

# Solid State

**SOLIDS** : Solids are characterised by definite shape, volume, rigidity, high density, low compressibility, mechanical strength, slow diffusion etc.

Solids can be classified into two types.

**CRYSTALLINE SOLIDS** : Here, constituent particles are arranged in definite geometrical pattern in three dimension.

**AMORPHOUS SOLIDS** : Here, constituent particles are in random arrangement. (amorphous - means without any form).

## DIFFERENCES BETWEEN CRYSTALLINE AND AMORPHOUS SOLIDS:

<b><i>Crystalline Solid</i></b>	<b><i>Amorphous Solid</i></b>
constituent particles are regularly arranged	constituent particles are randomly arranged
True solids	Pseudo solids or super cooled liquids
Have sharp melting point	Melts over a range of temperature
They are anisotropic i.e. their physical properties are different along different directions	They are isotropic i.e. their physical properties are same along all directions
Show clean cleavage planes	No clean cleavage planes
Have long range order	Can have short range order
Examples: Diamond, NaCl, etc.	Examples: Glass, Rubber, Plastic

### TYPES OF CRYSTALLINE SOLIDS BASED ON THE NATURE OF CONSTITUENT PARTICLES:

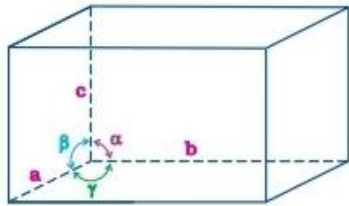
	<b>Ionic</b>	<b>Covalent</b>	<b>Molecular</b>	<b>Metallic</b>
Constituents	Positive and negative ions	Atoms	Molecules	Positive ions
Bonding	Electrovalent	Covalent	Van der waal, dipole-dipole attraction	Electrostatic force between karnels and electrons
Melting point	High	Very high	Low	Moderate to high
Example	CsCl, ZnS	Diamond	I <sub>2</sub> , dry ice	Fe, Zn.

**Crystal Lattice :**

If the three dimensional arrangement of constituent particles in a crystal is represented diagrammatically, in which each particle is depicted as a point, the arrangement is called crystal lattice. Thus, a regular three dimensional arrangement of points in space is called a crystal lattice.

**Unit Cell :**

Unit cell is the smallest portion of a crystal lattice which, when repeated in three dimension, generates the entire lattice.



A unit cell is characterised by:

- (i) its dimensions along the three edges, a, b and c. These edges may or may not be mutually perpendicular.
- (ii) angles between the edges,  $\alpha$  (between b and c)  $\beta$  (between a and c) and  $\gamma$  (between a and b).

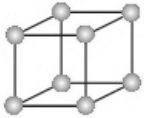
Thus, a unit cell is characterised by six parameters, a, b, c,  $\alpha$ ,  $\beta$  and  $\gamma$

**SEVEN CRYSTAL SYSTEMS** : There are about 230 crystal forms, which have been grouped into 14 types of space lattices called **BRAVAIS LATTICES** on the basis of their symmetry and 7 different crystal systems on the basis of interfacial angles and axes.

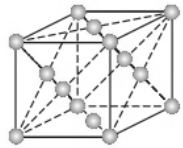
	Crystal system	Parameters of unit Cell		Bravais lattices
		Intercepts along crystallographic axes	Axial angles	
1	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	3 Primitive, Face Centred, Body centred
2	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	2 Primitive, Body centred
3	Rhombohedral	$a = b = c$	$\alpha = \beta = 90^\circ, \gamma \neq 90^\circ$	1 Primitive
4	Ortho Rhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	4 Primitive, Face centred, Body centred, End centred
5	Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90^\circ, \gamma \neq 90^\circ$	2 Primitive, End Centred
6	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	1 Primitive
7	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	1 Primitive

### TYPES OF UNIT CELL :

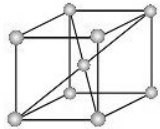
(i) Simple or primitive : Unit cell in which the particles are present at the corners only.



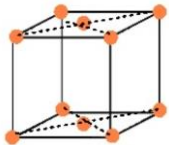
(ii) Face centred : In which the particles are present at the corners & at the centre of each of six faces



(iii) Body centred : In which the particles are present at the corners and in the centre



(iv) End face centred : In which the particles are present at the corners and at the centre of two opposite faces.



**NUMBER OF PARTICLES PER UNIT CELL (RANK OF UNIT CELL):**

UNIT CELL	NO OF PARTICLES AND THEIR CONTRIBUTIONS			TOTAL
	CORNER	FACE	CENTRE	
SIMPLE CUBIC	$8 \times \frac{1}{8} = 1$			1
FACE CENTERED	$8 \times \frac{1}{8} = 1$	$6 \times \frac{1}{2} = 3$		4
BODY CENTERED	$8 \times \frac{1}{8} = 1$		$1 \times 1 = 1$	2
END CENTERED	$8 \times \frac{1}{8} = 1$	$2 \times \frac{1}{2} = 1$		2

## PACKING FRACTION (PF):

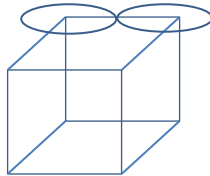
It is defined as the fraction of the volume of the unit cell that is occupied by the constituent particles.

### (i) Primitive cubic unit cell :

Here, number of atoms per unit cell = 1

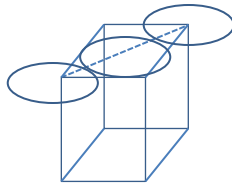
In the unit cell, particles touch each other along edges. Hence,  $r = \frac{a}{2}$  (where  $r$  = radius of atom and  $a$  = edge length).

$$\therefore PF = \frac{\frac{4}{3}\pi r^3}{(2r)^3} = 0.52$$



### (ii) Face centred cubic unit cell :

Number of atoms per unit cell = 4



Atoms touch each other along the face diagonal. Hence  $r = \frac{\sqrt{2}a}{4}$

$$\therefore PF = \frac{4 \times \frac{4}{3}\pi r^3}{\left(\frac{4r}{\frac{\sqrt{2}}{2}}\right)^3} = 0.74$$



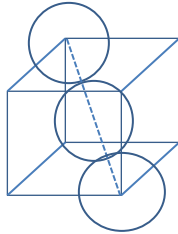
(iii) **Body centred cubic unit cell :**

Number of atoms per unit cell = 2

Here, atoms touch each other along the body diagonal.

