THE SOLID STATE

Introduction

- Solids are substances having definite shape and definite volume.
- In solids, the particles are closely packed and the force of attraction between the particles is strong. So solids are rigid and incompressible.
- Their constituent particles (atoms, molecules or ions) have fixed positions and can only vibrate about their mean positions.

Classification of solids

1. Crystalline solids

- In these solids, the constituent particles have a well ordered arrangement throughout the solid, i.e., they have a long range order.
- They consist of a large number of small crystals.
- They have a definite geometrical shape, melting point and heat of fusion.
- E.g.: Quartz, Diamond, Graphite, fullerene, NaCl, $CuSO_4.5H_2O$, ice, naphthalene, SiC etc.

2. Amorphous solids

- In these solids, the ordered arrangement of constituent particles is only at some portions of the solid, i.e., they have only a short range order.
- The structure of these solids is similar to that of liquids. They have no definite geometrical shape, melting point and heat of fusion. E.g.: Plastic, Glass (quartz glass), Rubber, amorphous silica, coal, charcoal, coke, PVC etc.
- Like liquids amorphous solids have a tendency to flow, though very slowly. Therefore, sometimes these are also called pseudo solids or super cooled liquids.
- ***Glass panes fixed to windows or doors of old buildings are slightly thicker at the bottom than at the top. This is because the glass flows down very slowly and makes the bottom portion slightly thicker.***
- ***Amorphous solids on heating become crystalline at some temperature. Some glass objects from ancient civilizations are found to become milky in appearance due to some crystallization.***

Anisotropic and isotropic substances

Anisotropic substances

- *Solids in which the physical properties like electrical conductance, refractive index etc are different when measured in different directions are said to be anisotropic in nature.*
- This is due to the different arrangement of particles in different directions.
- Crystalline solids are anisotropic.

Isotropic substances

- *Solids in which the physical properties are same along any direction are said to be isotropic in nature.*
- This is due to the irregular arrangement of particles along different directions. Amorphous solids are isotropic.
- Amorphous solids are isotropic.

Differences between Crystalline solids and Amorphous solids

Properties	Crystalline solids	Amorphous solids
Orderly arrangement of particles	Long range order	Only short range order
Geometrical shape	Definite characteristic geometrical shape	No definite Geometrical shape
Melting point	Definite m.p	No definite m.p
Heat of fusion	Definite	Not definite
Mode of cleavage	Give regular cleavage on cutting	Give irregular cleavage on cutting
Nature	True solids	Pseudo solids
Isotropy/anisotropy	Anisotropic in nature	Isotropic in nature

Classification of crystalline solids

On the basis of nature of particles and binding force between the particles, crystalline solids are classified into four types- molecular solids, ionic solids, metallic solids and covalent solids.

1. Molecular Solids: Here the constituent particles are molecules.

These are further sub-divided into three:

i. Non-polar molecular solids:

- Here the constituent particles are either atoms like Ar, He etc. or non-polar molecules like H_2, Cl_2, I_2 etc and the binding force between the particles is London dispersion forces or weak van der Waal's forces.
- These are soft solids and are non-conductors of electricity.
- They have low melting points and are usually liquid or gaseous state at room temperature and pressure.

ii. Polar molecular solids:

- Here the constituent particles are polar molecules like HCl, CO_2, SO_2 etc. and the binding force between the particles is relatively stronger dipole-dipole interactions.
- These are soft and non-conductors of electricity.
- Their melting points are higher than those of non-polar molecular solids.
- Most of them are gases or liquids at room temperature and pressure.

iii. Hydrogen bonded molecular solids:

- Here the constituent particles are molecules which contain atoms like H and F, O or N.
- The binding force between the particles is strong hydrogen bond.
- They are nonconductors of electricity and are volatile solids or soft solids at room temperature and pressure.
- E.g.: H_2O, NH_3 etc.

2. Ionic Solids:

- Here the constituent particles are ions and the binding force between the particles is strong electrostatic force of attraction (ionic bond).
- They are hard and brittle and have high m.p & b.p.

- They are electrical insulators in the solid state, since the ions are not free to move about. But in the molten or solution state, the ions become free to move about and they conduct electricity.
- E.g.: NaCl, KCl, $CaCl_2$ etc.

3. Metallic Solids:

- They contain a large number of metal ions which are surrounded by a sea of electrons.
- The particles are held together by strong electrostatic force of attraction (metallic bond).
- Due to the presence of a large number of free electrons, they are good conductors of heat and electricity, malleable and ductile and show metallic lustre.
- E.g. All metals

4. Covalent or Network Solids:

- Here the constituent particles are atoms and the binding force between the particles is strong covalent bond.
- They are very strong and brittle, have extremely high melting point and are electrical insulators.
- E.g. Diamond, Silicon Carbide (SiC, commonly known as Carborundum), Quartz, Graphite etc.
- Graphite has exceptional properties i.e., it is soft and good conductor of electricity. In graphite carbon atoms are arranged in different layers and each atom is covalently bonded to three adjacent carbon atoms. The fourth electron is free to move about between different layers. So Graphite is a good conductor of electricity. The different layers are held together by weak van der Waal's force of attractions. So each layer can slide over the other and hence it is soft and used as a good lubricant.

Cubic Lattices and Unit Cells

Unit cell: A unit cell is the smallest repeating unit of a crystal lattice which, when repeated in three dimension we get a whole crystal. Or, it is the building block of a crystal.

Different Types of unit Cells:
Unit cells can be broadly divided into two - primitive and centred unit cells.

