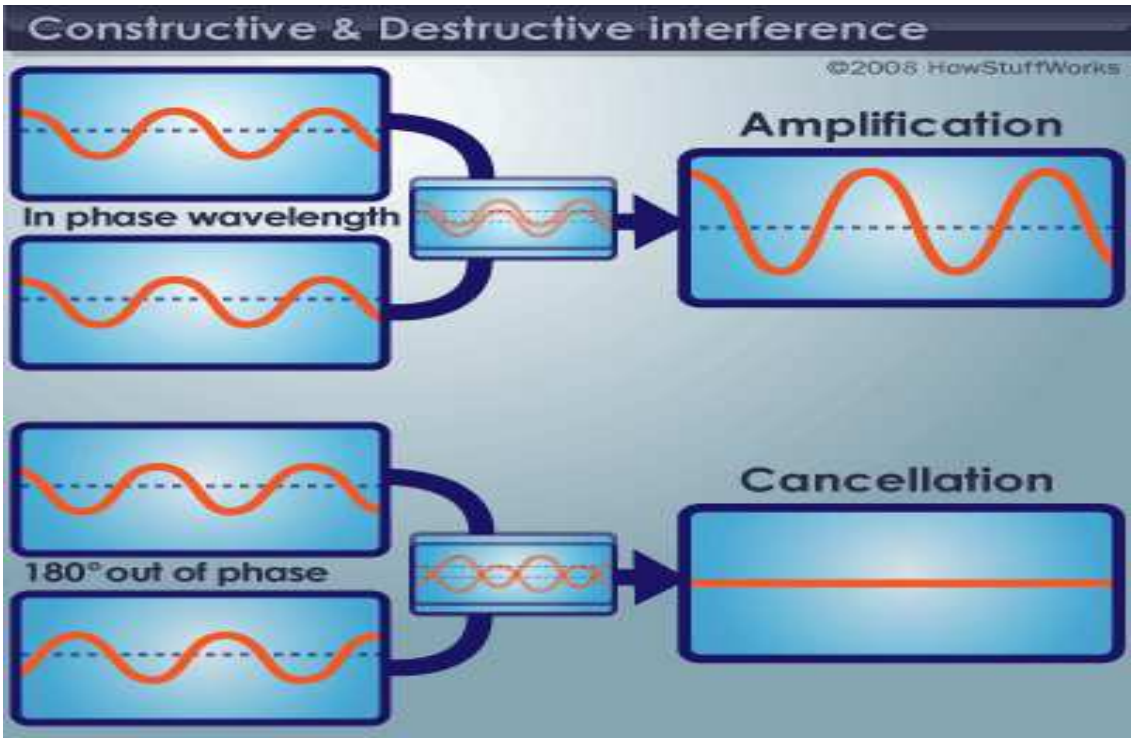
SHORT ANSWER QUESTIONS

1. **Explain when the diffracted rays may constructive and destructive interference?**

Ans:

In constructive interference,

- Two waves are in the same phase
- Mxima and minima of two waves mutually interfere with one another
- One wave reinforces the other wave.



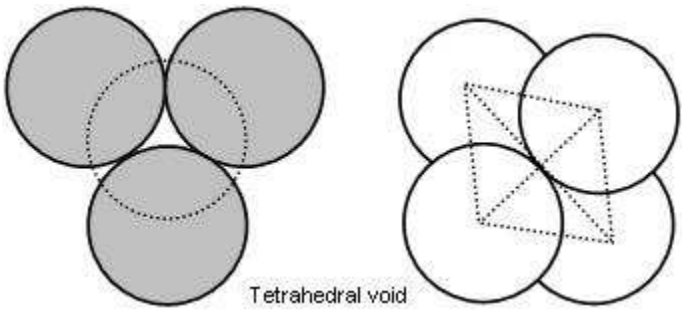
In destructive interference,

- Two waves are not in the same phase i.e. out of phase
- One wave nullifies the other

2. What is tetrahedral hole?

Tetrahedral hole

In close packing arrangement, each sphere in the second layer rests on the hollow (triangular void) in three touching spheres in the first layer. The centres of theses four spheres are at the corners of a regular tetrahedral. The vacant space between these four touching spheres is called tetrahedral void. In a close packing, the number of tetrahedral void is double the number of spheres, so there are two tetrahedral voids for each sphere



Radius of the tetrahedral void relative to the radius of the sphere is 0.225

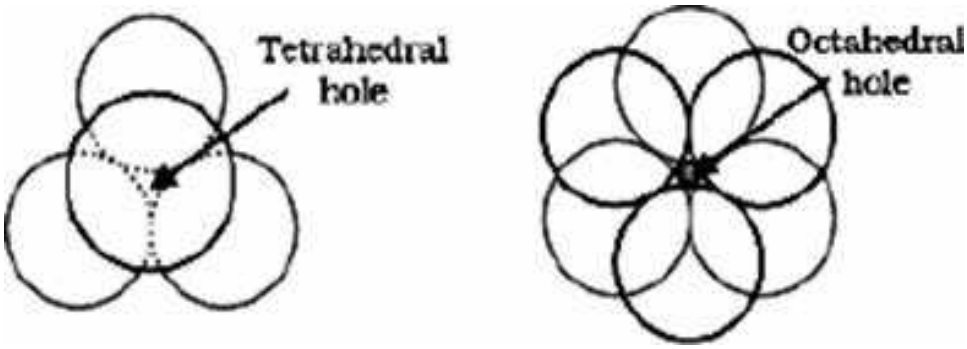
i.e. $r_{void} / r_{sphere} = 0.225$

In a multi layered close packed structure , there is a tetrahedral hole above and below each atom hence there is twice as many tetrahedral holes as there are in close packed atoms