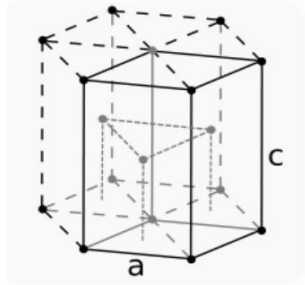
$$\text{Hence } r = \frac{\sqrt{3}a}{4}$$

$$\therefore PF = \frac{2 \times \frac{4}{3} \pi r^3}{\left(\frac{4r}{\sqrt{3}}\right)^3} = 0.68$$



(iv) **Hexagonal primitive unit cell :**

Each corner atom is being shared by 6 other unit cells therefore their contribution to one unit cell would be  $\frac{1}{6}$ .



$$\text{Total number of atoms per unit cell} = \frac{1}{6} \times 12 + 3 + \frac{1}{2} \times 2 = 6$$

$$\text{Height of unit cell } C = 4r \sqrt{\frac{2}{3}}$$

$$\text{Length of unit cell } a = 2r$$

Area of base = area of six equilateral triangles

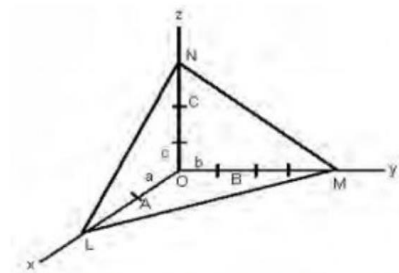
$$= 6 \times \left(\frac{\sqrt{3}}{4}\right) (2r)^2$$

$$\text{Volume of unit cell} = \left\{ 6 \times \left(\frac{\sqrt{3}}{4}\right) (2r)^2 \right\} \times \left\{ 4r \sqrt{\frac{2}{3}} \right\}$$

$$\therefore \text{PF} = \frac{6 \times \frac{4}{3} \pi r^3}{\left\{ 6 \times \left(\frac{\sqrt{3}}{4}\right) (2r)^2 \right\} \times \left\{ 4r \sqrt{\frac{2}{3}} \right\}} = 0.74$$

## LAW OF RATIONAL INDICES :

The ratio between intercepts on crystallographic axes for the different faces of a crystal can always be expressed by rational numbers.



The plane LMN has intercepts OL, OM and ON along X, Y and Z axes of lengths 2a, 4b and 3c respectively. When  $OA = a$ ,  $OB = b$  and  $OC = c$  are taken as unit distances, the intercepts are in the ratio  $2a : 4b : 3c$  and coefficients of a, b and c are known as **WEISS INDICES**. Weiss indices may have any values integers, fractional or infinity.

**MILLER INDICES** : Reciprocals of Weiss indices and multiplying throughout by smallest number to make integers are known Miller indices and represented by h, k and l and the plane as (hkl). For example, in (112) plane  $h = 1$ ,  $k = 1$  and  $l = 2$ .

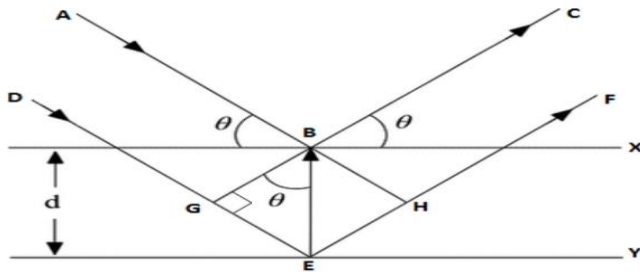
The distance between the parallel planes in a crystal is designated as  $d_{hkl}$ . For different cubic lattices the interplanar distances are given by

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}, \text{ where } a = \text{length of cube side and } h, k \text{ and } l \text{ are Miller indices.}$$

## X-RAY DIFFRACTION (BRAGG'S EQUATION) AND DETERMINATION OF INTER PLANAR DISTANCE:

When X-rays strike the parallel planes of the crystal at an angle  $\theta$ , they are reflected from different planes. The resulting reflected beam will be strong if all reflected rays are in phase.

For maximum reflection condition (defined above) path difference =  $n \times \text{wavelength } (\lambda)$



Now from figure the path difference =  $GE + EH$

$$= d \sin \theta + d \sin \theta$$

$$= 2 d \sin \theta$$

$\therefore \boxed{2 d \sin \theta = n \lambda}$ , This is Bragg's equation.

### **SYMMETRY IN CRYSTAL SYSTEMS :**

- (i) Plane of symmetry : Which divides a crystal in two parts in such a way that one part is the mirror image of the other.
- (ii) Axis of symmetry : It is a line about which the crystal may be rotated such that it presents the same appearance more than once during complete revolution.
- (iii) Centre of symmetry : It is a point such that any line drawn through it intersects the surface of the crystal at equal distances in both directions.

## CLOSE PACKING OF CONSTITUENT PARTICLES IN CRYSTALS :

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

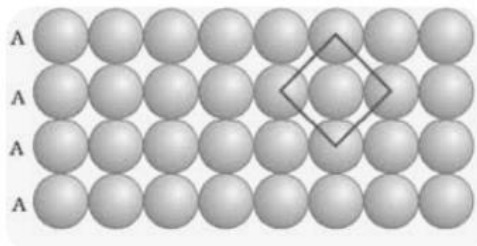
**(a) Close Packing in One Dimension :** There is only one way of arranging spheres in a one dimensional close packed structure, that is to arrange them in a row and touching each other.



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

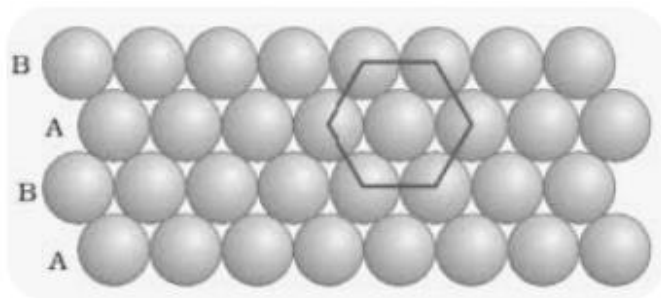
(b) **Close Packing in Two Dimensions:** Two dimensional close packed structure can be generated by stacking (placing) the rows of close packed spheres. This can be done in two different ways.

