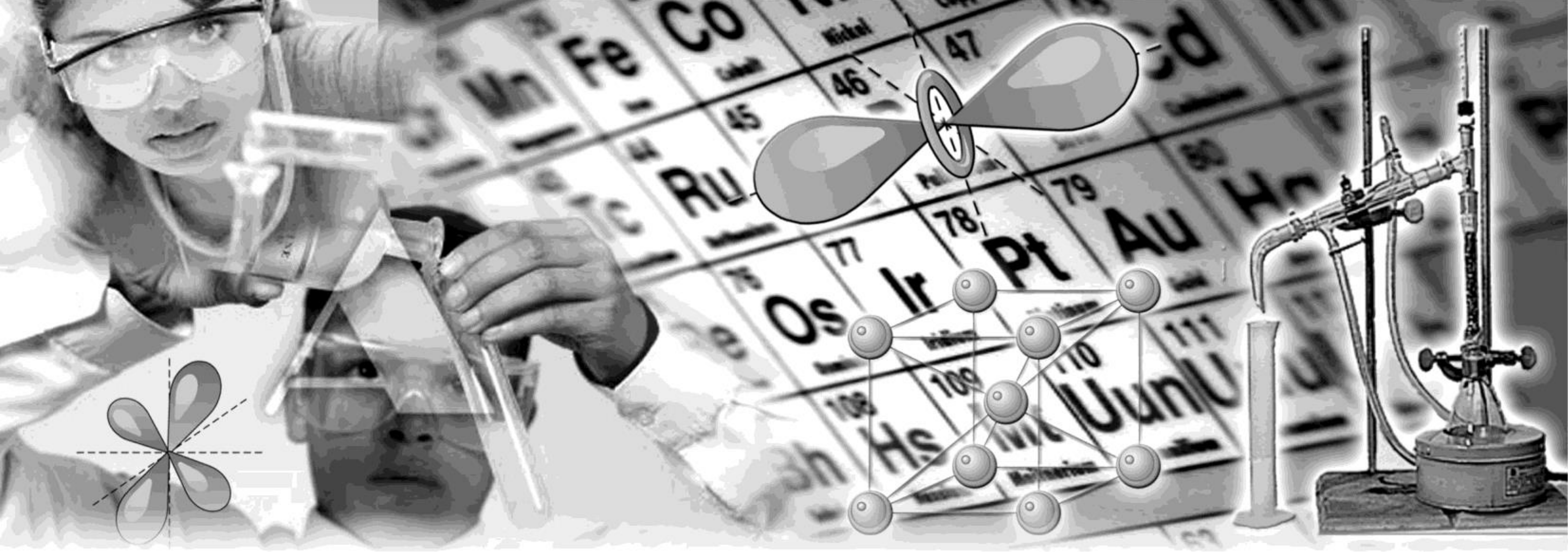


Chapter 5

Solid State

The solids are the substances which have definite volume and definite shape. In terms of kinetic molecular model, solids have regular order of their constituent particles (atoms, molecules or ions). These particles are held together by fairly strong forces, therefore, they are present at fixed positions. The properties of the solids not only depend upon the nature of the constituents but also on their arrangements.

Types and Classification of solids

(1) **Types of solids**

Solids can be broadly classified into following two types,

(i) Crystalline solids/True solids,

(ii) Amorphous solids/Pseudo solids

Crystalline solids	Amorphous solids
They have long range order.	*They have short range order.*
They have definite melting point	Not have definite melting point
They have a definite heat of fusion	Not have definite heat of fusion
They are rigid and incompressible	Not be compressed to any appreciable extent
They are given cleavage *i.e.* they break into two pieces with plane surfaces	They are given irregular cleavage *i.e.* they break into two pieces with irregular surface
They are anisotropic because of these substances show different property in different direction	*They are isotropic because of these substances show same property in all directions*
There is a sudden change in volume when it melts.	There is no sudden change in volume on melting.
These possess symmetry	Not possess any symmetry.
These possess interfacial angles.	Not possess interfacial angles.

(2) **Crystalline and amorphous silica** (SiO_2)

Silica occurs in crystalline as well as amorphous states. Quartz is a typical example of crystalline silica. Quartz and the amorphous silica differ considerably in their properties.

Quartz	Amorphous silica
It is crystalline in nature	It is light (fluffy) white powder
All four corners of SiO_4^{4-} tetrahedron are shared by others to give a network solid	The SiO_4^{4-} tetrahedra are randomly joined, giving rise to polymeric chains, sheets or three-dimensional units
It has high and sharp melting point (1710°C)	It does not have sharp melting point

(3) **Diamond and graphite**

Diamond and graphite are tow allotropes of carbon. Diamond and graphite both are covalent crystals. But, they differ considerably in their properties.

Diamond	Graphite
It occurs naturally in free state	It occurs naturally, as well as manufactured artificially

It is the hardest natural substance known.	It is soft and greasy to touch
It has high relative density (about 3.5)	Its relative density is 2.3
It is transparent and has high refractive index (2.45)	It has black in colour and opaque
It is non-conductor of heat and electricity.	Graphite is a good conductor of heat and electricity
It burns in air at 900°C to give CO_2	It burns in air at 700°C to give CO_2
It occurs as octahedral crystals	It occurs as hexagonal crystals

(4) **Classification of crystalline solids**

Table : 5.1 Some characteristics of different types of crystalline solids

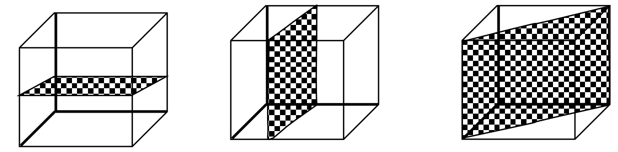
Types of Solid	Constituents	Bonding	Examples	Physical Nature	M.P.	B.P.	Electrical Conductivity
Ionic	Positive and negative ions network systematically arranged	Coulombic	$NaCl$, KCl, CaO, MgO, LiF, ZnS, $BaSO_4$ and K_2SO_4 etc.	Hard but brittle	High ($\simeq$1000K)	High ($\simeq$2000K)	Conductor (in molten state and in aqueous solution)
Covalent	Atoms connected in covalent bonds	Electron sharing	SiO_2 (Quartz), SiC, C (diamond), C(graphite) etc.	Hard Hard Hard	Very high ($\simeq$4000K)	Very high ($\simeq$5000K)	Insulator except graphite
Molecular	Polar or non-polar molecules	(i) Molecular interactions (intermolecular forces) (ii) Hydrogen bonding	I_2,S_8, P_4, CO_2, CH_4, CCl_4 etc. Starch, sucrose, water, dry ice or drycold (solid CO_2) etc.	Soft Soft	Low ($\simeq$300K to 600K) Low ($\simeq$400K)	Low ($\simeq$ 450 to 800 K) Low ($\simeq$373K to 500K)	Insulator Insulator
Metallic	Cations in a sea of electrons	Metallic	Sodium , Au, Cu, magnesium, metals and alloys	Ductile malleable	High ($\simeq$800K to 1000 K)	High ($\simeq$1500K to 2000K)	Conductor
Atomic	Atoms	London dispersion force	Noble gases	Soft	Very low	Very low	Poor thermal and electrical conductors

Crystallography

"*The branch of science that deals with the study of structure, geometry and properties of crystals is called crystallography*".

(1) **Symmetry in Crystal :** A crystal possess following three types of symmetry,

(i) ***Plane of symmetry*** **:** It is an imaginary plane which passes through the centre of a crystal can divides it into two equal portions which are exactly the mirror images of each other.

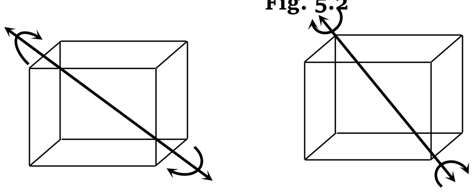


Plane of symmetry Rectangular plane of symmetry Diagonal plane of symmetry

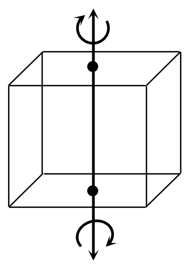
Fig. 5.1

(ii) ***Axis of symmetry*** **:** An axis of symmetry or axis of rotation is an imaginary line, passing through the crystal such that when the crystal is rotated about this line, it presents the same appearance more than once in one complete revolution *i.e.*, in a rotation through 360°. Suppose, the same appearance of crystal is repeated, on rotating it through an angle of 360°/n, around an imaginary axis, is called an ***n*-fold axis** where, n is known as the order of axis. By order is meant the value of n in $2\pi/n$ so that rotation through $2\pi/n$, gives an equivalent configuration.

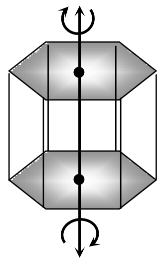
Fig. 5.2



Axis of two fold Axis of three f old symmetry



Axis of four fold symmetry



Axis of six fold

(iii) ***Centre of symmetry* :** It is an imaginary point in the crystal that any line drawn through it intersects the surface of the crystal at equal distance on either side.

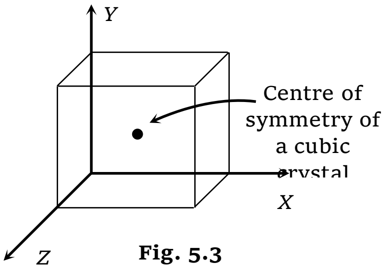


Fig. 5.3

Only simple cubic system have one centre of symmetry. Other system do not have centre of symmetry.

The total number of planes, axes and centre of symmetries possessed by a crystal is termed as **elements of symmetry**.

A cubic crystal possesses total 23 elements of symmetry.

Plane of symmetry	(3 + 6)	= 9
Axes of symmetry	(3 + 4 + 6)	= 13
Centre of symmetry	(1)	= 1
	Total symmetry = 23	

(2) **Laws of crystallography :** Crystallography is based on three fundamental laws.

(i) ***Law of constancy of interfacial angles* :** This law states that angle between adjacent corresponding faces is inter facial angles of the crystal of a particular substance is always constant inspite of different shapes and sizes and mode of growth of crystal. The size and shape of crystal depend upon the conditions of crystallisation. This law is also known as **Steno's Law**.