3. What is octahedral hole?

Ans:

The interstitial void, formed by combination of two triangular voids of the first and second layer is called octahedral void because this is enclosed between six spheres centres of which occupy corners of a regular octahedron



4. Write a brief account of VBT of metal bonding?

Ans:

VBT is also called as resonance theory proposed by 'Pauling'. According to this theory;

- Metallic bond is essentially polar or non-polar covalent bond.
- The covalent bond involves resonance between a number of structures one electron and electron pair bonds
- There is a possibility of insufficient valence electrons for the formation of electron pair bonds with each atom of the metal; it is assumed that resonance takes place through out the solid metal.
- The atoms undergo hybridization.

Defects of the theory:

- This theory does not explain the conduction of heat in solids or their luster or retention of metallic properties in either the liquid or in the solution.

LONG ANSWER QUESTIONS

1. **Describe Bragg's method for determining the structure of a regular crystalline solid?**

The German physicist M Von Laue (1879 – 1960) in 1913 suggested the possibility of diffraction of X – Rays by crystals. The reason for this suggestion was that the wavelength of X – Rays was of about the same order as the inter atomic distances in a crystal. Then if these X – Rays was allowed to strike the crystal the rays will penetrate into the crystal and will be scattered by the electrons of the atoms or the ions of the crystal. The rays reflected from different layers of the atoms, due to wave nature will then undergo interference (constructive and destructive) to produce a diffraction pattern just as it happens in case of light passing through a grating containing a large number of closely spaced lines. In other words, crystals should act as a three dimensional grating for X – Rays. Bragg applied this fact in determining structure and dimensions of crystal.

W.L. Bragg and his father W.H. Bragg determined the cubic structure of NaCl using X – Rays. According to Bragg, a crystal (Composed of series of equally spaced atomic planes) could be employed not only as a transmission grating (as suggested by Laue) but also as a reflection grating. In Bragg's treatment, the X – rays strike the crystal at angle **q**, these penetrates into the crystal and are reflected by different parallel layers of particles in the crystal.

A strong reflected (constructive) beam will result only if all the reflected rays are in phase. The reflected waves by different layer planes will be in phase with one another only if the difference in the path length of the waves reflected from the successive planes is equal to an integral number of wavelengths.

2. **Derive bragg's equation for X-rays of wavelength (λ) and diffraction angle Θ for an nth order reflection**?

It may be noted from the fig. that the beams of X – rays which are reflected from deeper layers travel more to reach the detector. Two X – Ray waves in phase are shown to be approaching the crystal. One wave is reflected from the first layer of atoms while the second wave is reflected from the second layer of atoms. The wave reflected from the second layer travels more distance before emerging from the crystal than the first wave. The extra distance travelled is equal to
LN + NM. For constructive interference to take place the extra distance travelled by the more penetrating beam must be on integral multiple of the wavelength

Path difference = LN + NM

LN = nγ (n = 1, 2, 3 ….)

Since the triangles OLN and OMN are congruent hence LN = NM

So, path difference = 2LN

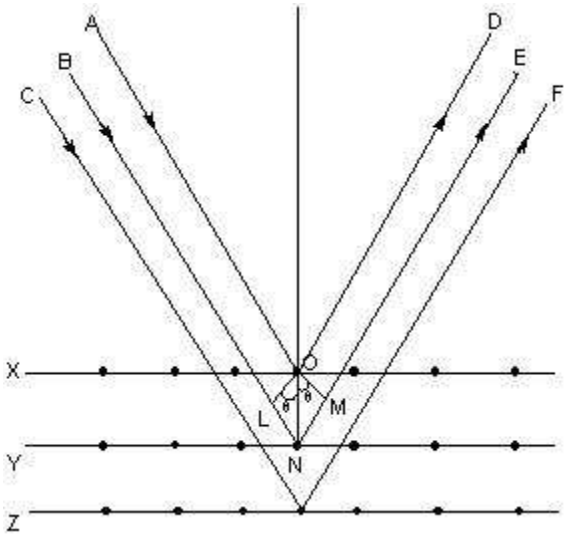
LN = d Sinq where d is the distance between two planes

So, path difference = 2d Sinθ

For constructive interference 2 d Sinq must be equal to nl

Or, **nγ = 2 d Sin**θ

This relation is called Bragg's equation. Distance between two successive planes d can be calculated form this equation. With X – Ray of definite wavelength, reflection at various angles will be observed for a given set of planes separated by a distance 'd'. These reflections correspond to n = 1, 2 , 3 and so on and are spoken of as first order, second order, third order and so on the
angle q increases as the intensity of the reflected beams weakens



X – Ray reflection from crystals

NUMERICALS

1. An X- ray beam (wavelength = 70.93 pm) was scattered by a crystalline solid. The angle (2θ) of diffraction for a second order reflection is 14.66^{o}. Calculate the distance between parallel planes of atoms from which the scattered beam appears to have been reflected?