1. Simple or Primitive Unit Cells:
Here the constituent particles are present only at the corners of the unit cell.

2. Centred Unit Cells:
Here the constituent particles are present at the corners and other positions of the unit cell.
These are of three types:

- ***Body-centred unit cells:*** Here the constituent particles are present at the body centre and at the corners of the unit cell.

- ***Face-centred unit cells:*** Here the constituent particles are present at the centre of each faces and at the corners of the unit cell.

- ***End-centred unit cells:*** Here the constituent particles are present at the centre of any two opposite faces and at the corners of the unit cell.

Calculation of Number of atoms in a unit cell (z)
1. Primitive cubic (Simple Cubic) unit cell:
- Here atoms are present only at the corners of the cube. Each corner atom is shared by 8 unit cells.
- Therefore, contribution to one unit cell = 1/8
- Since each unit cell has 8 atoms at the corners, the total number of atoms in one unit cell = 8×1/8 = 1
- So for a primitive (simple cubic) unit cell, z = 1

2. Body-centred cubic (bcc) unit cell:
- Here the particles are present at the corners of the cube and also one atom at the body centre.

2

- The number of atoms at the corner = 8×1/8 = 1
- The atom present at the centre of the body is not shared by other atoms.
  So the number of atoms at the body-centre = 1
- Therefore, total number of atoms in the unit cell = 1+1=2
  So, for a bcc, z = 2

3. Face-centred cubic (fcc) unit cell:

- Here the atoms are present at the corners and also at the centre of each faces. Each corner atom is shared by 8 unit cells and each face centre atom is shared by 2 unit cells.
- Number of corner atoms = 8×1/8 = 1
  Number of face-centre atoms = 6×1/2 = 3
- Therefore, total number of atoms = 1+3 = 4
  So, for an fcc, z = 4

Solved Problems:

1. A cubic solid is made up of elements P and Q. Atoms P are at the corners of the cube and Q at the body centre.
a. Identify the formula of the compound.
b. If an additional P atom is added to the body centre, what would be the formula of the compound?

Ans:
a. no: of P atoms = 1/8 x 8 = 1
    no: of Q atoms = 1
Therefore molecular of the compounds is PQ.
b. P_2Q

2. NaCl has fcc structure. Calculate the number of NaCl units in a unit cell of NaCl.

Soln. An fcc structure has particles at the corners and at the face centres.
No. of particles at the corners = 8 x 1/8 = 1
No. of particles at the corners = 6 x ½ = 3
Therefore, total number of particles per unit cell = 1 + 3 = 4 particles.

3. A crystal is formed by two elements X and Y in cubic structure. X atoms are at the corners of a cube while Y atoms are at the face centre. The formula of the compound will be_____

Soln: No. of X atoms at the corners = 8 x 1/8 = 1

No. of Y atoms (fcc) = 6 x ½ = 3

Hence, the formula is = XY_3

Calculation of Density of the unit cell (Solid)

Consider a cubic unit cell with edge length 'a'. Then volume of the unit cell = a^3.

Let 'M' be the atomic mass of the element in the unit cell (i.e. mass of Avogadro number (N_A) of atoms).

Then mass of one atom = M/N_A.
Let the number of particles present per unit cell = z
Then mass of the unit cell = z x M/N_A

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

i.e. density (d) = $\dfrac{z \times M/N_A}{a^3}$

or , d = $\dfrac{z.M}{N_A.a^3}$

Solved Problems

Question 1.

Silver crystallises in fcc lattice. If edge length of the cell is 4.07×10^{-8} cm and density is 10.5 g cm^{-3}, calculate the atomic mass of silver.

Answer

It is given that the edge length, $a = 4.077 \times 10^{-8}$ cm
Density, $d = 10.5$ g cm^{-3}

As the lattice is fcc type, the number of atoms per unit cell, z = 4
We also know that, $N_A = 6.022 \times 10^{23}$ mol^{-1}
Using the relation:

$$d = \frac{zM}{a^3 N_A}$$

$$\Rightarrow M = \frac{d\,a^3\,N_A}{z}$$

$$= \frac{10.5 \text{ gcm}^{-3} \times \left(4.077 \times 10^{-8} \text{ cm}\right)^3 \times 6.022 \times 10^{23} \text{ mol}^{-1}}{4}$$

= 107.13 gmol^{-1}
Therefore, atomic mass of silver = 107.13 u

The Solid State

Question 2

Copper crystallises into a fcc lattice with edge length 3.61×10^{-8} cm. Show that the calculated density is in agreement with its measured value of 8.92 g cm^{-3}.

Answer

Edge length, $a = 3.61 \times 10^{-8}$ cm

As the lattice is fcc type, the number of atoms per unit cell, $z = 4$
Atomic mass, $M = 63.5$ g mol^{-1}

We also know that, $N_A = 6.022 \times 10^{23}$ mol^{-1}
Applying the relation:

$$d = \frac{zM}{a^3 N_A}$$

$$= \frac{4 \times 63.5 \text{ g mol}^{-1}}{(3.61 \times 10^{-8} \text{ cm})^3 \times 6.022 \times 10^{23} \text{mol}^{-1}}$$

$$= 8.97 \text{ g cm}^{-3}$$

The measured value of density is given as 8.92 g cm^{-3}. Hence, the calculated density 8.97 g cm^{-3} is in agreement with its measured value.