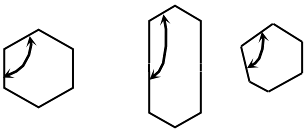


Fig. 5.4. Constancy of interfacial

(ii) ***Law of rational indices* :** This law states that the ratio of intercepts of different faces of a crystal with the three axes are constant and can be expressed by rational numbers that the intercepts of any face of a crystal along the crystallographic axes are either equal to unit intercepts (i.e., intercepts made by unit cell) a, b, c or some simple whole number multiples of them e.g., na, $n'\,b$, $n''c$, where n, n' and n'' are simple whole numbers. The whole numbers n, n' and n'' are called **Weiss indices.** This law was given by **Hauy.**

(iii) ***Law of constancy of symmetry* :** According to this law, all crystals of a substance have the same elements of symmetry is plane of symmetry, axis of symmetry and centre of symmetry.

Miller indices : Planes in crystals are described by a set of integers (h, k and l) known as Miller indices. Miller indices of a plane are the reciprocals of the fractional intercepts of that plane on the various crystallographic axes. For calculating Miller indices, a reference plane, known as parametral plane, is selected having intercepts a, b and c along x, y and z-axes, respectively. Then, the intercepts of the unknown plane are given with respect to a, b and c of the parametral plane.

Thus, the Miller indices are :

$$h = \frac{a}{\text{intercept of the plane along } x\text{ - axis}}$$

$$k = \frac{b}{\text{intercept of the plane along } y\text{ - axis}}$$

$$l = \frac{c}{\text{intercept of the plane along } z\text{ - axis}}$$

The distance between the parallel planes in crystals are designated as d_{hkl}. For different cubic lattices these interplanar spacing are given by the general formula,

$$d_{(hkl)} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Where a is the length of cube side while h, k and l are the Miller indices of the plane.

When a plane is parallel to an axis, its intercept with that axis is taken as infinite and the Miller will be zero.

Negative signs in the Miller indices is indicated by placing a bar on the intercept. All parallel planes have same Miller indices.

Space lattice and Unit cell

Crystal is a homogeneous portion of a crystalline substance, composed of a regular pattern of structural units (ions, atoms or molecules) by plane surfaces making definite angles with each other giving a regular geometric form.

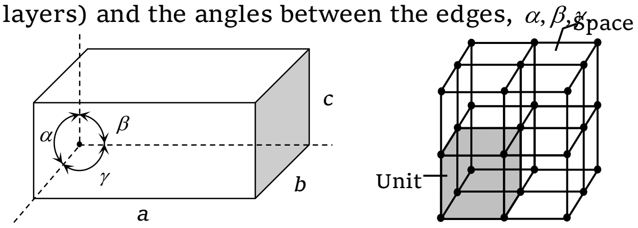
A regular array of points (showing atoms/ions) in three dimensions is commonly called as a **space lattice**, or lattice.

Each point in a space lattice represents an atom or a group of atoms.

Each point in a space lattice has identical surroundings throughout.

A three dimensional group of lattice points which when repeated in space generates the crystal called **unit cell**.

The unit cell is described by the lengths of its edges, *a*, *b*, *c* (which are related to the spacing between layers) and the angles between the edges, α, β, γ



Unit cell

Fig. 5.5

Space lattice & unit

Types of units cells

A units cell is obtained by joining the lattice points. The choice of lattice points to draw a unit cell is made on the basis of the external geometry of the crystal, and symmetry of the lattice. There are four different types of unit cells. These are,

(1) **Primitive or simple cubic** (sc) **:** Atoms are arranged only at the corners of the unit cell.

(2) **Body centred cubic** (bcc) **:** Atoms are arranged at the corners and at the centre of the unit cell.

(3) **Face centred cubic** (fcc) **:** Atoms are arranged at the corners and at the centre of each faces of the unit cell.

(4) **Side centered :** Atoms are arranged at the centre of only one set of faces in addition to the atoms at the corner of the unit cell.

Formation of crystal and Crystal systems

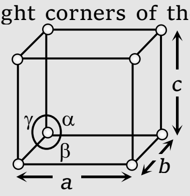
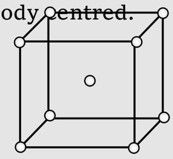
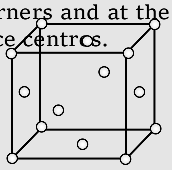
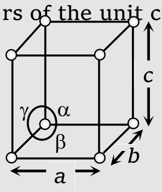
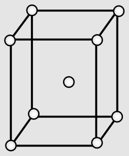
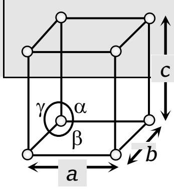
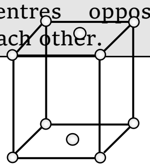
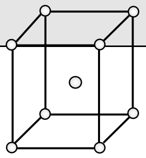
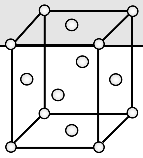
The crystals of the substance are obtained by cooling the liquid (or the melt) of the solution of that substance. The size of the crystal depends upon the rate of cooling. If cooling is carried out slowly, crystals of large size are obtained because the particles (ions, atoms or molecules) get sufficient time to arrange themselves in proper positions.

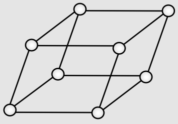
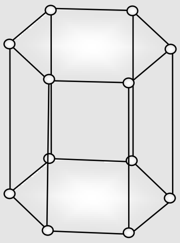
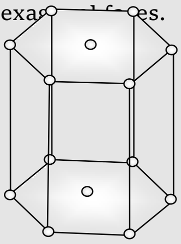
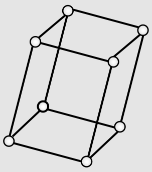
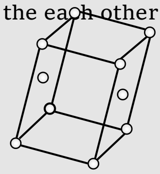
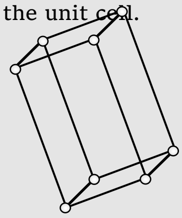
$$\text{Atoms of molecules} \xrightarrow{\text{Dissolved}} \text{cluster} \xrightarrow{\text{dissolved}} \text{dissolved embryo} \rightarrow \underset{\text{(unstable)}}{\text{nucleus}} \rightarrow \text{crystal}$$

(If loosing units dissolves as embryo and if gaining unit grow as a crystals).

Bravais (1848) showed from geometrical considerations that there can be only 14 different ways in which similar points can be arranged. Thus, there can be only 14 different space lattices. These 14 types of lattices are known as **Bravais Lattices**. But on the other hand Bravais showed that there are only seven types of crystal systems.

Table : 5.2 Bravais lattices corresponding to different crystal systems

Crystal system	Space lattice				Examples
Cubic $a = b = c$, $\alpha = \beta = \gamma = 90^o$	**Simple :** Lattice points at the eight corners of the unit cells. 	**Body centered :** Points at the eight corners and at the body centred. 	**Face centered :** Points at the eight corners and at the six face centres. 		$Pb, Hg, Ag,$ Au, Cu, ZnS , diamond, $KCl,$ $CsCl, NaCl,$ Cu_2O, CaF_2 and alums. etc.
Tetragonal $a = b \neq c$, $\alpha = \beta = \gamma = 90^o$	**Simple :** Points at the eight corners of the unit cell. 	**Body centered :** Points at the eight corners and at the body centre 			$SnO_2, TiO_2,$ $ZnO_2, NiSO_4$ $ZrSiO_4 . PbWO_4$, white Sn etc.
Orthorhombic (Rhombic) $a \neq b \neq c$, $\alpha = \beta = \gamma = 90^o$	**Simple:** Points at the eight corners of the unit cell. 	**End centered :** Also called side centered or base centered. Points at the eight corners and at two face centres opposite to each other. 	**Body centered :** Points at the eight corners and at the body centre 	**Face centered:** Points at the eight corners and at the six face centres. 	KNO_3, K_2SO_4 , $PbCO_3, BaSO_4$, rhombic sulphur, $MgSO_4 . 7H_2O$ etc.

Rhombohedral or **Trigonal** $a = b = c$, $\alpha = \beta = \gamma \neq 90^\circ$	**Simple :** Points at the eight corners of the unit cell 		$NaNO_3$, $CaSO_4$, calcite, quartz, As, Sb, Bi etc.
Hexagonal $a = b \neq c$, $\alpha = \beta = 90^o$ $\gamma = 120^o$	**Simple :** Points at the twelve corners of the unit cell out lined by thick line. 	**or** Points at the twelve corners of the hexagonal prism and at the centres of the two hexagonal faces. 	ZnO, PbS, CdS, HgS, graphite, ice, Mg, Zn, Cd etc.
Monoclinic $a \neq b \neq c$, $\alpha = \gamma = 90^o, \beta \neq 90^o$	**Simple :** Points at the eight corners of the unit cell 	**End centered :** Point at the eight corners and at two face centres opposite to the each other. 	$Na_2SO_4.10H_2O$, $Na_2B_4O_7.10H_2O$, $CaSO_4.2H_2O$, monoclinic sulphur etc.
Triclinic $a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90^o$	**Simple :** Points at the eight corners of the unit cell. 		$CaSO_4.5H_2O$, $K_2Cr_2O_7$, H_3BO_3 etc.

Analysis of cubic system

(1) **Number of atoms in per unit cell**

The total number of atoms contained in the unit cell for a simple cubic called the unit cell content.

The simplest relation can determine for it is, $\frac{n_c}{8} + \frac{n_f}{2} + \frac{n_i}{1}$

Where $n_c =$ Number of atoms at the corners of the cube=8

$n_f =$ Number of atoms at six faces of the cube = 6

$n_i =$ Number of atoms inside the cube = 1

Cubic unit cell	n_c	n_f	n_i	Total atom in per unit cell
Simple cubic (*sc*)	8	0	0	1
body centered cubic (*bcc*)	8	0	1	2
Face centered cubic (*fcc*)	8	6	0	4

(2) **Co-ordination number (C.N.) :** It is defined as the number of nearest neighbours or touching particles with other particle present in a crystal is called its co-ordination number. It depends upon structure of the crystal.

For simple cubic system C.N. = 6.

For body centred cubic system C.N. = 8

For face centred cubic system C.N. = 12.

(3) **Density of the unit cell** (ρ) **:** It is defined as the ratio of mass per unit cell to the total volume of unit cell.

$$\rho = \frac{Z \times M}{a^3 \times N_0}$$

Where Z = Number of particles per unit cell

M = Atomic mass or molecular mass

$N_0 =$ Avogadro number $(6.023 \times 10^{23} mol^{-1})$

$a =$ Edge length of the unit cell= $a\ pm = a \times 10^{-10}\ cm$

$a^3 =$ volume of the unit cell

i.e. $\rho = \dfrac{Z \times M}{a^3 \times N_0 \times 10^{-30}} g/cm^3$

The density of the substance is same as the density of the unit cell.