(i) **Square close packing in two dimensions:** The second row may be placed in contact with the first one such that the spheres of the second row are exactly above those of the first row. The spheres of the two rows are aligned horizontally as well as vertically. If we call the first row as 'A' type row, the second row being exactly the same as the first one, is also of 'A' type. Similarly, we may place more rows to obtain **AAA** type of arrangement. In this arrangement, each sphere is in contact with four of its neighbours. Thus, the two dimensional coordination number is 4. Also, if the centres of these 4 immediate neighbouring spheres are joined, a square is formed. Hence this packing is called square close packing in two dimensions.



Square close packing in 2D

(ii) **Hexagonal close packing in 2D:** The second row may be placed above the first one in a staggered manner such that its spheres fit in the depressions of the first row. If the arrangement of spheres in the first row is called 'A' type, the one in the second row is different and may be called 'B' type. When the third row is placed adjacent to the second in staggered manner, its spheres are aligned with those of the first layer. Hence this layer is also of 'A' type. The spheres of similarly placed fourth row will be aligned with those of the second row ('B' type). Hence this arrangement is of **ABAB type** (as shown above). This packing is more efficient than the square close packing. Each sphere is in contact with six of its neighbours and the two dimensional coordination number is 6. The centres of these six spheres are at the corners of a regular hexagon hence this packing is called two dimensional hexagonal close packing. In this layer there are some voids (empty spaces). These are triangular in shape. The triangular voids are of two different types. In one row, the apex of the triangles are pointing upwards and in the next layer downwards

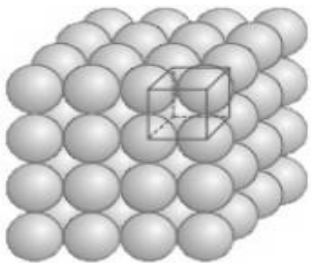


Hexagonal close packing in 2D



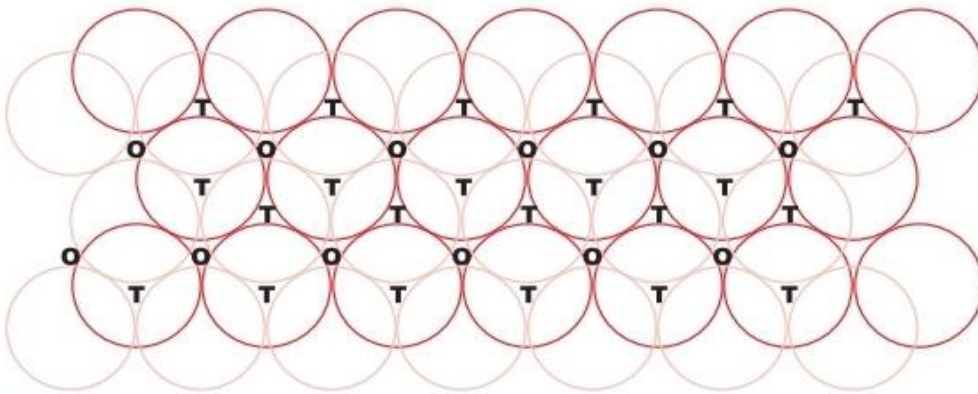
**(c) Close Packing in Three Dimensions:** All real structures are three dimensional structures. They can be obtained by stacking two dimensional layers one above the other.

**(i) Three dimensional close packing from two dimensional square close-packed layers:** While placing the second square close-packed layer above the first we follow the same rule that was followed when one row was placed adjacent to the other. Thus this lattice has **AAA.... type pattern**. The lattice thus generated is the simple cubic lattice, and its **unit cell is the primitive cubic unit cell**.



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

**(a) Placing second layer over the first layer:** Let us take a two dimensional hexagonal close packed layer 'A' and place a similar layer above it such that the spheres of the second layer are placed in the depressions of the first layer. Since the spheres of the two layers are aligned differently, let us call the second layer as B. It can be observed that not all the triangular voids of the first layer are covered by the spheres of the second layer. This gives rise to different arrangements.



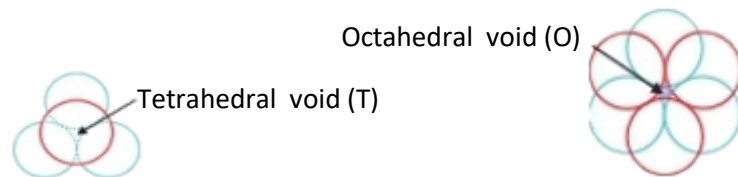
Wherever a sphere of the second layer is above the void of the first layer (or vice versa) a tetrahedral void is formed. These voids are called tetrahedral voids because a tetrahedron is formed when the centres of these four spheres are joined. They have been marked as 'T'. At other places, the triangular voids in the second layer are above the triangular voids in the first layer, and the triangular shapes of these do not overlap. One of them has the apex of the triangle pointing upwards and the other downwards. These voids have been marked as 'O'. Such voids are surrounded by six spheres and are called octahedral voids.

The number of these two types of voids depend upon the number of close packed spheres.

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

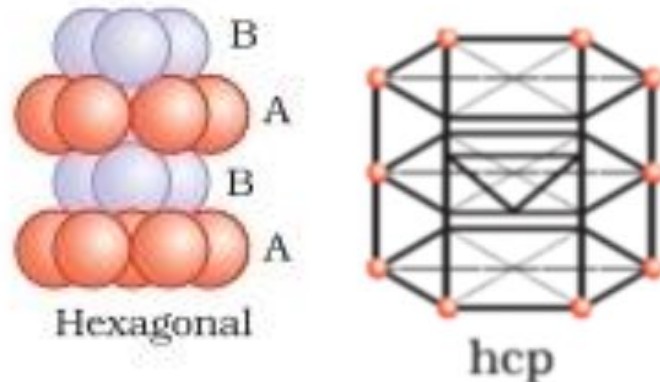
The number of octahedral voids generated =  $N$

The number of tetrahedral voids generated =  $2N$

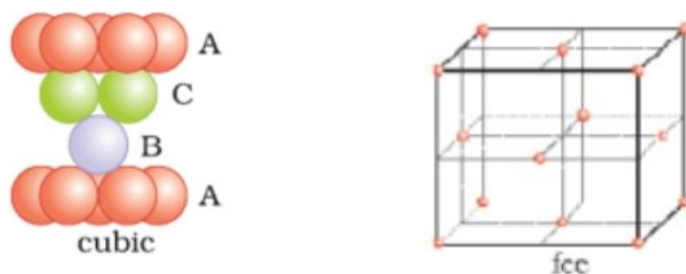


**(b) Placing third layer over the second layer:** When third layer is placed over the second, there are two possibilities.