Question 3

An element with molar mass 2.7×10^{-2} kg mol^{-1} forms a cubic unit cell with edge length 405 pm. If its density is 2.7×103 kg m^{-3}, what is the nature of the cubic unit cell? Answer

It is given that density of the element, $d = 2.7 \times 10^3$ kg m^{-3}
Molar mass, $M = 2.7 \times 10^{-2}$ kg mol^{-1}

Edge length, $a = 405$ pm $= 405 \times 10^{-12}$ m $= 4.05 \times 10^{-10}$ m

It is known that, Avogadro's number, $N_A = 6.022 \times 1023$ mol^{-1}
Applying the relation,

$$d = \frac{z.M}{a^3 \cdot N_A}$$

$$z = \frac{d \cdot a^3 N_A}{M}$$

$$= \frac{2.7 \times 10^3 \text{kg m}^{-3} \times (4.05 \times 10^{-10} \text{ m})^3 \times 6.022 \times 10^{23} \text{mol}^{-1}}{2.7 \times 10^{-2} \text{kg mol}^{-1}}$$

$$= 4.004$$

$$= 4$$

This implies that four atoms of the element are present per unit cell. Hence, the unit cell is face-centred cubic (*fcc*) or cubic close-packed (*ccp*).

Question 4:

Lead sulphide crystal has NaCl structure. What is its density? The edge length of the unit cell of PbS crystal is 500pm. (N_A = 6.022 x 10^{23} mol^{-1} and atomic mass of Pb = 207.2, S = 32)

Answer

Edge length, a = 500 pm = 500 x 10-10 cm

N_A = 6.022 x 10^{23} mol^{-1}

Molecular mass of PbS = 207.2 + 32 = 239.2 g/mol.

Since, NaCl has f.c.c lattice, PbS also has f.c.c lattice.

Therefore, z = 4

$$d = \frac{z.M}{a^3.N_A} = \frac{4 \times 239.2}{(500 \times 10^{-10})^3 \times 6.022 \times 10^{23}} = 12.71 \text{ gcm}^{-3}.$$

Question 5:

Copper crystal has a face centred cubic lattice structure. Its density is 8.93 gcm^{-3}. What is the edge length of the unit cell? Atomic mass of copper, M = 63.5 g/mol.

Answer:

z = 4   d = 8.93 g/cm^3 N_A = 6.022 × 10^{23} mol^{-1}

Density, $d = \dfrac{z.M}{a^3.N_A}$

$$a^3 = \frac{z.M}{d.N_A}; \qquad a = \left(\frac{z.M}{d.N_A}\right)^{1/3} cm = \left(\frac{4\times63.5}{6.022\times10^{23}\times8.93}\right)^{1/3} cm$$

= 3.61 x 10⁻⁸ cm =361 x 10⁻¹⁰ cm = 361 pm

Question 6:

Assuming that Al (atomic mass 27) has a density of 2.6 g/cm³ and its unit cell has an edge length of 405 pm, what type of crystal lattice is for the metal?

Answer:

d = 2.6 g/cm³, M = 27 g/mol, a = 405 pm = 405 x 10⁻¹⁰ cm,

$N_A = 6.022 \times 10^{23}$

Density, $d = \dfrac{z.M}{a^3.N_A}$

$$z = \frac{da^3.N_A}{M} = \frac{2.6\times\left(405\times10^{-10}\right)^3\times6.022\times10^{23}}{27} = 4$$

Hence, Al has face centred unit cell.

Question 7:

The density of chromium is 7.2 g/cm³. Edge length is 289 pm. Determine the number of atoms in the unit cell.

Answer: 2 (Do it your self)

Question 8:

An element crystallizes in bcc structure the edge length of its unit cell is 288 pm. Density is 7.2 g/cm³. How many atoms of this element are present in 100 gm.

Answer: 11.62 x 10²³

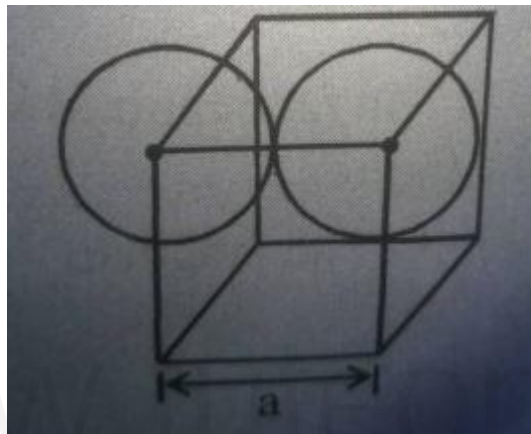**(Do it yourself using the formula X = $\frac{zM}{da^3}$. Similar question is discussed in video class part 4 question 3)**

Packing Efficiency

The percentage of total space filled by the particles in a crystal lattice is known as packing efficiency.

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

1. Packing Efficiency in simple cubic lattice

In simple cubic, the atoms touch each other along the edges as shown in the figure.