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

Given second order reflection, n = 2

λ = wavelength of X – ray = 70.93 pm = 70.93 x 10^{-12} m

d = distance between planes = ?

Given $2\theta = 14.66^{0} \Rightarrow \theta = \frac{14.66}{2} = 7.33^{0}$

$\sin\theta = \sin 7.33^{0} = 0.127$

$n\lambda = 2d \sin\theta \Rightarrow d = \frac{n\lambda}{2 \sin\theta} = \frac{2 \times 70.93 \times 10^{-12}}{2 \times 0.127} = 558 \times 10^{-12}$m

$\therefore$ Distance between the planes (d) = 558 x 10^{-12}m = 558pm.

2. crystal when examined by the Bragg's technique using X – rays of wavelength 2.29 A^{o} gave on X – ray reflection at an angle of 23^{o}20'. Calculate the inter planar spacing; with another X – ray source, the reflection was observed at 15^{o} 26'. What was the wave length of the X – rays of the second source?

Ans. Case -1 : $n\lambda = 2d \sin\theta$

n = 1

λ = 2.29 A^{o} = 2.29 x 10^{-10}m

d = ?

θ = 23^{o}20' $\Rightarrow \sin\theta = \sin 23^{o}20' = 0.393$

$$n\lambda = 2d\sin\theta \Rightarrow d = \frac{n\lambda}{2\sin\theta} = \frac{1 \times 2.29 \times 10^{-10}\text{m}}{2 \times 0.393} = 2.92 \times 10^{-10}\text{m}$$

$\therefore$ Inter planar spacing (d) = 2.92×10^{-10}m = 2.92 A^o

Case -II

n = 1

λ = ?

d = 2.92×10^{-10}m (calculated in case – 1)

$\theta = 15^o\ 26' \Rightarrow \sin\theta = \sin 15^o\ 26' = 0.267$

$$n\lambda = 2d\sin\theta \Rightarrow \lambda = \frac{2d\sin\theta}{n} = \frac{2 \times 2.92 \times 10^{-10} \times 0.267}{1} = 1.55 \times 10^{-10}\text{m}$$

$\therefore$ Wave length of X – rays (λ) = 1.55×10^{-10}m = 1.55 A^o

3. X – rays of wavelength 5460 A^o are incident on a grating with 5700 lines per cm. Find the angles of reflection for the 1st and 2nd order diffraction maximum?

Ans. Case -1

Wave length of X – rays (λ) = 5460 A^o = 5460×10^{-8} cm

$$\text{Inter planar spacing (d)} = \frac{1\text{cm}}{5700}$$

n = 1, angle of reflection (θ_1) = ?

$$n\lambda \qquad 1 \times 5460 \times 10^{-8}$$

$$\therefore n\lambda = 2d \sin\theta_1 \Rightarrow \sin\theta_1 = \frac{n\lambda}{2d} = \frac{1 \times 5460 \times 10^{-8}}{2 \times \frac{1}{5700}} = 0.155$$

$$\sin\theta_1 = 0.155$$

$$\theta_1 = 8.95^o$$

$\therefore$ Angle of reflection (θ_1) for 1st order diffraction = 8.95^o

Case –II: $\lambda = 5460\ A^o = 5460 \times 10^{-8}$ cm

$$d = \frac{1}{5700} \text{ cm}$$

$$n = 2$$

Angle of reflection (θ_2) = ?

$$\therefore n\lambda = 2d \sin\theta_2 \Rightarrow \sin\theta_2 = \frac{n\lambda}{2d} = \frac{1 \times 5460 \times 10^{-8}}{2 \times \frac{1}{5700}} = 0.3115$$

$$\sin\theta_2 = 0.3115$$

$$\therefore \theta_2 = 18.15$$

$\therefore$ Angle of reflection (θ_2) for 2nd order diffraction = 18.15^o

4. The inter planar distance in a crystal used for X – ray diffraction is 0.2 nm. The angle of incidence (θ) of x – rays is 9.0^0. If the diffraction is of first order, find the wavelength of the X p rays. ?

Sol. Given: $d = 0.2\ nm = 0.2 \times 10^{-9}\ m$

$n = 1$ (given as first order)

$\lambda = ?$

$\theta = 9.0^o \Rightarrow \sin\theta = \sin 9.0^o = 0.156$

Bragg's equation is $\Rightarrow n\lambda = 2d\sin\theta$

$$\Rightarrow \lambda = \frac{2d\sin\theta}{n} = \frac{0.2 \times 0.2 \times 10^{-9} \times 0.156}{1}$$

$$\Rightarrow \lambda = 0.0625 \times 10^{-9}\ m$$

$$= 0.0625 \times 10^{-9} \times 10^{-10}\ A^o$$

$$= 0.0625 \times 10A^o$$

$$= 0.625\ A^o$$

$\therefore$ Wavelength of the X – rays = $0.625\ A^o$

5. Silicon crystallizes in face centered cubic lattice. At 22.5°C, a single crystal of very pure 'Si' has the following characteristics Mol. wt = 28.09; unit cell length = 5.43 A^0, Z = 8 (Total no. of constituent particles per unit cell). Find the density of the crystal?