(4) **Packing fraction** (P.F.) **:** It is defined as ratio of the volume of the unit cell that is occupied by spheres of the unit cell to the total volume of the unit cell.

Let radius of the atom in the packing $= r$

Edge length of the cube = *a*

Volume of the cube *V* = a^3

Volume of the atom (spherical) $v = \dfrac{4}{3}\pi r^3$

Packing density $= \dfrac{vZ}{V} = \dfrac{\frac{4}{3}\pi r^3 Z}{a^3}$

Structure	***r* related to a**	**Volume of the atom (*v*)**	**Packing density**	**% of void**
Simple cubic	$r = \dfrac{a}{2}$	$\dfrac{4}{3}\pi\left(\dfrac{a}{2}\right)^3$	$\dfrac{\pi}{6} = 0.52$	100–52 = 48%
Face-centred cubic	$r = \dfrac{a}{2\sqrt{2}}$	$\dfrac{4}{3}\pi\left(\dfrac{a}{2\sqrt{2}}\right)^3$	$\dfrac{\sqrt{2}\pi}{6} = 0.74$	100 – 74 = 26%
Body-centred cubic	$r = \dfrac{\sqrt{3}a}{4}$	$\dfrac{4}{3}\pi\left(\dfrac{\sqrt{3}a}{4}\right)^3$	$\dfrac{\sqrt{3}\pi}{8} = 0.68$	100 – 68 = 32%

X-ray study of crystal structure

Study of internal structure of crystal can be done with the help of X-rays. The distance of the constituent particles can be determined from diffraction value by **Bragg's equation.**

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

where, λ = Wave length of X-rays, *n* = order of reflection, $\theta =$ Angle of reflection, *d* = Distance between two parallel surfaces

The above equation is known as **Bragg's equation** or **Bragg's law**. The reflection corresponding to *n* = 1 (for a given family of planes) is called first order reflection; the reflection corresponding to *n* = 2 is the second order reflection and so on. Thus by measuring *n* (the order of reflection of the X-rays) and the incidence angle θ, we can know d/λ.

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

From this, *d* can be calculated if λ is known and vice versa. In X-ray reflections, *n* is generally set as equal to 1. Thus Bragg's equation may alternatively be written as

$$\lambda = 2d\sin\theta = 2\, d_{hkl}\sin\theta$$

Where d_{hkl} denotes the perpendicular distance between adjacent planes with the indices *hkl*.

Close packing in crystalline solids

In the formation of crystals, the constituent particles (atoms, ions or molecules) get closely packed together. The closely packed arrangement is that in which maximum available space is occupied. This corresponds to a state of maximum density. The closer the packing, the greater is the stability of the packed system.

(1) **Close packing in two dimensions :** The two possible arrangement of close packing in two dimensions.

(i) ***Square close packing*** : In which the spheres in the adjacent row lie just one over the other and show a horizontal as well as vertical alignment and form square. In this arrangement each sphere is in contact with four spheres.

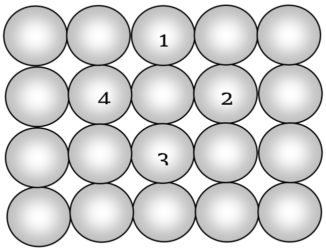


Fig. 5.6. Square close packing

(ii) ***Hexagonal close packing*** **:** In which the spheres in every second row are seated in the depression between the spheres of first row. The spheres in the third row are vertically aligned with spheres in first row. The similar pattern is noticed throughout the crystal structure. In this arrangement each sphere is in [illegible]heres.

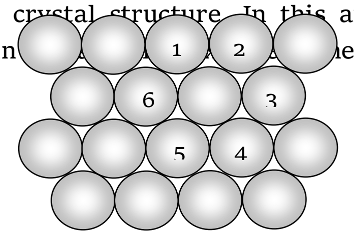


Fig. 5.7. Hexagonal close packing

(2) **Close packing in three dimensions :** In order to develop three dimensional close packing, let us retain the hexagonal close packing in the first layer. For close packing, each spheres in the second layer rests in the hollow at the centre of three touching spheres in the layer as shown in figure. The spheres in the first layer are shown by solid lines while those in

second layer are shown by broken lines. It may be noted that only half of the triangular voids in the first layer are occupied by spheres in the second layer (*i.e.*, either b or c). The unoccupied hollows or voids in the first layer are indicated by (c) in figure.

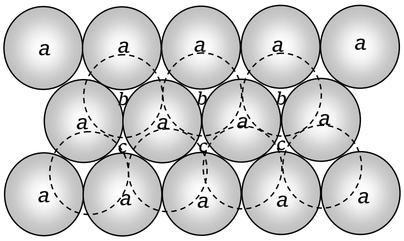


Fig. 5.8. Close packing in three dimensions

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

(i) ***Hexagonal close packing*** **:** The third layer lies vertically above the first and the spheres in third layer rest in one set of hollows on the top of the second layer. This arrangement is called **ABAB ....** type and 74% of the available space is occupied by spheres. This arrangement is found in *Be, Mg, Zn, Cd, Sc, Y, Ti, Zr, Tc, Ru.*

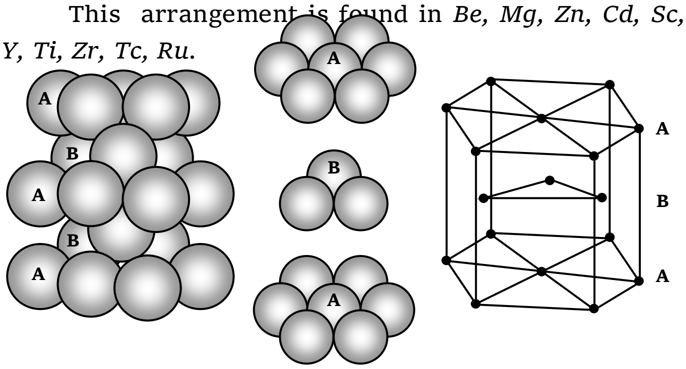


Fig. 5.9. Hexagonal close packing (*hcp*) in three

(ii) ***Cubic close packing*** **:** The third layer is different from the first and the spheres in the third layer lie on the other set of hollows marked 'C' in the first layer. This arrangement is called **ABCABC.....** type and in this also 74% of the available space is occupied by spheres. The cubic close packing has face centred cubic (*fcc*) unit cell. This arrangement is found in *Cu, Ag, Au, Ni, Pt, Pd, Co, Rh, Ca, Sr.*

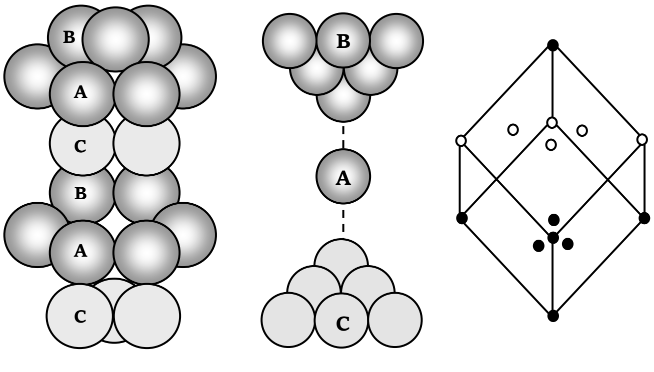


Fig. 5.10. Cubic close packing (*ccp* or *fcc*) in three

(iii) ***Body centred cubic*** **:** This arrangement of spheres (or atoms) is not exactly close packed. This structure can be obtained if spheres in the first layer (A) of close packing are slightly opened up. As a result none of these spheres are in contact with each other. The second layer of spheres (B) can be placed on top of the first layer so that each sphere of the second layer is in contact with four spheres of the layer below it. Successive building of the third will be exactly like the first layer. If this pattern of building layers is repeated infinitely we get an arrangement as shown in figure. This arrangement is found in *Li, Na, K, Rb, Ba, Cs, V, Nb, Cr, Mo, Fe.*

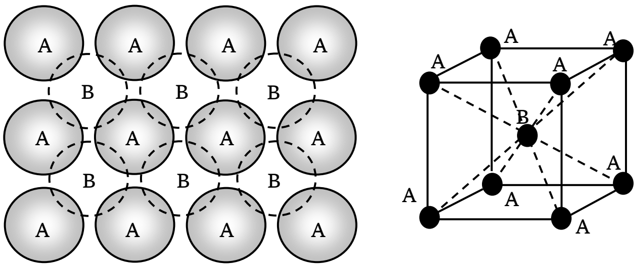


Fig. 5.11. Body centred cubic (*bcc*) close packing in three dimensions

Table : 5.3 Comparison of *hcp*, *ccp* and *bcc*

Property	***hcp***	***ccp***	***bcc***
Arrangement of packing	Close packed	Close packed	Not close packed
Type of packing	AB AB A...	ABC ABC A...	AB AB A...
Available space occupied	74%	74%	68%
Coordination number	12	12	8
Malleability and ductility	Less malleable, hard, brittle	Malleable and ductile	

Interstitial sites in close packing

Even in the close packing of spheres, there is left some empty space between the spheres. This empty space in the crystal lattice is called site or void or hole. Voids are of following types,

(1) **Trigonal void :** This site is formed when three spheres lie at the vertices of an equilateral triangle. Size of the trigonal site is given by the following relation,

$$r = 0.155\,R$$

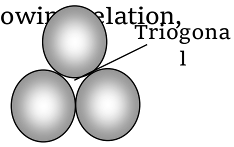


Fig. 5.12

r = Radius of the spherical trigonal void

R = Radius of closely packed spheres

(2) **Tetrahedral void :** A tetrahedral void is developed when triangular voids (made by three spheres in one layer touching each other) have contact with one sphere either in the upper layer or in the lower layer.

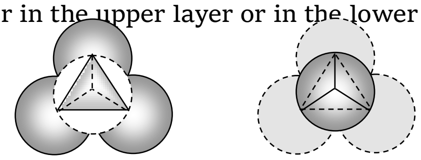


Fig. 5.13. Tetrahedral void

The number of tetrahedral voids is double the number of spheres in the crystal structure.

$$\frac{r}{R} = 0.225$$

where, r is the radius of the tetrahedral void or atom occupying tetrahedral void.