The edge length of the unit cell is equal to 2r, i.e., **a = 2r**

[Therefore, r = a/2]

Volume of spheres $= \frac{4}{3}\pi r^3$
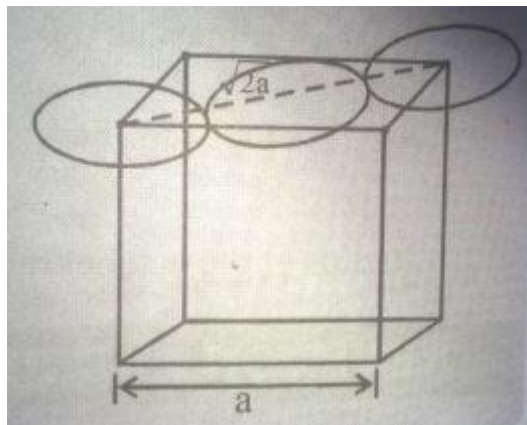
Volume of the unit cell $= a^3 = (2r)^3$

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

$$= \frac{\frac{4}{3}\pi r^3 \times 100}{(2r)^3}\% = 52.4\%$$

2. Packing Efficiency in *f.c.c* structure:

Both hcp and ccp are equally efficient. The ccp arrangement of spheres has face centred unit cells.

In face centred cubic, the atoms touch each other along the face diagonals of the cube shown in the figure.

The length of the face diagonal is equal to 4r.

$4r = \sqrt{2}a$

$a = \dfrac{4r}{\sqrt{2}} = 2\sqrt{2}\ r$ (or r = $\dfrac{a}{2\sqrt{2}}$)
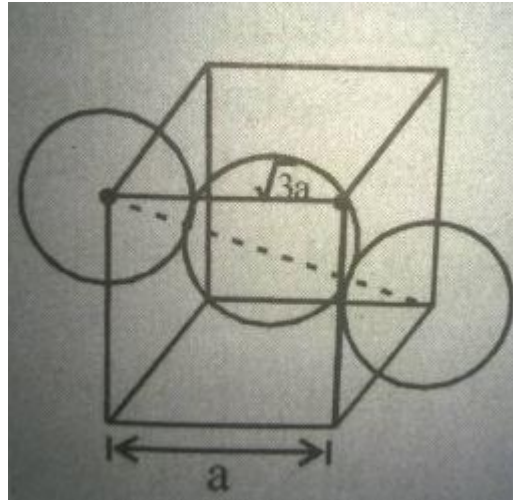
We know that each *f.c.c* unit cell has 4 spheres.

Therefore, total volume of four spheres = $4 \times \dfrac{4}{3}\pi r^3$

Volume of the cube = $a^3 = (2\sqrt{2}\ r)^3$

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

$$= \dfrac{4 \times \left(\dfrac{4}{3}\right)\pi r^3 \times 100}{\left(2\sqrt{2}r\right)^3}\% = 74\%$$

Packing efficiency in body centred cubic *(b.c.c)* structure

In body centred cubic, the atoms touch each other along the body diagonal of the cube as shown in the figure.

The length of body diagonal is equal to 4r.

i.e., $\sqrt{3}$ a = 4r

r = $\dfrac{\sqrt{3}}{4}$ a   ; a = $\dfrac{4r}{\sqrt{3}}$

We know that each *b.c.c* unit cell has 2 spheres.

Therefore, total volume of 2 spheres = $2 \times \left(\dfrac{4}{3}\right)\pi r^3$

Volume of the cube = a³ = $\left(\dfrac{4r}{\sqrt{3}}\right)^3$

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

$= \dfrac{2 \times \left(\frac{4}{3}\right)\pi r^3 \times 100}{\left(\frac{4r}{\sqrt{3}}\right)^3}\% = 68\%$

Note:

Nearest neighbour distance of simple cubic unit cell = d = 2r

Nearest neighbour distance of f.c.c or c.c.p = d =2r = $\dfrac{a}{\sqrt{2}}$

Nearest neighbour distance of b.c.c = d =2r = $\dfrac{\sqrt{3}\,a}{2}$

Solved Problems:

1. A metal _X_ crystallizes in a face – centred cubic arrangement with the edge length 862 pm. What is the shortest separation of any two nuclei of the atom?

Ans:

For fcc arrangement, distance of nearest neighbour is

d = $\dfrac{a}{\sqrt{2}}$ = $\dfrac{862}{1.414}$ = **609. 6 pm**

2. Edge length of unit cell of chromium metal is 287 pm with bcc arrangement. The atomic radius of the order _____

Ans:

In _b.c.c_ Lattice, r = $\dfrac{\sqrt{3}\,a}{4}$ = $\dfrac{1.732 \times 287}{4}$ = 124.27 pm

3. Total volume of atoms present in a fcc unit cell of a metal with radius r is

a) $\dfrac{12}{3}\pi r^3$ b) $\dfrac{16}{3}\pi r^3$ c) $\dfrac{20}{3}\pi r^3$ d) $\dfrac{24}{3}\pi r^3$

Ans:

No. of spheres in f.c.c = 4

Volume of four spheres = 4 x $\dfrac{4}{3}\pi r^3$ = $\dfrac{16}{3}\pi r^3$

Close packing in solids

In solids the particles are closely packed. In close packed structures the particles are considered as hard spheres. Solids are three dimensional and the 3 dimensional structure can be obtained by the following three steps:

1. **Close packing in One Dimensions**
    ➢ Here the spheres are arranged in a row touching each other.
    ➢ In this arrangement each sphere is in contact with 2 adjacent spheres.
   ➢ Therefore, co-ordination number of each sphere is 2.