Sol. Given:

$M = 28.09$

$Z = 8$

$A = 5.43\ A^o = 5.43 \times 10^{-8}$ cm

Formula

$$\text{Density of the crystal (P)} = \frac{Z\,M}{N_o a^3}$$

Where N_o = Avogadro's number = 6.023×10^{-23}

$$ZM = 8 \times 28.09$$

$$\therefore P = \frac{}{N_o a3} = \frac{}{6.023 \times 10^{23} \times (5.43 \times 10^{-8})^3 \text{ cm}^3}$$

$$= \frac{224.72}{6.023 \times (5.43)^3 \times 10^{23} \times 10^{-24}}$$

$$= \frac{224.72}{6.023 \times 160} \times 10$$

$$= 2.33 \text{ g / cm}^3$$

$\therefore$ Density of given crystal = 2.33 g / cc

6. Elementary Silver crystallizes in a face centered cubic lattice with unit cell length 0.4086nm. Calculate the density and hence the atomic radius of 'Ag'? (At.wt. of Ag = 107.88)

Sol. Given:

$a = 0.4086\text{nm}$

$= 0.4086 \times 10^{-9}\text{ m}$

$M = 107.88$

We have,

$N_o = 6.023 \times 10^{23}$

$Z = 4$(for f.c.c.)

$$\therefore \text{Density (P)} = \frac{Z\,M}{N_o\, a3}$$

$$P = \frac{4 \times 107.88 \times 10^{-3}\ kg}{6.023 \times 10^{23} \times (0.4086 \times 10\text{-}^{9})^3\ m^3}$$

$$= \frac{4315}{0.4108}$$

$$= 10503 \text{ (or) } 1.0503 \times 10^4\ kg/m^3$$

$\therefore$ Density of given metal = $1.0503 \times 10^4\ kg/m^3$

For f.c.c. lattice, radius of metal atom $= \frac{a}{2\sqrt{2}}$

Given, $a = 0.4086nm = 4.086\ A^o$

Radius of metal atom $= \frac{a}{2\sqrt{2}} = \frac{4.086}{2\sqrt{2}}$

$$= \frac{4.086}{2.828}$$

$$= 1.444\ A^o$$

7. X – rays of wavelength equal to 0.134 nm gave a first order diffraction from the surface of a crystal. The 'θ' value was found to be 10.5^o. Calculate the distance between the planes in the crystal?

Sol. Given:

$\lambda = 0.134nm$

$n = 1$ (for first order)

$\theta = 10.5^o \Rightarrow \sin\theta = \sin 10.5^o = 0.182$

$d = ?$

Bragg's equation $n\lambda = 2d \sin\theta$

$$\Rightarrow d = \frac{n\lambda}{2\sin\theta} = \frac{1 \times 0.134}{2 \times 0.182}$$

$$= 0.36\text{nm}$$

$\therefore$ Distance between the planes of crystal = 0.36nm.

8. Aluminium crystallizes with an fcc lattice. If the closest approach of aluminium atoms in the crystal is 0.4054 nm, find the density of aluminium ?(At. wt. of Al = 26.98).

Sol. Given:

Closest approach distance = 0.4054nm

$$\therefore \text{Radius (r)} = \frac{0.4054}{2} = 0.2027\text{nm}$$

We have $r = \frac{a}{2\sqrt{2}}$ (for fcc)

$$\Rightarrow 0.2027 = \frac{a}{2\sqrt{2}}$$

$$\Rightarrow \text{Unit cell length (a)} = 0.2027 \times 2\sqrt{2}$$

$$= 0.2027 \times 2.828$$

$$= 0.573\text{nm}$$

$$= 0.573 \times 10^{-9}\ \text{m}$$

We have $\text{Density (p)} = \frac{Z\,M}{N_o\, a3}$

$Z = 4$ (for fcc), $M = 26.98$, $N_o = 6.023 \times 10^{23}$

$a = 0.573 \times 10^{-9} m$ (calculated)

$$\therefore p = \frac{4 \times 26.98}{6.023 \times 10^{23} \times (0.573 \times 10^{-9})^3 \, m^3} = 95.318 \times -10^4 \, g / m^3$$

$\therefore$ Density of the given metal is $= 95.318 \times -10^4 \, g / m^3$

Solutions:

The crystalline sodium has body centered cubic unit cell with a = 0.424nm at 298 k. Calculate the density of sodium metal.