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



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



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

**INTERSTITIAL VOIDS :** The space left after hcp and ccp (74.0% in each case) is known as interstitial voids. They are of two types:

(i) Tetrahedral voids: The vacant space touching four spheres is called tetrahedral void. The radius ratio is

$$\frac{r_{void}}{r_{sphere}}=0.225$$

(ii) Octahedral voids: The vacant space touching six spheres is called octahedral void. The radius ratio is

$$\frac{r_{void}}{r_{sphere}}=0.414$$

**LIMITING RADIUS RATIO :** Cations tend to get surrounded by the largest number of anions therefore the larger the  $\frac{r_{void}}{r_{sphere}}$  ratio, the larger is the coordination number.

Limiting radius ratio( $r_+ / r_-$ )	Geometry	Coordination number
0.155 – 0.225	Planar triangle	3
0.225 – 0.414	Tetrahedral	4
0.414 – 0.732	Octahedral	6
0.732 – 1.000	Body Centred Cubic	8

### STRUCTURE OF SOME SIMPLE IONIC COMPOUNDS :

Crystal Structure	Packing	C.N. of cation & anion	Location of cation in unit cell	Location of anion in unit cell	No. of formula Units per unit cell
Rock Salt (NaCl)	$\text{Cl}^-$ in ccp & $\text{Na}^+$ in all octahedral voids	6,6	12 at edges, 1 in body	8 at corners, 6 at faces	4
Zinc blends (ZnS)	$\text{S}^{2-}$ in ccp & $\text{Zn}^{2+}$ in alternate tetrahedral voids	4,4	4 in body	8 at corners, 6 at faces	4
CsCl	$\text{Cl}^-$ at corners of cube & $\text{Cs}^+$ in all cubical voids or vice versa	8,8	1 in body	8 at corners	1
Fluorite ( $\text{CaF}_2$ )	$\text{Ca}^{2+}$ in ccp & $\text{F}^-$ in all tetrahedral voids	8,4	8 at corners, 6 at faces	8 in body	4
Antifluorite ( $\text{Na}_2\text{O}$ )	$\text{O}^{2-}$ in ccp & $\text{Na}^+$ in all tetrahedral voids	4,8	8 in body	8 at corners, 6 at faces	4

### DENSITY OF UNIT CELL :

$$\begin{aligned}\text{Density of the unit cell} &= \frac{\text{Mass of Unit Cell}}{\text{Volume of Unit Cell}} \\ &= \frac{zm}{a^3} \text{ [z= Rank of unit cell, m=mass of one constituent particle, a= edge length of unit cell]} \\ &= \frac{zM}{a^3 N_A} \text{ [M=Formula mass of constituent, } N_A \text{ =Avogadro Number]}\end{aligned}$$

Remember, the density of the unit cell is the same as the density of the substance.



**IMPERFECTIONS IN SOLIDS** : The defects are basically irregularities in the arrangement of constituent particles. They are of two types.

(i) **Electronic imperfections** : At temperatures above  $0\text{K}$  , some electrons are released from covalent bonds in pure crystals which are now free to move in the crystal. The electron deficient bonds produced are known as holes. Electrons (e) and holes (h) in solids are considered to cause electronic imperfections. Concentrations of electrons (e) and holes (h) is represented by  $n$  and  $p$ .

(ii) **Atomic imperfections** : This defect arises from the missing or misplacing of constituent particles from their normal crystal site(s). They may be divided as

(a) **Point defects** : Point defects are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance.

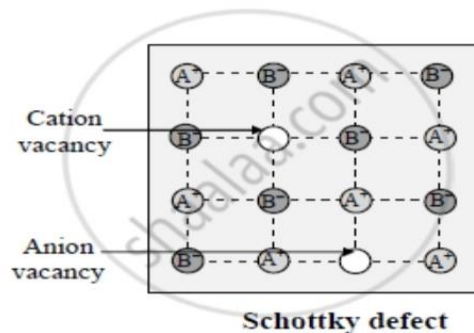
(c) **Line defects**: Line defects are the irregularities or deviations from ideal arrangement in entire rows of lattice points. These irregularities are called crystal defects.

(d) **Plane defects** : The lattice imperfections extend along surfaces of crystals.

**Types of Point Defects:** Point defects can be classified into three types :

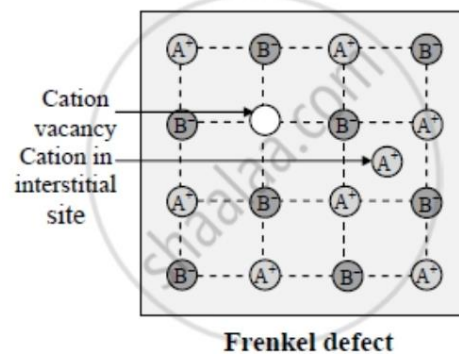
(i) **Stoichiometric defects** : These are the point defects that do not disturb the stoichiometry of the solid. They are also called intrinsic or thermodynamic defects. Basically these are of two types, vacancy defects and interstitial defects.

(i) **Schottky defect (vacancy defect)** : It is due to missing of ion pairs (one cation and one anion) from their lattice sites. It maintains the electrical neutrality. **Density of crystal** decrease as a result of this defect.



It is more common in compounds with high coordination number and when size of positive and negative ions is almost equal. Example NaCl, KCl, CsCl and KBr etc.

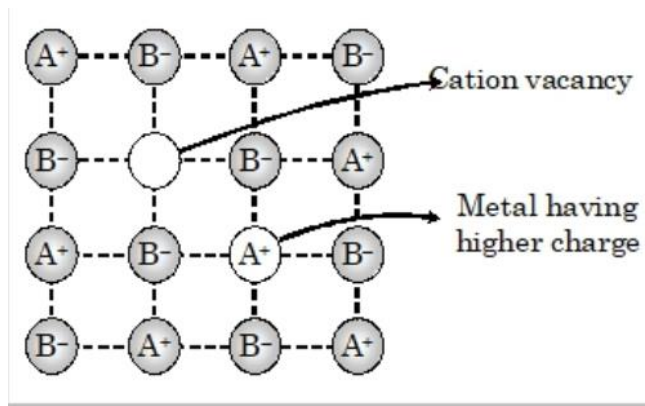
(ii) **Frenkel defect (dislocation defect)**: It is due to dislocation of ion from its usual site to interstitial position. **Density remains the same.**



It is common in compounds having low coordination number and large difference in size of +ve and –ve ions. Examples ZnS, AgCl, AgBr and AgI.