2. Close packing in Two Dimensions
Here the spheres are arranged in two directions – length-wise and breadth-wise. This can be done in two different ways.
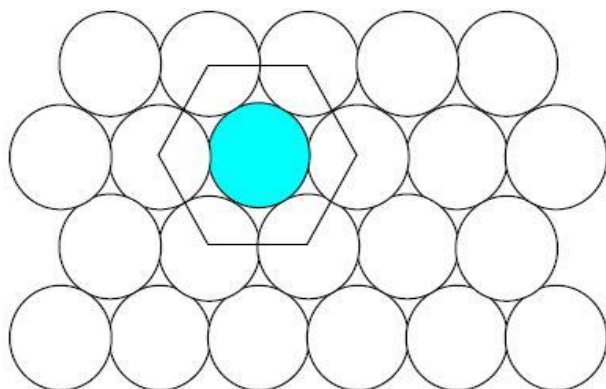
a. Square close packing:
    ✦ Here the spheres of second row are placed exactly above those of the first row.
    ✦ In this arrangement, each sphere is in contact with four adjacent spheres. So the co-ordination number of each sphere is 4.
    ✦ When we join the centres of these spheres, we get a square. So this close packing is called square close packing in two dimensions.
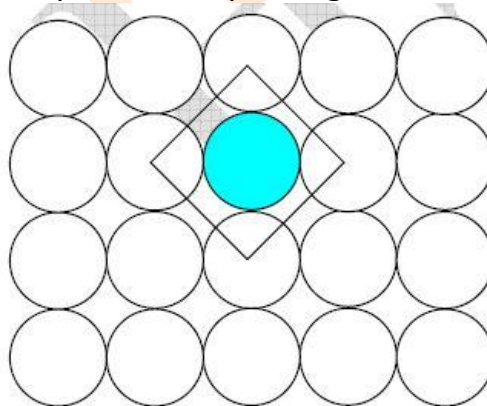
b. Hexagonal close packing:
    ✦ Here the spheres of the second row are placed in the depressions of the first row, the spheres of the third row are placed in the depressions of the second row and so on.

- In this arrangement, each sphere is in contact with six adjacent spheres. So the co-ordination number of each sphere is 6.
- When we join the centres of these spheres, we get a hexagon. So this close packing is called hexagonal close packing in two dimensions.

- ❖ Hexagonal close packing is more efficient than square close packing in two dimensions. This is because in Hexagonal close packing maximum space is occupied by spheres.

3. Close packing in Three Dimensions

i. Three dimensional close packing from two dimensional square close-packed layers:

- Here the spheres of the second layer are placed exactly above those of the first layer.
- In this arrangement spheres of both the layers are perfectly aligned horizontally as well as vertically.
- The spheres of the third layer are placed exactly above those of the second layer and so on.
- If the arrangement of the spheres in the first layer is denoted as 'A', all the layers are of 'A' type. So this arrangement forms AAA….. type pattern. The lattice thus generated is the simple cubic lattice and its unit cell is the primitive cubic unit cell.

ii. Three dimensional close packing from two dimensional hexagonal close-packed layers:

- Here the first layer is arranged as hexagonal manner.
- The second layer is placed above the depressions of the first layer. On placing the second layer there arises two types of voids (vacant spaces)

above the second layer – tetrahedral voids and octahedral voids. Thus when we place the third layer over the second there are two possibilities:

i. Covering tetrahedral voids:

❖ Here the spheres of the third layer are placed above the tetrahedral voids of the second layer.

❖ In this arrangement, the spheres of the third layer are vertically above those of the first layer, i.e. the first layer and the third layer are identical.

❖ If we call the first layer as 'A' and the second layer as 'B', then the third layer will be 'A', the fourth layer will be 'B' and so on. This will form the pattern ABAB…… This type of close packing is called *Hexagonal close packing (hcp) in three dimensions*.

❖ Examples: Mg, Zn, Mo, Be etc.

ii. Covering octahedral voids:

❖ Here the spheres of the third layer are placed above the octahedral voids of the second layer.

❖ In this arrangement, the third layer is different from the first or the second layer. But the spheres of the fourth layer are vertically above those of the first layer, i.e. the first layer and the fourth layer are identical.

❖ If we call the first layer as 'A', the second layer as 'B', and the third layer as 'C', then the fourth layer will be 'A', the fifth layer will be 'B' and so on.

❖ This will form the pattern ABCABC…… This type of close packing is called *Cubic close packing (ccp)* or *face-centred cubic(fcc) packing in three dimensions*.

❖ Examples: Fe, Ni, Cu, Ag, Au, Al

Hexagonal   cubic
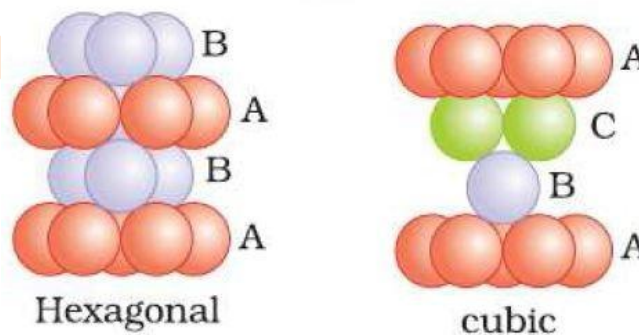
✓ *In both hcp and ccp 74% of the available space is occupied by spheres. So both are equally efficient.*

Co-ordination Number

➢ In a close packed arrangement the number of nearest neighbours with which a given sphere is in contact is called *the co-ordination number* of that sphere.

➢ In both *hcp* and *ccp* each sphere is in contact with 12 adjacent spheres. Thus the co-ordination number in both hcp and ccp is *12*.

Interstitial voids

The vacant space in close packed arrangement is called *voids*. These are of two types- tetrahedral voids and octahedral voids.

Tetrahedral void:

A void surrounded by *four* spheres in tetrahedral position is called tetrahedral void.