Ans.

$$\text{The density of sodium } (\rho) = \frac{Z \, M}{N_o \, a^3}$$

For body centered cubic substance z = 2

Molar mass (M) of sodium = 23g

$= 23 \times 10^{-3} \, kg$

Unit cell length (a) $= 0.424 \text{ nm}$

$= 0.424 \times 10^{-9} \, m$

Avogadro's number (N_o) $= 6.023 \times 10^{23}$

$$\therefore \rho = \frac{ZM}{N_o \, a^3} = \text{density of the unit cell}$$

$$= \frac{2 \, (23 \times 10^{-3} \text{ kg mol}^{-1})}{6.023 \times 10^{23} \times (0.424 \times 10^{-9})^3 \, m^3}$$

$= 1002 \text{ kg m}^{-3}$

$= 1.002 \times 10^3 \text{ kgm}^{-3}$

THE SOLID STATE

TOPIC-4
CRYSTAL DEFECTS, ELECTRICAL AND MAGNETIC PROPERTIES OF CRYSTALS

VERY SHORT ANSWER QUESTIONS

1. **What are point defects in crystal structures?**

Ans: When deviations exist from the regular (or periodic) arrangements around an atom or a group of atoms in a crystalline substance, the defects are called point defects.

Type of point defects – point defects in a crystal may be classified into three types

(a) Stoichiometric defects

(b) Non – stoichiometry defects

(c) Impurity defects

2. **Explain Ferro magnetic solid materials?**

Ans: **Ferromagnetic substances:** Substances which show permanent magnetism even in the absence of the magnetic field are called Ferromagnetic substances. e.g. Fe Ni. CO, CrO_2 show Ferromagnetism. Such substances remain permanently magnetised, once they have been magnetised. This type of magnetism arises due to spontaneous alignment of magnetic moment due to unpaired electrons in the same direction.

3. **What are Daltonide and Berthollide compounds?**

Ans: The stoichiometric compounds are called Daltonide compounds. The Non-stoichiometric compounds with variable compositions are called Berthollides.

SHORT ANSWER QUESTIONS

1. **What are crystal defects? Explain**?

Ans: **Atomic imperfections / point defects:**

When deviations exist from the regular (or periodic) arrangements around an atom or a group of atoms in a crystalline substance, the defects are called point defects.

Type of point defects – point defects in a crystal may be classified into three types

(a) Stoichiometric defects

(b) Non – stoichiometry defects

(c) Impurity defects

2. What are Schottky Defects? Explain?

Ans: **Schottky defect:** If in an ionic crystal of the type $A^+ B^-$, equal number of cations and anions are missing from their lattice. It is called Schottky defect.

This type of defect is shown by highly ionic compounds which have

(i) High Co – ordination number and

(ii) Small difference in the sizes of cations and anions

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

CONSEQUENCES OF SCHOTTKY DEFECT

(a) As the number of ions decreases as a result of this defect, the mass decreases whereas the volume remains the same. Hence density of the solid decreases

(b) The crystal begins to conduct electricity to a small extent by ionic mechanism

(c) The presence of too many voids lowers lattice energy and the stability of the crystal

3. What are Frenkel Defects? Explain?

Ans: **Frenkel defect:** If an ion is missing from its correct lattice sites (causing a vacancy or a hole) and occupies an interstitial site, electrical neutrality as well as stoichiometry of the compounds are maintained. This type of defect is called **Frenkel** defect. Since cations are usually smaller it is more common to find the cations occupying interstitial sites.

This type of defect is present in ionic compounds which have

(i) Low co ordinations number

(ii) Larger difference in size of cation and anions

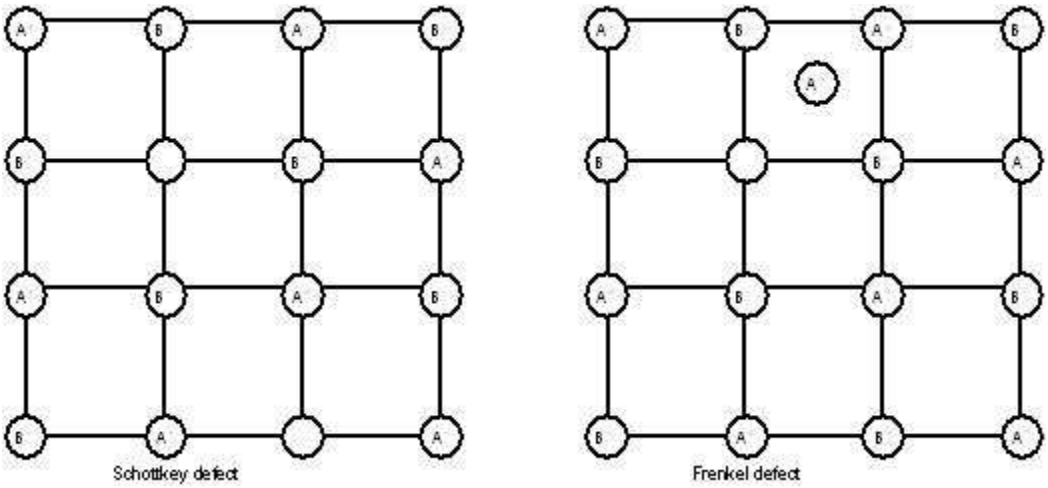
(iii) Compounds having highly polarising cation and easily polarisable anion. A few examples of ionic compounds exhibiting this defect are AgCl, AgBr, AgI, ZnS etc.