AgBr shows both of the above defects

(ii) **Impurity defects:** If molten NaCl containing a little amount of  $\text{SrCl}_2$  is crystallised, some of the sites of  $\text{Na}^+$  ions are occupied by  $\text{Sr}^{2+}$ . Each  $\text{Sr}^{2+}$  replaces two  $\text{Na}^+$  ions. It occupies the site of one ion and the other site remains vacant. The cationic vacancies thus produced are equal in number to that of  $\text{Sr}^{2+}$  ions. Another similar example is the solid solution of  $\text{CdCl}_2$  and  $\text{AgCl}$ .



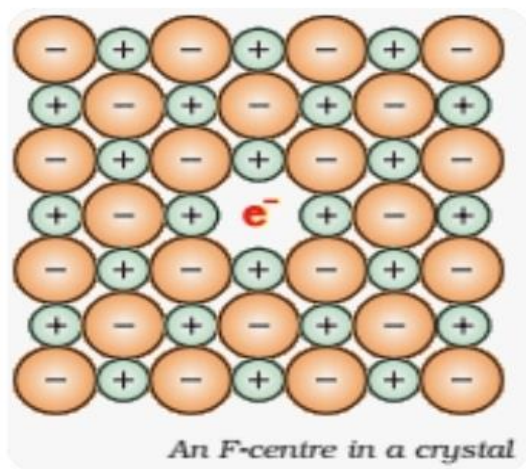
(iii) **Non-stoichiometric defects:** A large number of nonstoichiometric inorganic solids are known which contain the constituent elements in non-stoichiometric ratio due to defects in their crystal structures. These defects are of two types:

(i) Metal excess defect and

(ii) Metal deficiency defect.

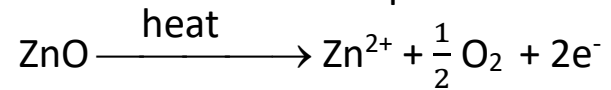
(i) **Metal Excess Defect :**

- **Metal excess defect due to anionic vacancies:** Alkali halides like NaCl and KCl show this type of defect. When crystals of NaCl are heated in an atmosphere of sodium vapour, the sodium atoms are deposited on the surface of the crystal. The  $\text{Cl}^-$  ions diffuse to the surface of the crystal and combine with Na atoms to give NaCl. This happens by loss of electron by sodium atoms to form  $\text{Na}^+$  ions. The released electrons diffuse into the crystal and occupy anionic sites

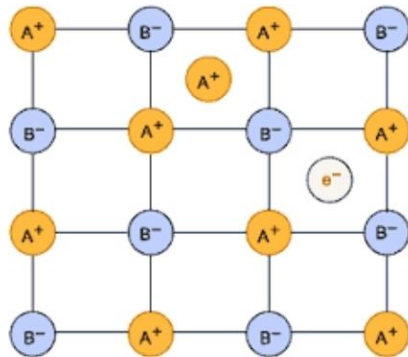


As a result the crystal now has an excess of sodium. The anionic sites occupied by unpaired electrons are called **F-centres** (from the German word Farbenzenter for colour centre). They impart yellow colour to the crystals of NaCl. The colour results by excitation of these electrons when they absorb energy from the visible light falling on the crystals. Similarly, excess of lithium makes LiCl crystals pink and excess of potassium makes KCl crystals violet (or lilac).

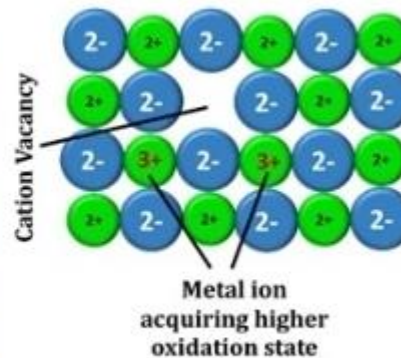
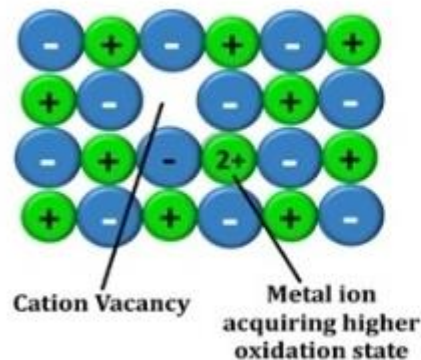
- **Metal excess defect due to the presence of extra cations at interstitial sites:** Zinc oxide is white in colour at room temperature. On heating it loses oxygen and turns yellow.



The excess  $\text{Zn}^{2+}$  ions move to interstitial sites and the electrons to neighbouring interstitial sites.



**(ii) Metal Deficiency Defect:** There are many solids which are difficult to prepare in the stoichiometric composition and contain less amount of the metal as compared to the stoichiometric proportion. A typical example of this type is FeO which is mostly found with a composition of  $\text{Fe}_{0.95}\text{O}$ . It may actually range from  $\text{Fe}_{0.93}\text{O}$  to  $\text{Fe}_{0.96}\text{O}$ . In crystals of FeO some  $\text{Fe}^{2+}$  cations are missing and the loss of positive charge is made up by the presence of required number of  $\text{Fe}^{3+}$  ions.





**Electrical Properties:** Solids exhibit an amazing range of electrical conductivities, extending over 27 orders of magnitude ranging from  $10^{-20}$  to  $10^7 \text{ ohm}^{-1} \text{ m}^{-1}$ . Solids can be classified into three types on the basis of their conductivities.