In a close packed arrangement the number of tetrahedral voids is double the number of spheres, i.e. there are two tetrahedral voids per sphere.

Octahedral voids:

A void surrounded by *six* spheres in octahedral position is called octahedral void.

In a close packed arrangement the number of octahedral voids is equal to the number of spheres, i.e. there is only one octahedral void per sphere.

> If there are N close packed spheres,
> The number of tetrahedral voids = 2N and
> The number of octahedral voids = N

Solved Problems

1. Calculate the number of tetrahedral and octahedral voids present in 0.5 mol of Be crystal.

Answer:

No. of Be atoms in 0.5 mol crystal = $0.5 \times 6.02 \times 10^{23}$

No. of octahedral voids = $0.5 \times 6.02 \times 10^{23} = 3.01 \times 10^{23}$

No. of tetrahedral voids = 2 x 0.5 x 6.02 x 10^{23} = 6.02 x 10^{23}

2. In a crystalline solid, the atom A are arranged in ccp array and atom B occupy all the octahedral voids and half of the tetrahedral voids. What is the formula of the compound?

Answer:

In a close packing, the number of octahedral voids is equal to the number of atoms and the number of tetrahedral voids is twice the number of atoms Since all the octahedral voids and half the tetrahedral voids are filled there will be one atom of B in tetrahedral void and one atom in octahedral void corresponding to each A. Thus, there will be two atoms of B corresponding to each A.

Hence, formula of the solid is AB_2.

3 .A compound is formed by two elements P and Q. atoms of Q (as anions) make hcp lattice and those of the element P (as cations) occupy all the tetrahedral voids. What is the formula of the compound?

Answer:

No. of atoms of Q = N

No. of atoms of P = 2N

Ratio of atoms of P and Q = 2 : 1

Therefore, the formula = P_2Q

4. A certain metal M crystallizes in f.c.c lattice. It forms a compound with elements A and B. A occupies all the octahedral voids and B occupies half of the tetrahedral voids. Find out the empirical formula of the compound.

Answer:

No. of M per unit cell = 4

No. of A per unit cell = 4

No. of B per unit cell $= \frac{1}{2} \times 2 \times 4 = 4$

Empirical Formula $= M_4A_4B_4 = MAB$

5. 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?

Answer:

The ccp lattice is formed by the element Y. The number of octahedral voids generated would be equal to the no. 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.

6. What is the formula of a compound in which the element Y forms hcp lattice and atoms of X occupy 2/3rd of tetrahedral voids?

Answer:

The number of tetrahedral voids formed is equal to twice the number of atoms of element Y. But only 2/3 of these tetrahedral voids are occupied by atoms of element X.

Therefore the ratio of number of atoms of X and Y is

2x(2/3) : 1 = 4 : 3

The formula of compound is X_4Y_3

7. A compound is formed by two elements P and Q. Atoms of Q (as anions) make hcp lattice and those of the element P (as cations) occupy all the tetrahedral voids. What is the formula of the compound?

Answer: Do it Your Self.

Defects or imperfections in solids

- The deviation from the regular orderly arrangement of particles of a solid is termed as *imperfections or crystal defects.*
- The crystal defects are broadly classified into two – point defects and line defects.
    - The imperfection around a point (an atom) in a crystalline substance, it is termed as **point defect**.
    - The imperfection along a row is termed as **line defect**.

Point defects
Point defects can be classified into three types:
Stoichiometric defects, Non-stoichiometric defects and Impurity defects.

1. Stoichiometric defects:
- These are point defects which do not disturb the stoichiometry of the solid.
- They are also called *intrinsic or thermodynamic defects*, because these defects can also develop when a substance is heated.

These are of two types – vacancy defects and interstitial defects
a. Vacancy defect: When some of the lattice sites are vacant, the crystal is said to have vacancy defect. This defect decreases the density of the solid.
**b. Interstitial defect**: When some constituent particles occupy an interstitial site, the crystal is said to have interstitial defect. This defect increases the density of the solid.

- The above two types of defects are shown by *non-ionic solids*.
- *Ionic solids* show two types of stoichiometric defects – **Schottky defect and Frenkel defect.**

i. Schottky defect:
- It is basically a vacancy defect.
- Equal number of cations and anions are missing from their lattice sites.
- This defect is shown by ionic solids which have
    - High coordination number.
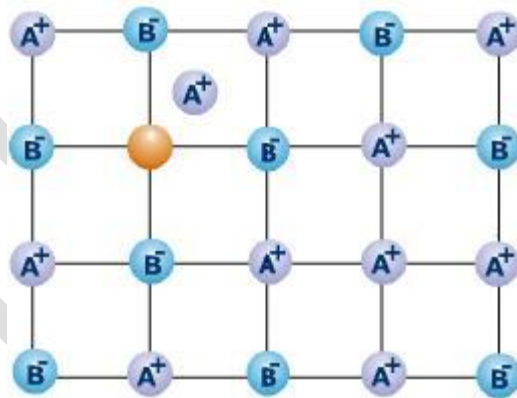   - Size of cations and anions are almost equal.
- NaCl, KCl, KBr, AgBr, CsCl.
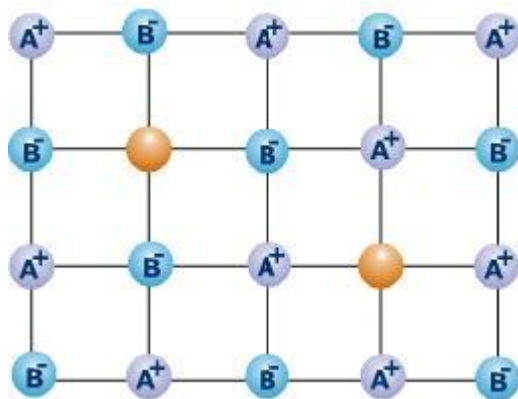
Consequences of Schottky defect:
1. Due to the presence of holes, solids having Schottky defect conduct electricity to a small extend.
2. As ions are missing from their lattice sites, density of the crystal decreases.