Consequences of Frenkel defect

(a) As no ions are missing from the crystal lattice as a whole, therefore density of the solid remains the same

(b) The closeness of like charges tends to increases the dielectric constant of the crystal

(c) The crystal conducts electricity to a small extent by ionic mechanism

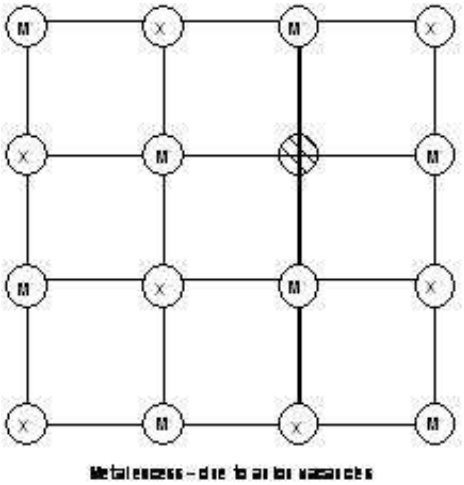


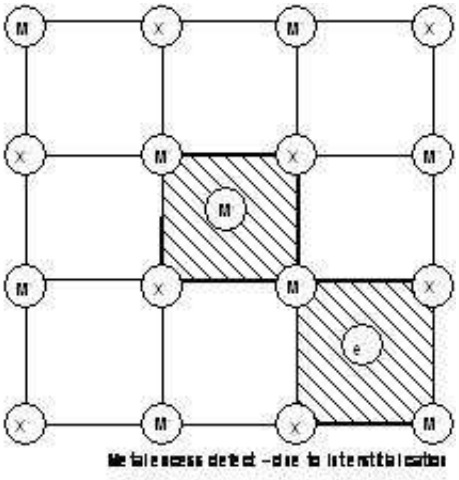
4. What are non-stoichiometric defects/ explain?

NON – STOICHIOMETRIC DEFECTS

If as a result of imperfection, the ratio of number of cation to anion becomes different from that indicated by the ideal chemical formula; the defects are called non – stoichiometric defects. These defects arise either due to excess of metal atoms or non metal atom or presence of impurities / foreign particle.

(a) **Metal excess defects due to anion vacancies**: - A compound may have excess metal ion if a negative ion is absent from its lattice site leaving a hole which is occupied by electron to maintain neutrality. The holes that are occupied by electrons are called ‘F’ centres (or colour centres) and are responsible for the colour of the compound and many interesting properties.





(ii) **Metal excess defects due to interstitial cations:** Metal excess may also be caused by an extra cation (positive ion) present in an interstitial site. Electrical neutrality is maintained by presence of an electron in another interstitial site. This defect is similar to Frenkel defect and is found in crystals having Frenkel defects.

(iii) **Metal deficiency due to cation vacancies: The** non-stoichiometric compounds may have metal deficiency due to the absence of a metal from its lattice site. The charge is balanced by an adjacent ion having higher positive charge. These types of defects are generally shown by compounds of transition elements.

(c) **Point defects due to the presence of foreign atoms**: These defects arise when foreign atoms are present at the lattice site (in place of host atoms) or at the vacant interstitial sites. In the former case, we get substitutional solid solutions. The formation of former depends upon the electronic structure of impurity while that of later on the size of impurity.

LONG ANSWER QUESTIONS

1. **How many types of semi-conductors are known? Explain the influence of doping on the conductivity of crystalline solids?**

Semi conductors: The solids with intermediate conductivities at the room temperature. Semi conductors allow a portion of electric current to flow through them.

Actually semi conductors are those solids which are perfect insulators at absolute zero, but conduct electric current at room temperature.

(1) **Intrinsic semi conductors** (semi-conductors due to thermal defects)

At zero Kelvin pure substance silicon and germanium act as insulators because electrons fixed in covalent bonds are not available for conduction. However at higher temperature some of the covalent bonds are broken and the electrons so released become free to move in the crystal and thus conduct electric current. This type of conduction is known as intrinsic conduction as it can be introduced in the crystal without adding an external substance.

(2) **Extrinsic semi conductors:** (semi conductors due to impurity defects)

The conductivity of pure silicon and germanium is very low at room temperature. The conductivity of silicon and germanium can be increased by doping with impurities producing n-type semiconductors or p – type semi conductors.

2. What do you mean by imperfections in solids? Write an essay on crystal defects. ?

Ans: **IMPERFECTIONS IN SOLIDS: DEFECTS IN CRYSTALS**

Atomic imperfections / point defects: When deviations exist from the regular (or periodic) arrangements around an atom or a group of atoms in a crystalline substance, the defects are called point defects. Type of point defects – point defects in a crystal may be classified into three types

(a) Stoichiometric defects

(b) Non – stoichiometry defects

(c) Impurity defects

Stoichiometry defect: The compounds in which the number of cation and anions are exactly in the same ratio as represented by their chemical formula are called stoichiometric compounds. The defects that do not disturb the ratio of cations and anions are called stoichiometric defect. These are of two types:

1. Schottky defect: If in an ionic crystal of the type $A^+ B^-$, equal number of cations and anions are missing from their lattice. It is called Schottky defect. This type of defect is shown by highly ionic compounds which have

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CONSEQUENCES OF SCHOTTKY DEFECT