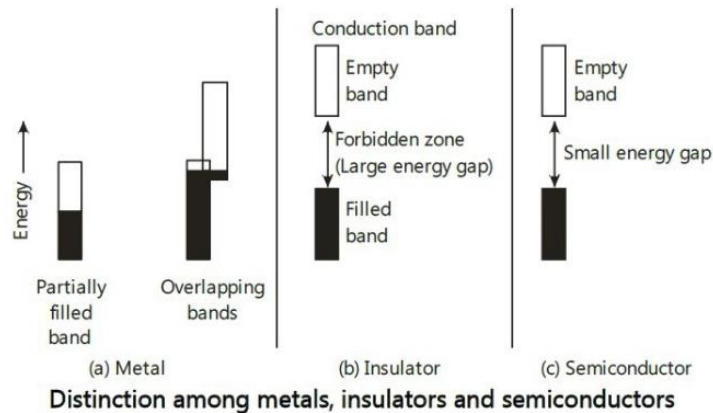
(i) **Conductors:** The solids with conductivities ranging between  $10^4$  to  $10^7 \text{ ohm}^{-1} \text{ m}^{-1}$  are called conductors. Metals have conductivities in the order of  $10^7 \text{ ohm}^{-1} \text{ m}^{-1}$  are good conductors.

(ii) **Insulators:** These are the solids with very low conductivities ranging between  $10^{-20}$  to  $10^{-10} \text{ ohm}^{-1} \text{ m}^{-1}$ .

(iii) **Semiconductors:** These are the solids with conductivities in the intermediate range from  $10^{-6}$  to  $10^4 \text{ ohm}^{-1} \text{ m}^{-1}$ .

## Conduction of Electricity in Metals:

A conductor may conduct electricity through movement of electrons or ions. Metallic conductors belong to the former category and electrolytes to the latter. Metals conduct electricity in solid as well as molten state. The conductivity of metals depend upon the number of valence electrons available per atom. The atomic orbitals of metal atoms form molecular orbitals which are so close in energy to each other as to form a **band**.



If this band is partially filled or it overlaps with a higher energy unoccupied conduction band, then electrons can flow easily under an applied electric field and the metal shows conductivity.

If the gap between filled valence band and the next higher unoccupied band (conduction band) is large, electrons cannot jump to it and such a substance has very small conductivity and it behaves as an insulator

### **Conduction of Electricity in Semiconductors:**

In case of semiconductors, the gap between the valence band and conduction band is small. Therefore, some electrons may jump to conduction band and show some conductivity. Electrical conductivity of semiconductors increases with rise in temperature, since more electrons can jump to the conduction band.

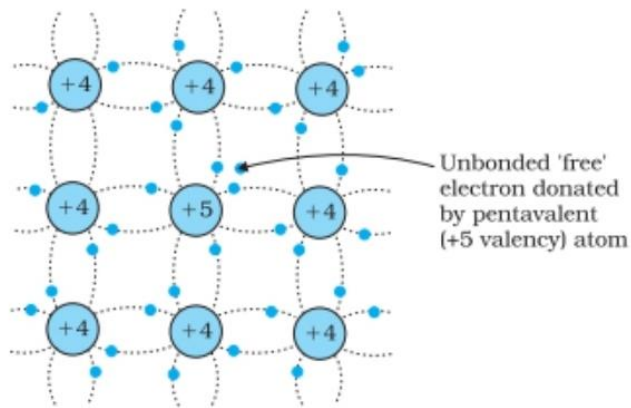
Substances like silicon and germanium show this type of behaviour and are called **intrinsic semiconductors**. The conductivity of these intrinsic semiconductors is too low to be of practical use.

Their conductivity is increased by adding an appropriate amount of suitable impurity. This process is called **doping**. Doping can be done with an impurity which is electron rich or electron deficient as compared to the intrinsic semiconductor silicon or germanium. Such impurities introduce electronic defects in them.

### (a) Electron – rich impurities:

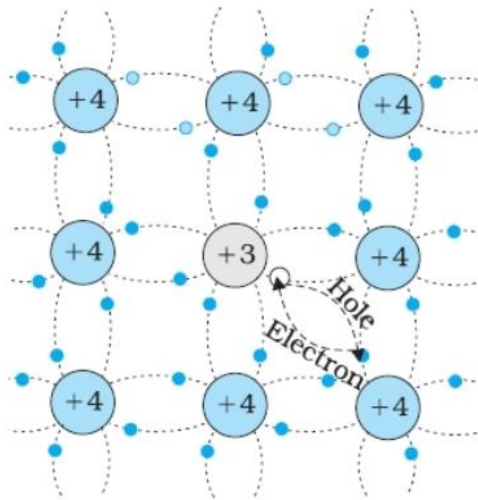
Silicon and germanium belong to group 14 of the periodic table and have four valence electrons each. In their crystals each atom forms four covalent bonds with its neighbours.

When doped with a group 15 element like P or As, which contains five valence electrons, they occupy some of the lattice sites in silicon or germanium crystal. Four out of five electrons are used in the formation of four covalent bonds with the four neighbouring silicon atoms. The fifth electron is extra and becomes delocalised. These delocalised electrons increase the conductivity of doped silicon (or germanium). Here the increase in conductivity is due to the negatively charged electron, hence silicon doped with electron-rich impurity is called **n-type semiconductor**.



**(b) Electron – deficit impurities:**

Silicon or germanium can also be doped with a group 13 element like B, Al or Ga which contains only three valence electrons. The place where the fourth valence electron is missing is called electron hole or electron vacancy. An electron from a neighbouring atom can come and fill the electron hole, but in doing so it would leave an electron hole at its original position. If it happens, it would appear as if the electron hole has moved in the direction opposite to that of the electron that filled it. Under the influence of electric field, electrons would move towards the positively charged plate through electronic holes, but it would appear as if electron holes are positively charged and are moving towards negatively charged plate. These types of semiconductors are called **p-type semiconductors**.



## **Applications of n-type and p-type semiconductors**

Various combinations of n-type and p-type semiconductors are used for making electronic components. Diode is a combination of n-type and p-type semiconductors and is used as a rectifier. Transistors are made by sandwiching a layer of one type of semiconductor between two layers of the other type of semiconductor. npn and pnp type of transistors are used to detect or amplify radio or audio signals. The solar cell is an efficient photo-diode used for conversion of light energy into electrical energy. Germanium and silicon are group 14 elements and therefore, have a characteristic valence of four and form four bonds as in diamond. A large variety of solid state materials have been prepared by combination of groups 13 and 15 or 12 and 16 to simulate average valence of four as in Ge or Si. Typical compounds of groups 13 – 15 are InSb, AlP and GaAs. Gallium arsenide (GaAs) semiconductors have very fast response and have revolutionised the design of semiconductor devices. ZnS, CdS, CdSe and HgTe are examples of groups 12 – 16 compounds. In these compounds, the bonds are not perfectly covalent and the ionic character depends on the electronegativities of the two elements. It is interesting to learn that transition metal oxides show marked differences in electrical properties. TiO, CrO<sub>2</sub> and ReO<sub>3</sub> behave like metals. Rhenium oxide, ReO<sub>3</sub> is like metallic copper in its conductivity and appearance. Certain other oxides like VO, VO<sub>2</sub>, VO<sub>3</sub> and TiO<sub>3</sub> show metallic or insulating properties depending on temperature.