ii. Frenkel defect (dislocation defect, interstitial defect):
- Some ions are missing from their lattice sites and they occupy the interstitial space.
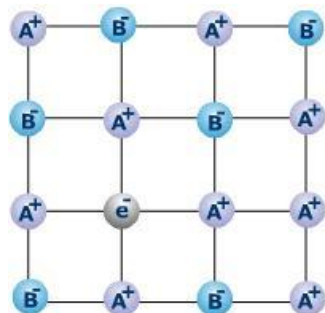- Usually cations occupy the interstitial space due to their small size.
- AgCl, AgBr, ZnS.

This defect is shown by ionic solids which have
1. Low coordination number
2. Large difference in the size of cations and anions.

Consequences of Frenkel defect:
1. Due to the presence of holes, solids having frenkel defect conduct electricity to small extend.

2. As no ions are missing from the lattice, density remains same.

   ✓ **Frenkel defect do not found in alkali metal halides, because alkali metal ions due to their large size cannot fit in to the interstitial space.**

2. Non-Stoichiometric defects:
These are point defects which change the stoichiometry of a solid.
These defects are of two types:
i) Metal excess defect and   ii) Metal deficiency defect

i) Metal excess Defect:
Here the number of cations is greater than the number of anions.

This arises in two ways:

Metal excess defect due to anionic vacancies:
- Here some of the anions are missing from the lattice site.
- The electrical neutrality is maintained by occupying electrons in the anionic sites. These electrons are called **f-centres** because they give colour to the crystal.
- This defect is shown by alkali metal halides.
- For example when NaCl is heated in an atmosphere of sodium vapour, some sodium atoms are deposited at the surface of the crystal. The Cl⁻ ions diffuse to the surface of the crystal and combines with Na atom to form NaCl.
- The electron so formed diffuse into the crystal and occupies the anion vacancy. These electrons absorb light energy and get excited. As a result the crystal becomes yellow in colour.
- Similarly, *excess of Li makes LiCl crystals pink and excess of K makes KCl crystals violet*.

Metal excess defect due to extra cations at interstitial sites:

- Here some cations occupy the interstitial sites. The electrical neutrality is maintained by occupying some electrons in adjacent interstitial sites.
- E.g. When ZnO crystals are heated, the white coloured crystals becomes yellow. This is because on heating, the crystal loses oxygen as follows:
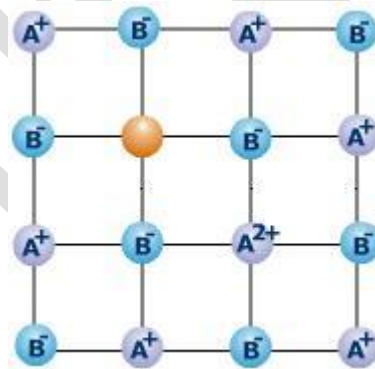
$$ZnO \rightarrow Zn^{2+} + \tfrac{1}{2} O_2 + 2e^-$$
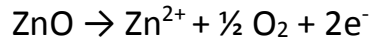
The Zn ions now move to the interstitial sites and the electrons to neighbouring interstitial sites.
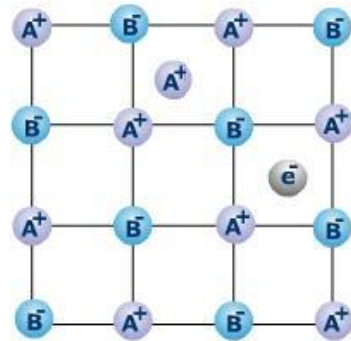
ii) **Metal deficiency Defect:**