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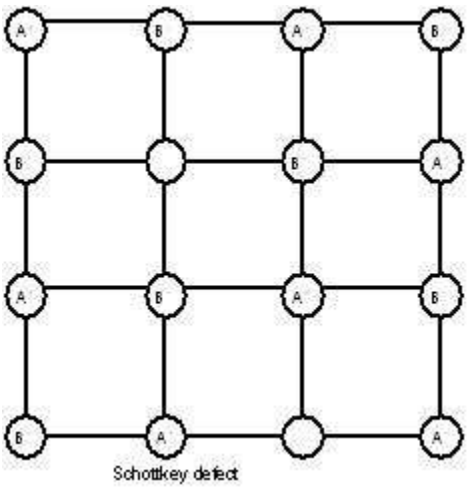
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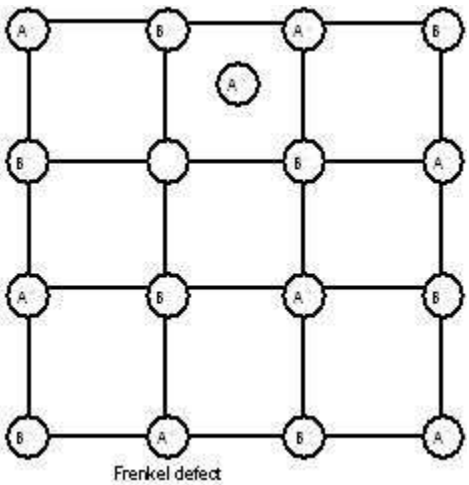
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Schottkey defect

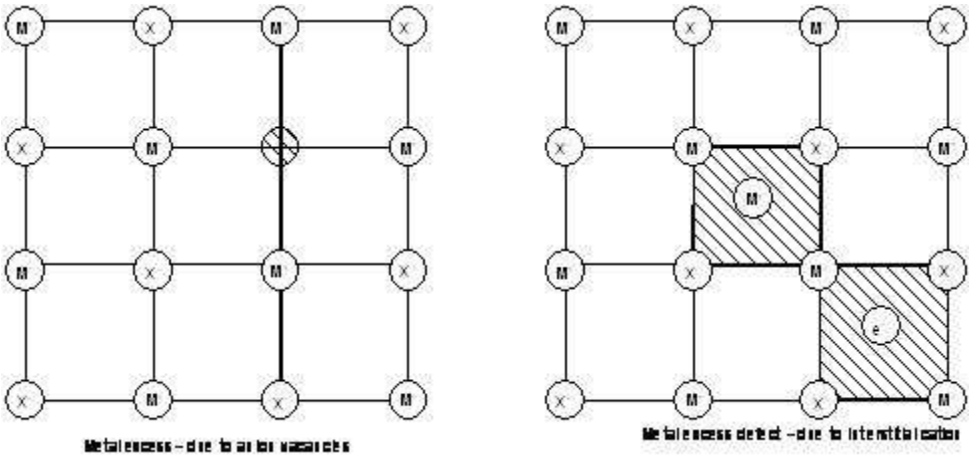


Frenkel defect

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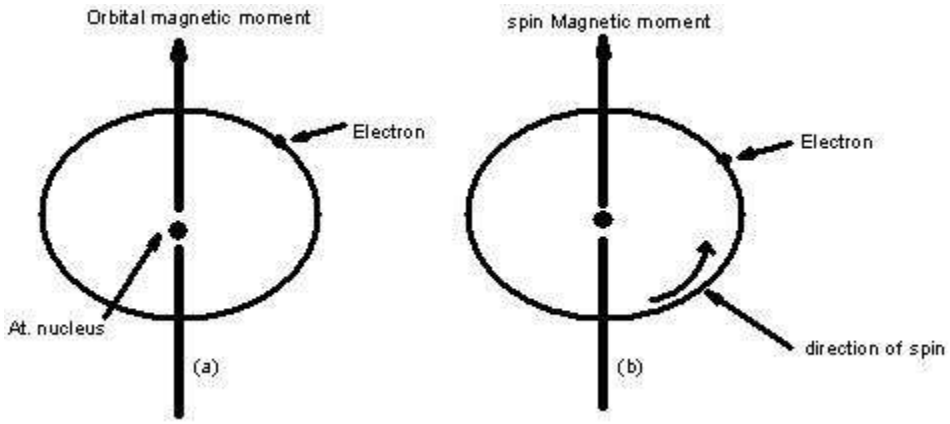
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3. Explain the magnetic properties of solids?

MAGNETIC PROPERTIES: The magnetic properties of different materials are studies in terms of their magnetic moments which arise due to the orbital motion and spinning motion of the electron. As electron is charged particle, the circular motion of the electric charge causes the electron to act as a tiny electro magnet. The magnetic moment of the magnetic field generated due to orbital motion of the electron is along the axis of rotation. The electron also possesses magnetic moment due to the spin which is directed along the spin axis.

Thus, magnetic moment of the electron is due to travelling in closed path (orbital motion) about the nucleus and spinning on its axis. For each electron spin magnetic moment is $\pm\mu_B$ where μ_B, Bohr Magneton is the fundamental unit of magnetic moment and is equal to 9.27×10^{-24} em^2. The magnetic moment due to orbital motion is equal to $M_l\mu_B$ where M_l is the magnetic quantum number of the electron.