R is the radius of spheres forming tetrahedral void.

(3) **Octahedral void :** This type of void is surrounded by six closely packed spheres, *i.e.* it is formed by six spheres.

The number of octahedral voids is equal to the number of spheres.

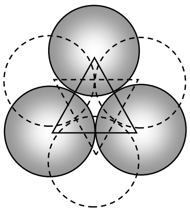


Fig. 5.14. Octahedral void

$$\frac{r}{R} = 0.414$$

(4) **Cubic void :** This type of void is formed between 8 closely packed spheres which occupy all the eight corner of cube.

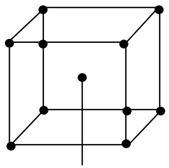


Fig. 5.15. Cubic void

$$\frac{r}{R} = 0.732$$

The decreasing order of the size of the various voids is,

Cubic > Octahedral > Tetrahedral > Trigonal

Ionic radii and Radius ratio

(1) **Ionic radii :** X-ray diffraction or electron diffraction techniques provides the necessary information regarding unit cell. From the dimensions of the unit cell, it is possible to calculate ionic radii.

Let, cube of edge length 'a' having cations and anions say $NaCl$ structure.

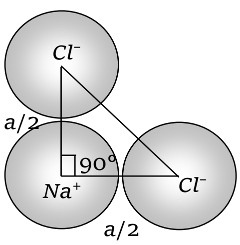


Fig. 5.16. Radii of chloride

Then, $r_c + r_a = a/2$

where r_c and r_a are radius of cation and anion.

$$\text{Radius of } Cl^- = \sqrt{\frac{(a/2)^2 + (a/2)^2}{2}} = \frac{a}{4}$$

$$\text{For bcc lattice say } CsCl. \ r_c + r_a = \frac{\sqrt{3}a}{2}$$

(2) **Radius ratio :** Ionic compounds occur in crystalline forms. Ionic compounds are made of cations and anions. These ions are arranged in three dimensional array to form an aggregate of the type $(A^+B^-)_n$. Since, the Coulombic forces are non-directional, hence the structures of such crystals are mainly governed by the ratio of the radius of cation (r_+) to that of anion (r_-). The ratio r_+ to r_- (r_+/r_-) is called as radius ratio.

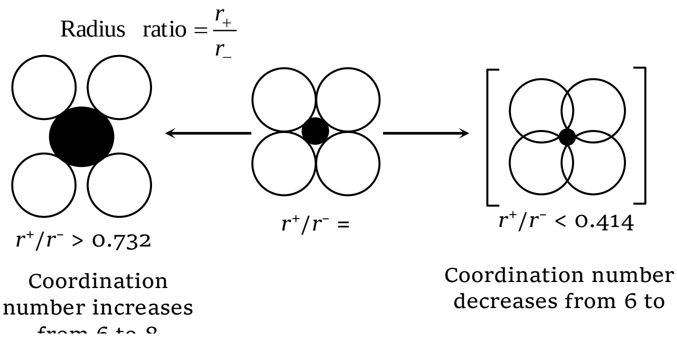


Fig. 5.17. Effect of radius ratio on co-ordination number

Table : 5.4 Limiting Radius ratios and Structure

Limiting radius ratio $(r^+)/(r^-)$	C.N.	Shape
< 0.155	2	Linear
0.155 – 0.225	3	Planar triangle
0.225 – 0.414	4	Tetrahedral
0.414 – 0.732	6	Octahedral
0.732 – 0.999 or 1	8	Body-centered cubic

Effect of temperature and Pressure on C.N.

On applying high pressure $NaCl$ structure having $6:6$ co-ordination changes to $CsCl$ structure having $8:8$ co-ordination. Thus, increase in pressure increases the co-ordination number.

Similarly, $CsCl$ structure on heating to about 760 K, changes to $NaCl$ structure. In other words, increase of temperature decreases the co-ordination number.

$$\underset{\text{Temp}}{\overset{\text{Pressur}}{\rightleftharpoons}}$$

$\underset{(6:6)}{NaCl}$ $\underset{(8:8)}{CsCl}$

Structure of ionic crystals

Table : 5.5 Types of ionic crystal with description

Crystal structure type	Brief description	Examples	Co-ordination number	Number of formula units per unit cell
Type AB *Rock salt (NaCl) type*	It has *fcc* arrangement in which Cl^- ions occupy the corners and face centres of a cube while Na^+ ions are present at the body and edge of centres.	Halides of *Li*, *Na*, *K*, *Rb*, *AgF*, *AgBr*, NH_4Cl, NH_4Br, NH_4I etc.	$Na^+ = 6$ $Cl^- = 6$	4
Zinc blende (ZnS) type	It has *ccp* arrangement in which S^{2-} ions form *fcc* and each Zn^{2+} ion is surrounded tetrahedrally by four S^{2-} ions and vice versa.	$CuCl, CuBr, CuI, AgI, BeS$	$Zn^{2+} = 4$ $S^{2-} = 4$	4
Type AB_2 *Fluorite (CaF_2) type*	It has arrangement in which Ca^{2+} ions form *fcc* with each Ca^{2+} ions surrounded by $8F^-$ ions and each F^- ions by $4Ca^{2+}$ ions.	$BaF_2, BaCl_2, SrF_2$ $SrCl_2, CdF_2, PbF_2$	$Ca^{2+} = 8$ $F^- = 4$	4
Antifluorite type	Here negative ions form the *ccp* arrangement so that each positive ion is surrounded by 4 negative ions and each negative ion by 8 positive ions	Na_2O	$Na^+ = 4$ $O^{2-} = 8$	4
Caesium chloride (CsCl) type	It has the *bcc* arrangement with Cs^+ at the body centre and Cl^- ions at the corners of a cube or vice versa.	$CsCl, CsBr, CsI, CsCN$, $TlCl, TlBr, TlI$ and $TlCN$	$Cs^+ = 8$ $Cl^- = 8$	1

Defects or Imperfections in solids

Any deviation from the perfectly ordered arrangement constitutes a defect or imperfection. These defects sometimes called thermodynamic defects because the number of these defects depend on the temperature.

(1) **Electronic imperfections :** Generally, electrons are present in fully occupied lowest energy states. But at high temperatures, some of the electrons may occupy higher energy state depending upon the temperature. For example, in the crystals of pure *Si* or *Ge* some electrons are released thermally from the covalent bonds at temperature above 0 K. these electrons are free to move in the crystal and are responsible for electrical conductivity. This type of conduction is known as **intrinsic conduction**. The electron deficient bond formed by the release of an electron is called a hole. In the presence of electric field the positive holes move in a direction opposite to that of the electrons and conduct electricity. The electrons and holes in solids gives rise to electronic imperfections.

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

(i) ***Stoichiometric defects*** **:** The compounds in which the number of positive and negative ions are exactly in the ratios indicated by their chemical formulae are called stoichiometric compounds. The defects do not disturb the stoichiometry (the ratio of numbers of positive and negative ions) are called stoichiometric defects. These are of following types,

(a) Interstitial defect : This type of defect is caused due to the presence of ions in the normally vacant interstitial sites in the crystals.

(b) Schottky defect : This type of defect when equal number of cations and anions are missing from their lattice sites so that the electrical neutrality is maintained. This type of defect occurs in highly ionic compounds which have high co-ordination number and cations and anions of similar sizes. *e.g.*, *NaCl, KCl, CsCl* and *KBr* etc.

(c) Frenkel defect : This type of defect arises when an ion is missing from its lattice site and occupies an interstitial position**.** The crystal as a whole remains electrically neutral because the number of anions and cations remain same. Since cations are usually smaller than anions, they occupy interstitial sites. This type of defect occurs in the compounds which have low co-ordination number and cations and anions of different sizes. *e.g., ZnS, AgCl* and *AgI* etc. Frenkel defect are not found in pure alkali metal halides because the cations due to larger size cannot get into the interstitial sites. ***In AgBr both Schottky and Frenkel defects occur simultaneously.***

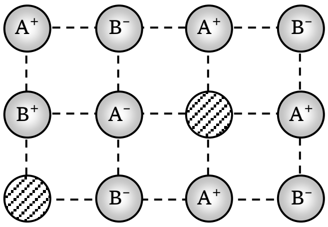


Fig. 5.18. Schottky defect

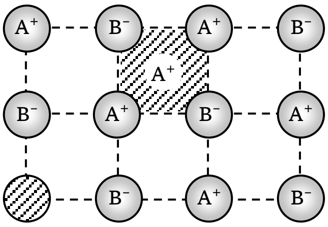


Fig. 5.19. Frenkel defect

Consequences of Schottky and Frenkel defects

Presence of large number of Schottky defect lowers the density of the crystal. When Frenkel defect alone is present, there is no decrease in density. The closeness of the charge brought about by Frenkel defect tends to increase the dielectric constant of the crystal. Compounds having such defect conduct electricity to a small extent. When electric field is applied, an ion moves from its lattice site to occupy a hole, it creates a new hole. In this way, a hole moves from one end to the other. Thus, it conducts electricity across the crystal. Due to the presence of holes, stability (or the lattice energy) of the crystal decreases.

(ii) ***Non-stoichiometric defects*** **:** The defects which disturb the stoichiometry of the compounds are called non-stoichiometry defects. These defects are either due to the presence of excess metal ions or deficiency of metal ions.

(a) *Metal excess defects due to anion vacancies* : A compound may have excess metal anion if a negative ion is absent from its lattice site, leaving a '*hole*', which is occupied by electron to maintain electrical neutrality. This type of defects are found in crystals which are likely to possess **Schottky defects**. Anion vacancies in alkali metal halides are reduced by heating the alkali metal halides crystals in an atmosphere of alkali metal vapours. The '*holes*' occupy by electrons are called ***F*-centres** (or colour centres).

(b) *Metal excess defects due to interstitial cations* : Another way in which metal excess defects may occur is, if an extra positive ion is present in an interstitial site. Electrical neutrality is maintained by the presence of an electron in the interstitial site. This type of defects are exhibit by the crystals which are likely to exhibit **Frenkel defects** *e.g.*, when *ZnO* is heated, it loses oxygen reversibly. The excess is accommodated in interstitial sites, with electrons trapped in the neighborhood. **The yellow colour and the electrical conductivity of the non-stoichiometric *ZnO* is due to these trapped electrons.**

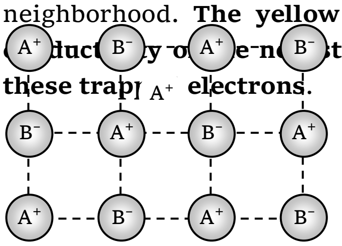


Fig. 5.20. Metal excess defect due to extra cation

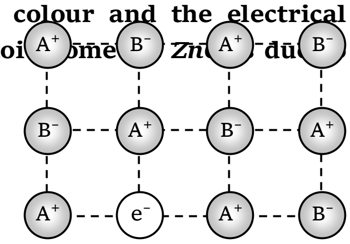


Fig. 5.21. Metal excess defect due to anion vacancy

Consequences of Metal excess defects

The crystals with metal excess defects are generally coloured due to the presence of free electrons in them.