Here the number of cations is smaller than the number of anions. This is mainly arises due to cation vacancies. This type of defect is commonly shown by transition metal compounds. E.g. FeO
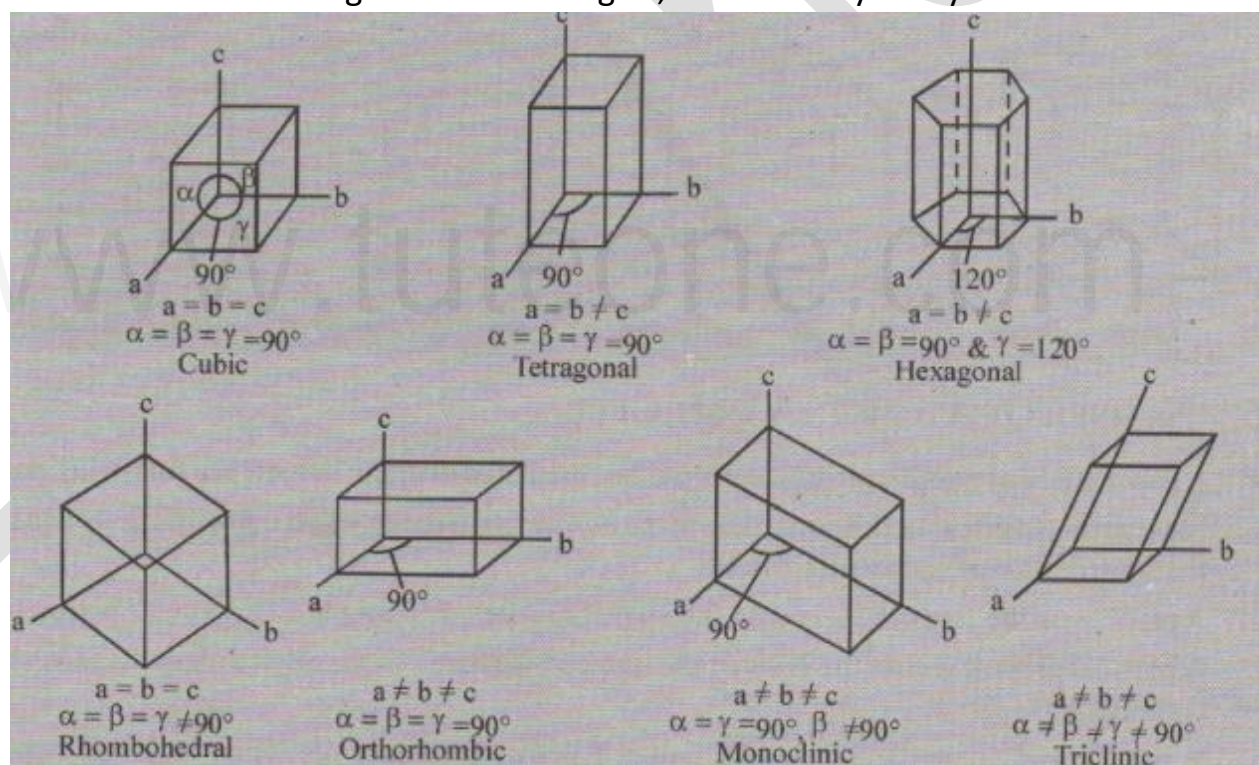

c) *Impurity Defects*:

It is the defect arising due to the presence of foreign particles in a crystal. For example if molten NaCl containing a little amount of $SrCl_2$ is crystallised, some of the sites of Na^+ ions are occupied by Sr^{2+}. Each Sr^{2+} replaces two Na^+ ions. It occupies the site of one ion and the other site remains vacant. The cationic vacancies thus produced are equal to the number of Sr^{2+} ions. Another similar example is a solid solution of $CdCl_2$ and AgCl.
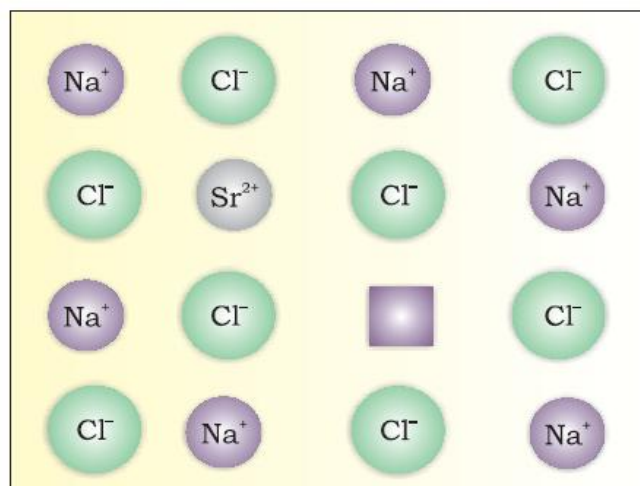
Space lattice or Crystal lattice

+ A regular three dimensional arrangement of particles in space is called space lattice (crystal lattice).
+ There are 14 possible crystal lattices. They are called Bravaise lattices.
+ The points in the crystal lattice at which the constituent particles are present are called lattice sites or lattice points.
+ The smallest portion of a crystal lattice which when repeated in different directions produces the complete lattice is called unit cell.
+ A unit cell is represented by three egdes a,b,c and angles between the egdes a,b,c and angles between the edges α, β, γ.

Based on the three edges and three angles, there are crystal systems.

$a = b = c$
$\alpha = \beta = \gamma = 90°$
Cubic

$a = b \neq c$
$\alpha = \beta = \gamma = 90°$
Tetragonal

$a = b \neq c$
$\alpha = \beta = 90° \ \& \ \gamma = 120°$
Hexagonal

$a = b = c$
$\alpha = \beta = \gamma \neq 90°$
Rhombohedral

$a \neq b \neq c$
$\alpha = \beta = \gamma = 90°$
Orthorhombic

$a \neq b \neq c$
$\alpha = \gamma = 90° \ \beta \neq 90°$
Monoclinic

$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90°$
Triclinic

System	Axial distance	Axial angles	Examples
1. Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	ZnS, KCl, $NaCl$, Cu, Alums, diamond
2. Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	Sn, SnO_2, TiO_2, $CaSO_4$
3. Orthorhombic or rhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	Rhombic Sulphur, KNO_3, K_2SO_4, $BaSO_4$
4. Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°$ $\beta \neq 90°$	Monoclinic sulphur, $Na_2SO_4 \cdot 10\,H_2O$, $FeSO_4$
5. Trigonal or Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	$NaNO_3$, Sb, As, Calcite ($CaCO_3$), HgS(Cinnabar)
6. Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°$ $\gamma = 120°$	HgS, Ice, ZnO, CdS, Graphite.
7. Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	$CuSO_4 \cdot 5H_2O$, $K_2Cr_2O_7$, H_3BO_3