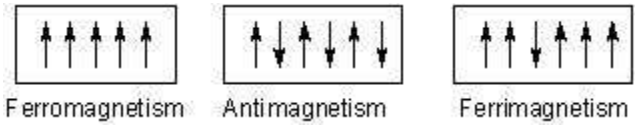
As magnetic moment is a vector quantity, the net magnetic moment of an electron may be represented by an arrow. Thus a material may be considered to contain a number of magnetic dipoles (similar to a bar magnet with north and south poles). Due to the magnetic moment of the electrons different substances behave differently towards the external applied magnetic field. Based on the behaviour in the external magnetic field, the substances are divided into different categories as explained below.

(i) **Diamagnetic substance:** Substances which are weakly repelled by the external magnetic fields are called diamagnetic field e.g. TiO_2, NaCl, benzene etc. Diamagnetic substances have all their electrons paired.

(ii) **Paramagnetic substances:** Substances which are weakly attracted by magnetic field are called paramagnetic substances. These substance have permanent magnetic

dipoles due to the presence of some species (atoms, ions or molecules) with unpaired electron. The paramagnetic substances lose their magnetism in the absence of magnetic field. For e.g. TiO, VO_2 and CuO, O_2, Cu^{+2}, Fe^{+3} etc.

(iii) **Ferromagnetic substances:** Substances which show permanent magnetism even in the absence of the magnetic field are called Ferromagnetic substances. e.g. Fe Ni. CO, CrO_2 show Ferromagnetism. Such substances remain permanently magnetised, once they have been magnetised. This type of magnetism arises due to spontaneous alignment of magnetic moment due to unpaired electrons in the same direction.



(iv) **Anti Ferromagnetic substance:** Substances which are expected to possess paramagnetism or Ferromagnetism on the basis of unpaired electron but actually they posses zero net magnetic moment are called anti Ferromagnetic substances e.g. MnO, Mn_2O_3, MnO_2.

Anit Ferromagnetism is due to presence of equal number of magnetic moments in the opposite direction.

(v) **Ferrimagnetic substances:** Substance which are expected to posses large magnetism on the basis of the unpaired electrons but actually have small net magnetic moments are called Ferrimagnetic substances e.g. Fe_3O_3

(3) **Dielectric properties:** A dielectric substance is, in which an electric field gives rise to no net flow of electric charge. This is due to the reason that electrons in dielectric substances are tightly held by individual atoms. However when electric field is applied, Polarization takes place because nuclei are attracted to one side and the electron cloud to the other side. In addition to these dipoles, there may also be permanent dipoles in the crystal.

The alignment of these dipoles may be in compensatory way i.e. the net dipole moment is zero or non compensatory way i.e. has a net dipole moment. The net dipole moment leads to certain characteristic properties to solids.

(a) **Piezoelectricity (or pressure electricity):** When mechanical stress is applied on crystals so as to deform them, electricity is produced due to displacement of ions. The electricity thus produced is called piezoelectricity and the crystals are called piezoelectric crystals. Conversely, if electric field is applied to such crystals, atomic displacement takes place resulting into mechanical strain. This is sometimes called **Inverse piezoelectric effect.**

The crystals are used as pick – ups in record players where they produce electrical signals by application of pressure. Examples of piezoelectric crystals include titanates of barium and lead, lead zirconate ($PbZrO_3$), ammonium dihydrogen phosphate ($NH_4H_2PO_4$) and quartz. They are also used in microphones, ultrasonic generators and sonar detectors.

(b) **Pyroelectricity:** Some piezoelectric crystals when heated produce a small electric current. The electricity thus produced is called pyroelectricity.

(c) **Ferroelectricity:** In some of the piezoelectric crystals, the dipoles are permanently polarized even in the absence of the electric field. However on applying electric field, the direction of polarization changes e.g. Barium titanate ($BaTiO_3$) sodium potassium tartarate (Rochelle salt) and potassium dihydrogen phosphate (KH_2PO_4). All ferroelectric solids are piezoelectric but the reverse is not true.

(d) **Anti Ferroelectricity:** In some crystals, the dipoles align themselves in such a way, that alternately; they point up and down so that the crystal does not posses any net dipole moment. Such crystal are said to be anti Ferroelectric e.g. Lead zirconate ($PbZrO_3$)

IMPOTANT QUESTIONS

I . Very short answer questions.

1. Name an element that forms mono clinic crystals?
2. What are point defects in crystal structure?
3. Do amorphous solids have unit cell in them?
4. What will be magnitude of the vapour pressure of these ionic crystals?
5. Which group and period of the periodic table does polonium occupy?

II. Short answer questions.

1. Derive bragg's equation**?**
2. What are octahedral holes? How are they formed?
3. Expalin Schottky defect in solids?
4. Define Co-ordination number in a crystalline solid. What is the co-ordination number in a body centered cubic lattice?

III. Long answer questions.

1. What do you know about amorphous substances? Discuss.

2. Describe Bragg's method for determination of structure of a regular solid?

3. Derive Bragg's equation for X-rays of wavelength (λ) and a diffraction angle (Θ) for nth order reflection?

4. How many types of semi-conductors are known? Explain the influence of doping on the conductivity of crystalline solids?