The crystals with metal excess defects conduct electricity due to the presence of free electrons and are *semiconductors*. As the electric transport is mainly by "excess" electrons, these are called *n*-type (*n* for negative) semiconductor.

The crystals with metal excess defects are generally paramagnetic due to the presence of unpaired electrons at lattice sites.

When the crystal is irradiated with white light, the trapped electron absorbs some component of white light for excitation from ground state to the excited state. This gives rise to colour. Such points are called ***F*-centres**. (German word Farbe which means colour) such excess ions are accompanied by positive ion vacancies. These vacancies serve to trap holes in the same way as the anion vacancies trapped electrons. The colour centres thus produced are called ***V*-centres**.

(c) *Metal deficiency defect by cation vacancy* : In this a cation is missing from its lattice site. To maintain electrical neutrality, one of the nearest metal ion acquires two positive charge. This type of defect occurs in compounds where metal can exhibit variable valency. *e.g.,* Transition metal compounds like *NiO*, *FeO*, *FeS* etc.

(d) *By having extra anion occupying interstitial site* : In this, an extra anion is present in the interstitial position. The extra negative charge is balanced by one extra positive charge on the adjacent metal ion. Since anions are usually larger it could not occupy an interstitial site. Thus, this structure has only a theoretical possibility. No example is known so far.

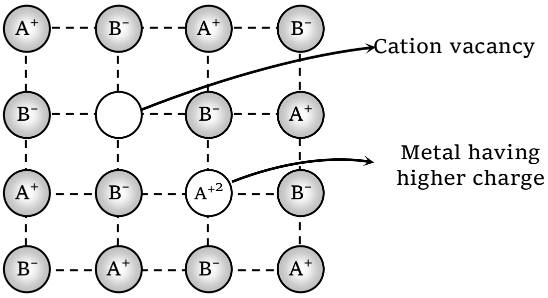


Fig. 5.22

Consequences of metal deficiency defects

Due to the movement of electron, an ion A^+ changes to A^{+2} ions. Thus, the movement of an electron from A^+ ion is an apparent of positive hole and the substances are called *p*-type semiconductor

(iii) ***Impurity defect* :** 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 while in the latter case, we get interstitial solid solution. The formation of the former depends upon the electronic structure of the impurity while that of the later on the size of the impurity.

Properties of solids

Some of the properties of solids which are useful in electronic and magnetic devices such as, transistor, computers, and telephones etc., are summarised below,

(1) **Electrical properties :** Solids are classified into following classes depending on the extent of conducting nature.

(i) ***Conductors* :** The solids which allow the electric current to pass through them are called conductors. These are further of two types; Metallic conductors and electrolytic conductors. The electrical conductivity of these solids is high in the range $10^4 - 10^6 ohm^{-1} cm^{-1}$. Their conductance decrease with increase in temperature.

(ii) ***Insulators* :** The solids which do not allow the current to pass through them are called insulators. *e.g.*, rubber, wood and plastic etc. the electrical conductivity of these solids is very low *i.e.,* $10^{-12} - 10^{-22} ohm^{-1} cm^{-1}$.

(iii) ***Semiconductors* :** The solids whose electrical conductivity lies between those of conductors and insulators are called semiconductors. The conductivity of these solid is due to the presence of impurities. *e.g.* Silicon and Germanium. Their conductance increase with increase in temperature. The electrical conductivity of these solids is increased by adding impurity. This is called **Doping**. When silicon is doped with *P* (or *As*, group 5th elements), we get *n*-type semiconductor. This is because *P* has five valence electrons. It forms 4 covalent bonds with silicon and the fifth electron remains free and is loosely bound. This give rise to *n*-type semiconductor because current is carried by electrons when silicon is doped with *Ga* (or in *In*/*Al*, group 3rd elements) we get *p*-type semiconductors.

Superconductivity : When any material loses its resistance for electric current, then it is called superconductor, **Kammerlingh Onnes (1913)** observed this phenomenon at 4*K* in mercury. The materials offering no resistance to the flow of current at very low temperature (2-5*K*) are called **superconducting materials** and phenomenon is called *superconductivity*.

Examples, Nb_3Ge alloy (Before 1986)

$La_{1.25}Ba_{0.15}CuO_4$ (1986)

$YBa_2Cu_3O_7$ (1987)

Following are the important applications of superconductivity,

(a) Electronics, (b) Building supermagnets,

(c) Aviation transportation, (d) Power transmission

"The temperature at which a material enters the superconducting state is called the superconducting transition temperature, (T_c)*". Superconductivity was also observed in lead (Pb) at 7.2 K and in tin (Sn) at*

3.7K. The phenomenon of superconductivity in other materials such as polymers and organic crystals. Examples are

$(SN)_x$, polythiazyl, the subscript x indicates a large number of variable size.

$(TMTSF)_2PF_6$, where $TMTSF$ is tetra methyl tetra selena fulvalene.

(2) **Magnetic properties :** Based on the behavior of substances when placed in the magnetic field, there are classified into five classes.

Table : 5.6 Magnetic properties of solids

Properties	Description	Alignment of Magnetic Dipoles	Examples	Applications
Diamagnetic	Feebly repelled by the magnetic fields. Non-metallic elements (excepts O_2, S) inert gases and species with paired electrons are diamagnetic	All paired electrons ↑↓ ↑↓ ↑↓	TiO_2, V_2O_5, $NaCl$, C_6H_6 (benzene)	Insulator
Paramagnetic	Attracted by the magnetic field due to the presence of permanent magnetic dipoles (unpaired electrons). In magnetic field, these tend to orient themselves parallel to the direction of the field and thus, produce magnetism in the substances.	↑↓ ↑ ↑ At least one unpaired electron	$O_2, Cu^{2+}, Fe^{3+}, TiO,$ Ti_2O_3, VO, VO_2, CuO	Electronic appliances
Ferromagnetic	Permanent magnetism even in the absence of magnetic field, Above a temperature called **Curie** temperature, there is no ferromagnetism.	Dipoles are aligned in the same direction ↑ ↑ ↑ ↑ ↑	Fe, Ni, Co, CrO_2	CrO_2 is used in audio and video tapes
Antiferromagnetic	This arises when the dipole alignment is zero due to equal and opposite alignment.	↑ ↓ ↑ ↓ ↑ ↓	MnO, MnO_2, Mn_2O, FeO, Fe_2O_3; NiO, Cr_2O_3, CoO, Co_3O_4,	–
Ferrimagnetic	This arises when there is net dipole moment	↑ ↓ ↓ ↓ ↑ ↓	Fe_3O_4, ferrites	–

(3) **Dielectric properties :** A dielectric substance is that which does not allow the electricity to pass through them but on applying the electric field, induced charges are produced on its faces. In an insulator, the electrons are strongly held by the individual atoms. When an electric field is applied polarization takes place because nuclei are attracted to one side and the electron cloud to the other side. As a result, dipoles are created. Such type of crystals shows the following properties,

(i) ***Piezoelectricity*** **:** In some of the crystals, the dipoles may align themselves is an ordered way so as to give some net dipole moment. When mechanical stress is applied in such crystals so as to deform them, electricity is produced due to the displacement of ions. The electricity thus produced is called piezoelectricity and the crystals are called piezoelectric crystals. Examples, Quartz, Rochelle's salt (sod. pot. tartarate). Piezoelectric crystals act as mechanical-electric transducer. These crystals are used as pick-ups in record players where they produce electric signals by application of pressure.

(ii) ***Pyroelectricity*** **:** On heating, some polar crystals produce a small electric current. The electricity thus produced is called pyroelectircity.

(iii) ***Ferroelectricity*** **:** In some of the piezoelectric crystals, a permanent alignment of the dipoles is always there even in the absence of the electric field, however, on applying field the direction of polarization changes. This phenomenon is called ferroelectricity and the crystals as ferroelectric crystal. Example, Potassium hydrogen phosphate (KH_2PO_4), Barium titanate $(BaTiO_3)$.

(iv) ***Antiferroelectricity*** **:** In some crystals, the dipoles in alternate polyhedra point up and down so that the crystals does not possess any net dipole moment. Such crystals are said to be antiferroelectric. Example, Lead zirconate $(PbZrO_3)$. Ferroelectrics are used in the preparation of small sized capacitors of high capacitance. Pyroelectric infrared detectors are based on such substances. These can be used in transistors, telephone, computer etc.

Tips & Tricks

- The reverse of crystallization is the melting of the solid.
- The slower the rate of formation of crystal, the bigger is the crystal.
- The hardness of metals increases with the number of electrons available for metallic bonding. Thus *Mg* is harder than sodium.
- Isomorphism is applied to those substances which are not only similar in their crystalline form, but also possess an equal number of atoms united in the similar manner. The existence of a substance in more than one crystalline form is known as polymorphism.