## **Magnetic Magnetic Properties Properties**

Every substance has some magnetic properties associated with it. The origin of these properties lies in the electrons. Each electron in an atom behaves like a tiny magnet. Its magnetic moment originates from two types of motions (i) its orbital motion around the nucleus and (ii) its spin around its own axis. Electron being a charged particle and undergoing these motions can be considered as a small loop of current which possesses a magnetic moment. Thus, each electron has a permanent spin and an orbital magnetic moment associated with it. Magnitude of this magnetic moment is very small and is measured in the unit called Bohr magneton,  $\mu_B$ . It is equal to  $9.27 \times 10^{-24} \text{A m}^2$ .

On the basis of their magnetic properties, substances can be classified into five categories:

(i) paramagnetic (ii) diamagnetic (iii) ferromagnetic (iv) antiferromagnetic and (v) ferrimagnetic.

(i) Paramagnetism: Paramagnetic substances are weakly attracted by a magnetic field. They are magnetised in a magnetic field in the same direction. They lose their magnetism in the absence of magnetic field. Paramagnetism is due to presence of one or more unpaired electrons which are attracted by the magnetic field.  $O_2$ ,  $Cu^{2+}$ ,  $Fe^{3+}$ ,  $Cr^{3+}$  are some examples of such substances.

(ii) Diamagnetism: Diamagnetic substances are weakly repelled by a magnetic field.  $H_2O$ ,  $NaCl$  and  $C_6H_6$  are some examples of such substances. They are weakly magnetised in a magnetic field in opposite direction. Diamagnetism is shown by those substances in which all the electrons are paired and there are no unpaired electrons. Pairing of electrons cancels their magnetic moments and they lose their magnetic character.



(iii) Ferromagnetism: A few substances like iron, cobalt, nickel, gadolinium and  $\text{CrO}_2$  are attracted very strongly by a magnetic field. Such substances are called ferromagnetic substances. Besides strong attractions, these substances can be permanently magnetised. In solid state, the metal ions of ferromagnetic substances are grouped together into small regions called domains. Thus, each domain acts as a tiny magnet. In an unmagnetised piece of a ferromagnetic substance the domains are randomly oriented and their magnetic moments get cancelled. When the substance is placed in a magnetic field all the domains get oriented in the direction of the magnetic field and a strong magnetic effect is produced. This ordering of domains persists even when the magnetic field is removed and the ferromagnetic substance becomes a permanent magnet.

(iv) Antiferromagnetism: Substances like  $\text{MnO}$  showing antiferromagnetism have domain structure similar to ferromagnetic substance, but their domains are oppositely oriented and cancel out each other's magnetic moment.

(v) Ferrimagnetism: Ferrimagnetism is observed when the magnetic moments of the domains in the substance are aligned in parallel and anti-parallel directions in unequal numbers. They are weakly attracted by magnetic field as compared to ferromagnetic substances.  $\text{Fe}_3\text{O}_4$  (magnetite) and ferrites like  $\text{MgFe}_2\text{O}_4$  and  $\text{ZnFe}_2\text{O}_4$  are examples of such substances. These substances also lose ferrimagnetism on heating and become paramagnetic.

## Some Important terms

**FOOL'S GOLD:** Some samples of Iron pyrites shine like gold due to exchange of electrons between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , which leads to metallic lustre. Such samples are known as fool's gold.

**PIEZOELECTRIC EFFECT AND PIEZOELECTRICITY:** The charge developed on the crystal due to mechanical stress is called piezoelectric effect and the current thus produced is called piezo electricity.

**PYROELECTRICITY:** The electric current produced by heating on the faces of a crystal is called pyroelectricity.

**LIQUID CRYSTALS (MESOMORPHIC OR PARA CRYSTALLINE) :** The substances having the properties of crystalline solids and flow properties of liquids. Examples: Para-azoxy anisole and Normal Octyl-para azoxy cinnamate. Such solids undergo two sharp phase transformations on fusion, first yielding turbid liquid and at higher temperature a clear liquid. The turbid liquids are called liquid crystals and are anisotropic in nature (a property of crystalline solid).

**MCQ (ONLY ONE OPTION IS CORRECT)**

1. A crystalline solid:

- (A) changes abruptly from solid to liquid when heated.
- (B) has no definite melting point.
- (C) undergoes deformation of its geometry easily
- (D) has irregular 3-dimensional arrangements.

2. Na and Mg crystallize in crystals of bcc and fcc form respectively and then the number of Na and Mg atoms present in their respective crystal unit cells is:

- (A) 4 and 2      (B) 9 and 14      (C) 14 and 9      (D) 2 and 4

3. For the orthorhombic system, axial ratios are  $a \neq b \neq c$  and the axial angles are:

- (A)  $\alpha = \beta = \gamma \neq 90^\circ$       (B)  $\alpha \neq \beta \neq \gamma \neq 90^\circ$   
(C)  $\alpha = \beta = \gamma = 90^\circ$       (D)  $\alpha \neq \beta \neq \gamma = 90^\circ$

4. The fraction of the total volume occupied by the atoms present in a simple cube is

- (a)  $\pi/4$       (b)  $\pi/6$       (c)  $\pi/3\sqrt{2}$       (d)  $\pi/4\sqrt{2}$

5. Edge length of unit cell of chromium metal is 287 pm with bcc arrangement. The atomic radius is of the order [Cr=52]

- (a) 287 pm      (b) 574 pm      (c) 124.27 pm      (d) 143.5 pm

6. The density of a metal which crystallises in bcc lattice with unit cell edge length 300 pm and molar mass 50 g mol<sup>-1</sup> will be

- (a) 10 g cm<sup>-3</sup>                      (b) 14.2 g cm<sup>-3</sup>                      (c) 6.15 g cm<sup>-3</sup>                      (d) 9.3 2 g cm<sup>-3</sup>

7. How many lithium atoms are present in a unit cell with edge length 3.5 Å and density 0.53 g cm<sup>-3</sup>?  
(Atomic mass of Li = 6.94):

- (a) 2                      (b) 1                      (c) 4                      (d) 6

8. Which of the following statements about amorphous solids is incorrect?

- (a) They melt over a range of temperature  
(b) They are anisotropic  
(c) There is no orderly arrangement of particles  
(d) They are rigid and incompressible

9. Most crystals show good cleavage because their atoms, ions or molecules are

- (a) weakly bonded together
- (b) strongly bonded together
- (c) spherically symmetrical
- (d) arranged in planes

10. Which of the following statement is not true about the hexagonal close packing?

- (a) The coordination number is 12.
- (b) It has 74% packing efficiency.
- (c) Tetrahedral voids of the second layer are covered by the spheres of the third layer.
- (d) In this arrangement spheres of the fourth layer are exactly aligned with those of the first layer.