Ordinary Thinking

Objective Questions

Properties and Types of solid

1. The three states of matter are solid, liquid and gas. Which of the following statement is/are true about them **[AIIMS 1991]**

(a) Gases and liquids have viscosity as a common property

(b) The molecules in all the three states possess random translational motion

(c) Gases cannot be converted into solids without passing through the liquid phase

(d) Solids and liquids have vapour pressure as a common property

2. A pure crystalline substance, on being heated gradually, first forms a turbid looking liquid and then the turbidity completely disappears. This behaviour is the characteristic of substances forming **[BHU 2000]**

(a) Isomeric crystals (b) Liquid crystals

(c) Isomorphous crystals (d) Allotropic crystals

3. Which of the following is ferroelectric compound **[AFMC 1997]**

(a) $BaTiO_3$ (b) $K_4[Fe(CN)_6]$

(c) Pb_2O_3 (d) $PbZrO_3$

4. Solid CO_2 is an example of

(a) Molecular crystal (b) Ionic crystal

(c) Covalent crystal (d) Metallic crystal

5. Value of heat of fusion of $NaCl$ is

(a) Very low

(b) Very high

(c) Not very low and not very high

(d) None of the above

6. Piezoelectric crystals are used in

(a) TV (b) Radio

(c) Record player (d) Freeze

7. Which of the following is true for diamond **[AFMC 1997]**

(a) Diamond is a good conductor of electricity

(b) Diamond is soft

(c) Diamond is a bad conductor of heat

(d) Diamond is made up of C, H and O

8. $NaCl$ is an example of

(a) Covalent solid (b) Ionic solid

(c) Molecular solid (d) Metallic solid

Assignment

Properties and Types of solid

1. The three states of matter are solid, liquid and gas. Which of the following statement is/are true about them **[AIIMS 1991]**

(a) Gases and liquids have viscosity as a common property

(b) The molecules in all the three states possess random translational motion

(c) Gases cannot be converted into solids without passing through the liquid phase

(d) Solids and liquids have vapour pressure as a common property

2. A pure crystalline substance, on being heated gradually, first forms a turbid looking liquid and then the turbidity completely disappears. This behaviour is the characteristic of substances forming **[BHU 2000]**

(a) Isomeric crystals (b) Liquid crystals

(c) Isomorphous crystals (d) Allotropic crystals

3. Which of the following is ferroelectric compound **[AFMC 1997]**

(a) $BaTiO_3$ (b) $K_4[Fe(CN)_6]$

(c) Pb_2O_3 (d) $PbZrO_3$

4. Solid CO_2 is an example of

(a) Molecular crystal (b) Ionic crystal

(c) Covalent crystal (d) Metallic crystal

5. Value of heat of fusion of $NaCl$ is

(a) Very low

(b) Very high

(c) Not very low and not very high

(d) None of the above

6. Piezoelectric crystals are used in

(a) TV (b) Radio

(c) Record player (d) Freeze

7. Which of the following is true for diamond

(a) Diamond is a good conductor of electricity

(b) Diamond is soft

(c) Diamond is a bad conductor of heat

(d) Diamond is made up of C, H and O

8. $NaCl$ is an example of

(a) Covalent solid (b) Ionic solid

(c) Molecular solid (d) Metallic solid

9. Amorphous substances show

(A) Short and long range order

(B) Short range order

(C) Long range order

(D) Have no sharp M.P.

(a) A and C are correct (b) B and C are correct

(c) C and D are correct (d) B and D are correct

10. The characteristic features of solids are **[AMU 1994]**

(a) Definite shape

(b) Definite size

(c) Definite shape and size

(d) Definite shape, size and rigidity

11. Which one of the following is a good conductor of electricity **[MP PMT 1994; AFMC 2002]**

(a) Diamond (b) Graphite

(c) Silicon (d) Amorphous carbon

12. A crystalline solid **[Kerala CET (Med.) 2003]**

(a) Changes abruptly from solid to liquid when heated

(b) Has no definite melting point

(c) Undergoes deformation of its geometry easily

(d) Has an irregular 3-dimensional arrangements

(e) Softens slowly

13. Diamond is an example of **[MP PET/PMT 1998; CET Pune 1998]**

(a) Solid with hydrogen bonding

(b) Electrovalent solid

(c) Covalent solid

(d) Glass

14. The solid $NaCl$ is a bad conductor of electricity since **[AIIMS 1980]**

(a) In solid $NaCl$ there are no ions

(b) Solid $NaCl$ is covalent

(c) In solid $NaCl$ there is no velocity of ions

(d) In solid $NaCl$ there are no electrons

15. The existence of a substance in more than one solid modifications is known as **or** Any compound having more than two crystal structures is called **[MP PMT 1993; MP PET 1999]**

(a) Polymorphism (b) Isomorphism

(c) Allotropy (d) Enantiomorphism

16. Which is not a property of solids **[MP PET 1995]**

(a) Solids are always crystalline in nature

(b) Solids have high density and low compressibility

(c) The diffusion of solids is very slow

(d) Solids have definite volume

17. Which solid will have the weakest intermolecular forces

(a) Ice (b) Phosphorus

(c) Naphthalene (d) Sodium fluoride

18. Dulong and Petit's law is valid only for **[KCET 2004]**

(a) Metals (b) Non-metals

(c) Gaseous elements (d) Solid elements

19. Which of the following is an example of metallic crystal solid

(a) C (b) Si

(c) W (d) $AgCl$

20. Under which category iodine crystals are placed among the following

(a) Ionic crystal (b) Metallic crystal

(c) Molecular crystal (d) Covalent crystal

21. Among solids the highest melting point is established by **[Kerala CET (Med.) 2002]**

(a) Covalent solids (b) Ionic solids

(c) Pseudo solids (d) Molecular solids

22. To get a *n*- type semiconductor, the impurity to be added to silicon should have which of the following number of valence electrons **[KCET (Engg.) 2001]**

(a) 1 (b) 2

(c) 3 (d) 5

23. Which of the following is non-crystalline solid

(a) $CsCl$ (b) $NaCl$

(c) CaF_2 (d) Glass

24. The lustre of a metal is due to **[AFMC 1998]**

(a) Its high density (b) Its high polishing

(c) Its chemical inertness (d) Presence of free electrons

25. A crystalline solid have **[DCE 2001]**

(a) Long range order (b) Short range order

(c) Disordered arrangement (d) None of these

26. Crystalline solids are **[Pb. PMT 1999]**

(a) Glass (b) Rubber

(c) Plastic (d) Sugar

27. Davy and Faraday proved that **[Kerala CET (Med.) 2002]**

(a) Diamond is a form of carbon

(b) The bond lengths of carbon containing compounds are always equal

(c) The strength of graphite is minimum compared to platinum

(d) Graphite is very hard

28. Which one of the following metal oxides is antiferromagnetic in nature **[MP PET 2002]**

(a) MnO_2 (b) TiO_2

(c) VO_2 (d) CrO_2

29. In graphite, carbon atoms are joined together due to **[AFMC 2002]**

(a) Ionic bonding (b) Vander Waal's forces

(c) Metallic bonding (d) Covalent bonding

30. Which of the following is not correct for ionic crystals **[Orissa JEE 2002]**

(a) They possess high melting point and boiling point

(b) All are electrolyte

(c) Exhibit the property of isomorphism

(d) Exhibit directional properties of the bond

31. Which of the following is a molecular crystal

(a) SiC (b) $NaCl$

(c) Graphite (d) Ice

32. Quartz is a crystalline variety of **[Pb. PMT 2000]**

(a) Silica (b) Sodium silicate

(c) Silicon carbide (d) Silicon

33. Which type of solid crystals will conduct heat and electricity **[RPET 2000]**

(a) Ionic (b) Covalent

(c) Metallic (d) Molecular

34. Which of the following is an example of covalent crystal solid

(a) Si (b) NaF

(c) Al (d) Ar

35. Which of the following is an example of ionic crystal solid

(a) Diamond (b) LiF

(c) Li (d) Silicon

36. Which one is an example of amorphous solid

(a) Glass (b) Salt

(c) Cesium chloride (d) Calcium fluoride

37. Silicon is **[MHCET 2004]**

(a) Semiconductor (b) Insulator

(c) Conductor (d) None of these

38. Which of the following statements about amorphous solids is incorrect **[KCET 2004]**

(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

39. The ability of a given substance to assume two or more crystalline structure is called **[DCE 2004]**

(a) Amorphism (b) Isomorphism

(c) Polymorphism (d) Isomerism

40. Glass is

(a) Supercooled liquid (b) Crystalline solid

(c) Amorphous solid (d) Liquid crystal

Crystallography and Lattice

1. The correct statement in the following is **[MP PET 1997]**

(a) The ionic crystal of $AgBr$ has Schottky defect

(b) The unit cell having crystal parameters, $a = b \neq c$, $\alpha = \beta = 90^o$, $\gamma = 120^o$ is hexagonal

(c) In ionic compounds having Frenkel defect the ratio $\frac{\gamma_+}{\gamma_-}$ is high

(d) The coordination number of Na^+ ion in $NaCl$ is 4

2. Which of the following is correct **[DPMT 1997]**

	Crystal system	**Axial distance**	**Axial angles**	**Examples**
(a)	Cubic	$a \neq b = c$	$\alpha = \beta \neq \gamma = 90^o$	Cu, KCl
(b)	Monoclinic	$a \neq b = c$	$\alpha = \beta = \gamma = 90^o$	$PbCrO_2$, $PbCrO_4$
(c)	Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^o$	$CaCO_3$, HgS
(d)	Triclinic	$a = b = c$	$\alpha \neq \beta = \gamma \neq 90^o$	$K_2Cr_2O_7$, $CuSO_4.5H_2O$

3. Tetragonal crystal system has the following unit cell dimensions **[MP PMT 1993]**

(a) $a = b = c$ and $\alpha = \beta = \gamma = 90^o$

(b) $a = b \neq c$ and $\alpha = \beta = \gamma = 90^o$

(c) $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^o$

(d) $a = b \neq c$ and $\alpha = \beta = 90^o$, $\gamma = 120^o$

4. Rhombic sulphur has the following structure

(a) Open chain

(b) Tetrahedral

(c) Puckered 6-membered ring
(d) Puckered 8-membered ring

5. Space lattice of CaF_2 is **[MP PMT 1993]**
(a) Face centred cubic
(b) Body centred cubic
(c) Simple cubic
(d) Hexagonal closed packing

6. For cubic coordination the value of radius ratio is
(a) $0.732 - 1.000$ (b) $0.225 - 0.414$
(c) $0.000 - 0.225$ (d) $0.414 - 0.732$

7. How many space lattices are obtainable from the different crystal systems **[MP PMT 1996; MP PET/PMT 1998]**
(a) 7 (b) 14
(c) 32 (d) 230

8. Example of unit cell with crystallographic dimensions $a \neq b \neq c,\ \alpha = \gamma = 90^o,\ \beta \neq 90^o$ is **[AFMC 1998]**
(a) Calcite (b) Graphite
(c) Rhombic sulphur (d) Monoclinic sulphur

9. In a face-centered cubic lattice, a unit cell is shared equally by how many unit cells **[CBSE PMT 2005]**
(a) 8 (b) 4
(c) 2 (d) 6

10. The maximum radius of sphere that can be fitted in the octahedral hole of cubical closed packing of sphere of radius r is
(a) 0.732 r (b) 0.414 r
(c) 0.225 r (d) 0.155 r

11. The unit cell of a $NaCl$ lattice
(a) Is body centred cube (b) Has $3Na^+$ ions
(c) Has $4NaCl$ units (d) Is electrically charged

12. For tetrahedral coordination number, the radius ratio $\frac{r_{c^+}}{r_{a^-}}$ is **[KCET 2000]**
(a) $0.732 - 1.000$ (b) $0.414 - 0.732$
(c) $0.225 - 0.414$ (d) $0.155 - 0.225$

13. What type of lattice is found in potassium chloride crystal **[MP PMT 1996]**
(a) Face centred cubic (b) Body centred cubic
(c) Simple cubic (d) Simple tetragonal

14. The three dimensional graph of lattice points which sets the pattern for the whole lattice is called
(a) Space lattice (b) Simple lattice
(c) Unit cell (d) Crystal lattice

15. Crystals can be classified into ...... basic crystal habits **[MP PMT 1994]**
(a) 3 (b) 7
(c) 14 (d) 4

16. How many molecules are there in the unit cell of sodium chloride **[MP PMT 1996; MP PET 1997]**
(a) 2 (b) 4
(c) 6 (d) 8

17. In a crystal, the atoms are located at the position of **[AMU 1985]**
(a) Maximum P.E. (b) Minimum P.E.
(c) Zero P.E. (d) Infinite P.E.

18. The total number of lattice arrangements in different crystal systems is **[KCET (Engg.) 2001]**
(a) 3 (b) 7
(c) 8 (d) 14

19. Monoclinic crystal has dimension **[DCE 2000]**
(a) $a \neq b \neq c, \alpha = \gamma = 90°, \beta \neq 90°$
(b) $a = b = c, \alpha = \beta = \gamma = 90°$
(c) $a = b \neq c, \alpha = \beta = \gamma = 90°$
(d) $a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90°$

20. The low solubility of $BaSO_4$ in water can be attributed to **[CBSE PMT 1991]**
(a) High lattice energy (b) Dissociation energy
(c) Low lattice energy (d) Ionic bond

21. Bravais lattices are of **[MP PMT 1997]**
(a) 8 types (b) 12 types
(c) 14 types (d) 9 types

22. The structure of $TlCl$ is similar to $CsCl$. What would be the radius ratio in $TlCl$
(a) $0.155 - 0.225$ (b) $0.225 - 0.414$
(c) $0.414 - 0.732$ (d) $0.732 - 1.000$

23. Structure similar to zinc blende is found in
(a) $AgCl$ (b) $NaCl$
(c) $CuCl$ (d) $TlCl$

24. The structure of Na_2O crystal is
(a) $CsCl$ type (b) $NaCl$ type
(c) ZnS type (d) Antifluorite

25. Structure of ZnS is
(a) Body centred cubic (b) Face centred cubic
(c) Simple cube (d) Fluorite structure

26. The crystal system of a compound with unit cell dimensions $a = 0.387$, $b = 0.387$ and $c = 0.504\,nm$ and $\alpha = \beta = 90^o$ and $\gamma = 120^o$ is **[AIIMS 2004]**
(a) Cubic (b) Hexagonal
(c) Orthorhombic (d) Rhombohedral

27. The number of tetrahedral voids in the unit cell of a face centered cubic lattice of similar atoms is **[Kerala PMT 2004]**
(a) 4 (b) 6
(c) 8 (d) 10

28. An fcc unit cell of aluminium contains the equivalent of how many atoms **[DCE 2003]**
(a) 1 (b) 2
(c) 3 (d) 4

Crystal packing

1. If 'Z' is the number of atoms in the unit cell that represents the closest packing sequence $---A\ B\ C\ A\ B\ C---$, the number of tetrahedral voids in the unit cell is equal to **[AIIMS 2005]**
(a) Z (b) $2Z$
(c) Z/2 (d) Z/4

2. The close packing represents ABC ABC...... order of
(a) Body centred cubic packing
(b) Face centred cubic packing
(c) Simple cubic packing
(d) Hexagonal cubic closed packing

3. The arrangement $ABC\,ABC\,ABC$ ..... is referred as **[MP PET 2001]**
(a) Octahedral close packing (b) Hexagonal close packing
(c) Tetragonal close packing (d) Cubic close packing

4. The number of close neighbour in a body-centred cubic lattice of identical sphere is **[MP PET 2001]**
(a) 8 (b) 6
(c) 4 (d) 2

5. The number of equidistant oppositely charged ions in a sodium chloride crystal is **[MP PET 2001]**
(a) 8 (b) 6
(c) 4 (d) 2

6. Na and Mg crystallize in *BCC* and *FCC* type crystals respectively, then the number of atoms of Na and Mg present in the unit cell of their respective crystal is **[AIEEE 2002]**

(a) 4 and 2 (b) 9 and 14
(c) 14 and 9 (d) 2 and 4

7. An AB_2 type structure is found in **[AIIMS 2002]**

(a) $NaCl$ (b) Al_2O_3
(c) CaF_2 (d) N_2O

8. Potassium crystallizes with a **[MP PET/PMT 1998]**

(a) Face-centred cubic lattice
(b) Body-centred cubic lattice
(c) Simple cubic lattice
(d) Orthorhombic lattice

9. If the number of atoms per unit in a crystal is 2, the structure of crystal is

(a) Octahedral
(b) Body centred cubic *bcc*
(c) Face centred cubic fcc
(d) simple cubic

10. The intermetallic compound $LiAg$ crystallizes in cubic lattice in which both lithium and silver have coordination number of eight. The crystal class is **[CBSE PMT 1997]**

(a) Simple cube (b) Body-centred cube
(c) Face-centred cube (d) None of these

11. The number of octahedral sites per sphere in a *fcc* structure is **[MP PMT 2000, 01]**

(a) 8 (b) 4
(c) 2 (d) 1

12. Hexagonal close packed arrangement of ions is described as **[MP PMT 1994]**

(a) ABC ABA (b) ABC ABC
(c) ABABA (d) ABBAB

13. An example of a body cube is **[AIIMS 1996]**

(a) Sodium (b) Magnesium
(c) Zinc (d) Copper

14. An example of fluorite structure is

(a) NaF (b) SrF_2
(c) $AlCl_3$ (d) SiF_4

15. In which of the following crystals alternate tetrahedral voids are occupied? **[IIT 2005]**

(a) $NaCl$ (b) ZnS
(c) CaF_2 (d) Na_2O

16. Which of the following contains rock salt structure

(a) SrF_2 (b) MgO
(c) Al_2O_3 (d) All

17. In the fluorite structure, the coordination number of Ca^{2+} ion is

(a) 4 (b) 6
(c) 8 (d) 3

18. The ratio of close-packed atoms to tetrahedral holes in cubic close packing is **[Pb. PMT 1998]**

(a) 1 : 1 (b) 1 : 2
(c) 1 : 3 (d) 2 : 1

19. A solid is made of two elements X and Z. The atoms Z are in CCP arrangement while the atom X occupy all the tetrahedral sites. What is the formula of the compound **[UPSEAT 2004]**

(a) XZ (b) XZ_2
(c) X_2Z (d) X_2Z_3

20. An ionic compound has a unit cell consisting of A ions at the corners of a cube and B ions on the centres of the faces of the cube. The empirical formula for this compound would be **[CBSE PMT 2004; AIEEE 2005]**

(a) AB (b) A_2B
(c) AB_3 (d) A_3B

21. The vacant space in the *bcc* unit cell is

(a) 32% (b) 23%
(c) 26% (d) None of these

22. The number of octahedral voids in a unit cell of a cubical closest packed structure is

(a) 1 (b) 2
(c) 4 (d) 8

23. In the closest packed structure of a metallic lattice, the number of nearest neighbours of a metallic atom is **[JIPMER 2002]**

(a) Twelve (b) Four
(c) Eight (d) Six

24. In the rock salt structure, the number of formula units per unit cell is equal to

(a) 1 (b) 2
(c) 3 (d) 4

25. Hexagonal close packing is found in crystal lattice of **[MH CET 2002]**

(a) Na (b) Mg
(c) Al (d) None of these

26. Which ion has the largest radius from the following ions

(a) Na^+ (b) Mg^{2+}
(c) Al^{3+} (d) Si^{4+}

Mathematical analysis of cubic system and Bragg's equation

1. The formula for determination of density of unit cell is

(a) $\frac{a^3 \times N_o}{N \times M}\, g\,cm^{-3}$ (b) $\frac{N \times M}{a^3 \times N_o}\, g\,cm^{-3}$
(c) $\frac{a^3 \times M}{N \times N_o}\, g\,cm^{-3}$ (d) $\frac{M \times N_o}{a^3 \times N}\, g\,cm^{-3}$

2. Potassium fluoride has $NaCl$ type structure. What is the distance between K^+ and F^- ions if cell edge is a cm

(a) $2a\ cm$ (b) $a/2\ cm$
(c) $4a\ cm$ (d) $a/4\ cm$

3. An element occurring in the *bcc* structure has 12.08×10^{23} unit cells. The total number of atoms of the element in these cells will be **[MP PET 1994]**

(a) 24.16×10^{23} (b) 36.18×10^{23}
(c) 6.04×10^{23} (d) 12.08×10^{23}

4. If an atom is present in the centre of the cube, the participation of that atom per unit cell is

(a) $\frac{1}{4}$ (b) 1
(c) $\frac{1}{2}$ (d) $\frac{1}{8}$

5. For an ionic crystal of the general formula AX and coordination number 6, the value of radius ratio will be **[MP PMT 1993]**

(a) Greater than 0.73
(b) In between 0.73 and 0.41
(c) In between 0.41 and 0.22
(d) Less than 0.22

6. The number of spheres contained (i) in one body centred cubic unit cell and (ii) in one face centred cubic unit cell, is

(a) In (i) 2 and in (ii) 4 (b) In (i) 3 and in (ii) 2
(c) In (i) 4 and in (ii) 2 (d) In (i) 2 and in (ii) 3

7. $CsBr$ crystal has bcc structure. It has an edge length of $4.3\ \text{Å}$. The shortest interionic distance between Cs^+ and Br^- ions is **[IIT 1995]**

(a) $1.86\ \text{Å}$ (b) $3.72\ \text{Å}$
(c) $4.3\ \text{Å}$ (d) $7.44\ \text{Å}$

8. In octahedral holes (voids)

(a) A simple triangular void surrounded by four spheres
(b) A bi-triangular void surrounded by four spheres
(c) A bi-triangular void surrounded by six spheres
(d) A bi-triangular void surrounded by eight spheres