11. "Crystalline solids are anisotropic in nature. What is the meaning of anisotropic in the given statement?

- (a) A regular pattern of arrangement of particles which repeats itself periodically over the entire crystal.
- (b) Different values of some of physical properties are shown when measured along different directions in the same crystals.
- (c) An irregular arrangement of particles over the entire crystal.
- (d) Same values of some of physical properties are shown when measured along different directions in the same crystals.

12. Which of the following is not a characteristic of a crystalline solid ?

- (a) Definite and characteristic heat of fusion.
- (b) Isotropic nature.
- (c) A regular periodically repeated pattern of arrangement of constituent particles in the entire crystal.
- (d) A true solid

13. In face-centred cubic lattice, a unit cell is shared equally by how many unit cells

- (a) 2          (b) 4          (c) 6          (d) 8

14. In which pair most efficient packing is present?

- (a) hcp and bcc          (b) hcp and ccp  
(c) bcc and ccp          (d) bcc and simple cubic cell

15. Iodine molecules are held in the crystals lattice by \_\_\_\_\_.

- (a) london forces          (b) dipole-dipole interactions  
(c) covalent bonds          (d) coulombic forces



16. Which of the following is a network solid?

- (a)  $\text{SO}_2$  (Solid)      (b)  $\text{I}_2$       (c) Diamond      (d)  $\text{H}_2\text{O}$  (Ice)

Q.17. A mixed oxide has ccp arrangement in which the cations 'X' occupy  $\frac{1}{3}$ rd of octahedral voids and the cations 'Y' occupy  $\frac{1}{3}$ rd of tetrahedral voids. The formula of oxide is:

- (A)  $\text{X}_2\text{Y}_3\text{O}_2$       (B)  $\text{XY}_3\text{O}$       (C)  $\text{X}_2\text{YO}_3$       (D)  $\text{XY}_2\text{O}_3$

Q.18. Alkali halides do not show Frenkel defect because

- (a) cations and anions have almost equal size  
(b) there is a large difference in size of cations and anions  
(c) cations and anions have low coordination number  
(d) anions cannot be accommodated in voids

Q.19. The point defect noticed when AgCl is doped with  $\text{CdCl}_2$  is :

- (A) Frenkel Defect
- (B) Vacancy Defect
- (C) Metal excess Defect
- (D) Impurity Defect

Q20. An element possess cubic close packing structure. Calculate the radius (r) of the atom in the unit cell. (The edge length of unit cell is  $a=252 \text{ nm}$ )

- (A) 89.36 nm
- (B) 126 nm
- (C) 152 nm
- (D) 109.1 nm

Q.21. In NaCl structure

- (a) all octahedral and tetrahedral sites are occupied
- (b) only octahedral sites are occupied
- (c) only tetrahedral sites are occupied
- (d) neither octahedral nor tetrahedral sites are occupied

Q.22. In Zinc blende structure

- (a) zinc ions occupy half of the tetrahedral sites
- (b) each  $\text{Zn}^{2+}$  ion is surrounded by six sulphide ions
- (c) each  $\text{S}^{2-}$  ion is surrounded by six  $\text{Zn}^{2+}$  ions
- (d) it has fcc structure

Q.23. The distance between  $\text{Na}^+$  and  $\text{Cl}^-$  ions in NaCl with a density  $2.165 \text{ g cm}^{-3}$  is

- (a) 564 pm
- (b) 282 pm
- (c) 234 pm
- (d) 538 pm

Q.24. What is the effect of Frenkel defect on the density of ionic solids?

- (a) The density of the crystal increases
- (b) The density of the crystal decreases
- (c) The density of the crystal remains unchanged
- (d) There is no relationship between density of a crystal and defect present in it

Q.25. How many unit cells are present in a cube-shaped ideal crystal of NaCl of mass 1.00 g? [Atomic masses : Na = 23, Cl = 35.5]

- (a)  $2.57 \times 10^{21}$  unit cells                      (b)  $5.14 \times 10^{21}$  unit cells  
(c)  $1.28 \times 10^{21}$  unit cells                      (d)  $1.71 \times 10^{21}$  unit cells

26. A metallic crystal crystallizes into a lattice containing a sequence of layers AB AB AB.....Any packing of spheres leaves out voids in the lattice. What percentage of volume of this lattice is empty space?

- (a) 74%                      (b) 26%                      (c) 50%                      (d) none of these.

27. The interionic distance for cesium chloride crystal will be

- (a)  $a$                       (b)  $a/2$                       (c)  $\sqrt{3}a/2$                       (d)  $2a/\sqrt{3}$

28. A semiconductor of Ge can be made p-type by adding

- (a) trivalent impurity      (b) tetravalent impurity  
(c) pentavalent impurity    (d) divalent impurity

29. The second order Bragg diffraction of X-rays with  $\lambda = 1.0 \text{ \AA}$  from a set of parallel planes in a metal occurs at an angle of  $60^\circ$ . The distance between the scattering planes in the crystal is

- (a)  $0.575 \text{ \AA}$  (b)  $1.00 \text{ \AA}$  (c)  $2.00 \text{ \AA}$  (d)  $1.15 \text{ \AA}$

30. If NaCl is doped with  $10^{-4}$  mol % of  $\text{SrCl}_2$ , the concentration of cation vacancies will be ( $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$ )

- (a)  $6.02 \times 10^{16} \text{ mol}^{-1}$       (b)  $6.02 \times 10^{17} \text{ mol}^{-1}$   
(c)  $6.02 \times 10^{14} \text{ mol}^{-1}$       (d)  $6.02 \times 10^{15} \text{ mol}^{-1}$