9. Bragg's law is given by the equation **[MP PMT 1995, 2002]**

(a) $n\lambda = 2\theta\sin\theta$ (b) $n\lambda = 2d\sin\theta$
(c) $2n\lambda = d\sin\theta$ (d) $n\frac{\theta}{2} = \frac{d}{2}\sin\theta$

10. The number of atoms in $100\ g$ of an fcc crystal with density $d = 10\ g/cm^3$ and cell edge equal to $100\ pm$, is equal to **[CBSE PMT 1994; KCET 2002]**

(a) 4×10^{25} (b) 3×10^{25}
(c) 2×10^{25} (d) 1×10^{25}

11. In the crystals of which of the following ionic compounds would you expect maximum distance between centres of cations and anions **[CBSE PMT 1998]**

(a) LiF (b) CsF
(c) CsI (d) LiI

12. The number of unit cells in $58.5\,g$ of $NaCl$ is nearly **[MP PMT 2000, 01]**

(a) 6×10^{20} (b) 3×10^{22}
(c) 1.5×10^{23} (d) 0.5×10^{24}

13. How many unit cells are present in a cube-shaped ideal crystal of $NaCl$ of mass $1.00\,g$ [Atomic masses: $Na = 23, Cl = 35.5$] **[AIEEE 2003]**

(a) 2.57×10^{21} unit cells (b) 5.14×10^{21} unit cells
(c) 1.28×10^{21} unit cells (d) 1.71×10^{21} unit cells

14. In the Bragg's equation for diffraction of X-rays, n represents for **[MP PMT 2000]**

(a) Quantum number (b) An integer
(c) Avogadro's numbers (d) Moles

15. In a face centred cubic cell, an atom at the face contributes to the unit cell **[Karnataka (Engg./Med.) 2000; AFMC 2001]**

(a) 1/4 part (b) 1/8 part
(c) 1 part (d) 1/2 part

16. The interionic distance for cesium chloride crystal will be **[MP PET 2002]**

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

17. Sodium metal crystallizes as a body centred cubic lattice with the cell edge 4.29 Å. What is the radius of sodium atom **[AIIMS 1999]**

(a) $1.857\times10^{-8}\,cm$ (b) $2.371\times10^{-7}\,cm$
(c) $3.817\times10^{-8}\,cm$ (d) $9.312\times10^{-7}\,cm$

18. For an ionic crystal of the type AB, the value of (limiting) radius ratio is 0.40. The value suggests that the crystal structure should be

(a) Octahedral (b) Tetrahedral
(c) Square planar (d) Plane triangle

19. Potassium has a bcc structure with nearest neighbour distance $4.52\ \text{Å}$. Its atomic weight is 39. Its density (in $kg\ m^{-3}$) will be **[AIIMS 1991]**

(a) 454 (b) 804
(c) 852 (d) 908

20. If the value of ionic radius ratio $\left(\frac{r_c}{r_a}\right)$ is 0.52 in an ionic compound, the geometrical arrangement of ions in crystal is

(a) Tetrahedral (b) Planar
(c) Octahedral (d) Pyramidal

21. The number of atoms/molecules contained in one face centred cubic unit cell of a monoatomic substance is **[CPMT 1989, 94; CBSE PMT 1989, 96; NCERT 1990; MP PET 1993; KCET 1999]**

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

22. The number of atoms/molecules contained in one body centered cubic unit cell is

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

23. It the distance between Na^+ and Cl^- ions in sodium chloride crystal is X pm, the length of the edge of the unit cell is **[KCET 2004]**

(a) 4X pm (b) X/4 pm
(c) X/2 pm (d) 2X pm

24. The edge of unit cell of FCC Xe crystal is $620\ pm$. The radius of Xe atom is **[MP PET 2004]**

(a) 219.25 Pm (b) 235.16 Pm
(c) 189.37 Pm (d) 209.87 Pm

25. In orthorhombic, the value of a, b and c are respectively $4.2\text{Å}, 8.6\text{Å}$ and 8.3Å. given the molecular mass of the solute is $155\ gm\ mol^{-1}$ and that of density is $3.3\,gm/cc$, the number of formula units per unit cell is **[Orrisa JEE 2005]**

(a) 2 (b) 3
(c) 4 (d) 6

26. A metal has bcc structure and the edge length of its unit cell is $3.04\,\text{Å}$. The volume of the unit cell in cm^3 will be **[Orrisa JEE 2005]**

(a) $1.6\times10^{21}\,cm^3$ (b) $2.81\times10^{-23}\,cm^3$
(c) $6.02\times10^{-23}\,cm^3$ (d) $6.6\times10^{-24}\,cm^3$

27. In face centred cubic unit cell edge length is **[DPMT 2005]**

(a) $\frac{4}{\sqrt{3}}r$ (b) $\frac{4}{\sqrt{2}}r$

(c) $2r$ (d) $\frac{\sqrt{3}}{2}r$

Crystal structure and Coordination number

1. A solid has a structure in which $'W'$ atoms are located at the corners of a cubic lattice $'O'$ atoms at the centre of edges and $'Na'$ atoms at the centre of the cube. The formula for the compound is **[KCET 1996]**

(a) $NaWO_2$ (b) $NaWO_3$

(c) Na_2WO_3 (d) $NaWO_4$

2. Potassium crystallizes in a bcc lattice, hence the coordination number of potassium in potassium metal is **[KCEE 1993]**

(a) 0 (b) 4

(c) 6 (d) 8

3. Body centered cubic lattice has a coordination number of **[AIIMS 1996; MP PMT 2002]**

(a) 4 (b) 8

(c) 12 (d) 6

4. A compound is formed by elements A and B. This crystallizes in the cubic structure when atoms A are the corners of the cube and atoms B are at the centre of the body. The simplest formula of the compounds is **[KCET 1993; CBSE PMT 2000; Kerala PMT 2002]**

(a) AB (b) AB_2

(c) A_2B (d) AB_4

5. Coordination number for Cu is **[AMU 1982]**

(a) 1 (b) 6

(c) 8 (d) 12

6. In the crystal of $CsCl$, the nearest neighbours of each Cs ion are **[MP PET 1993]**

(a) Six chloride ions (b) Eight chloride ions

(c) Six Cs ions (d) Eight Cs ions

7. In a cubic structure of compound which is made from X and Y, where X atoms are at the corners of the cube and Y at the face centres of the cube. The molecular formula of the compound is **[AIIMS 2000]**

(a) X_2Y (b) X_3Y

(c) XY_2 (d) XY_3

8. Ferrous oxide has a cubic structure and each edge of the unit cell is 5.0 Å. Assuming density of the oxide as $4.0 g-cm^{-3}$, then the number of Fe^{2+} and O^{2-} ions present in each unit cell will be **[MP PET 2000]**

(a) Four Fe^{2+} and four O^{2-}

(b) Two Fe^{2+} and four O^{2-}

(c) Four Fe^{2+} and two O^{2-}

(d) Three Fe^{2+} and three O^{2-}

9. Which of the following statements is not true about $NaCl$ structure **[DCE 2001]**

(a) Cl^- ions are in *fcc* arrangement

(b) Na^+ ions has coordination number 4

(c) Cl^- ions has coordination number 6

(d) Each unit cell contains $4 NaCl$ molecules

10. In $CsCl$ structure, the coordination number of Cs^+ is **[MP PMT 2001]**

(a) Equal to that of Cl^-, that is 6

(b) Equal to that of Cl^-, that is 8

(c) Not equal to that of Cl^-, that is 6

(d) Not equal to that of Cl^-, that is 8

11. In a solid '*AB*' having the $NaCl$ structure, '*A*' atoms occupy the corners of the cubic unit cell. If all the face-centered atoms along one of the axes are removed, then the resultant stoichiometry of the solid is **[IIT Screening 2001]**

(a) AB_2 (b) A_2B

(c) A_4B_3 (d) A_3B_4

12. In solid $CsCl$ each Cl is closely packed with how many Cs **[MP PET 2003]**

(a) 8 (b) 6

(c) 10 (d) 2

13. In A^+B^- ionic compound, radii of A^+ and B^- ions are $180\ pm$ and $187\ pm$ respectively. The crystal structure of this compound will be

(a) $NaCl$ type (b) $CsCl$ type

(c) ZnS type (d) Similar to diamond

14. In which of the following substances the carbon atom is arranged in a regular tetrahedral structure **[NCERT 1978]**

(a) Diamond (b) Benzene

(c) Graphite (d) Carbon black

15. The coordination number of a metal crystallizing in a hexagonal close packed structure is **[NCERT 1978; IIT 1999]**

(a) 4 (b) 12

(c) 8 (d) 6

16. The structure of MgO is similar to $NaCl$. What would be the coordination number of magnesium

(a) 2 (b) 4

(c) 6 (d) 8

17. How many chloride ions are there around sodium ion in sodium chloride crystal **[NCERT 1979, 80; CPMT 1988; BHU 1982, 87; MP PET 1995, 99]**

(a) 3 (b) 8

(c) 4 (d) 6

18. Most crystals show good cleavage because their atoms, ions or molecules are **[CBSE PMT 1991]**

(a) Weakly bonded together

(b) Strongly bonded together

(c) Spherically symmetrical

(d) Arranged in planes

19. An example of a non-stoichiometric compound is **[NCERT 1983]**

(a) Al_2O_3 (b) Fe_3O_4

(c) NiO_2 (d) PbO

20. If the radius ratio is in the range of $0.731-1$, then the coordination number will be

(a) 2 (b) 4

(c) 6 (d) 8

21. If the radius ratio is in the range of $0.414-0.732$, then the coordination number will be

(a) 2 (b) 4

(c) 6 (d) 8

22. What is the coordination number of sodium in Na_2O **[AIIMS 2003]**

(a) 6 (b) 4

(c) 8 (d) 2

23. The ratio of cationic radius to anionic radius in an ionic crystal is greater than 0.732. Its coordination number is **[KCET 2003]**

(a) 6 (b) 8
(c) 1 (d) 4

24. In $CsCl$ lattice the coordination number of Cs^+ ion is
(a) 2 (b) 4
(c) 8 (d) 12

25. Crystal structure of $NaCl$ is **[NCERT 1982; BHU 1995]**
(a) *fcc* (b) *bcc*
(c) Both (a) and (b) (d) None

26. In $NaCl$ lattice the coordination number of Cl^- ion is
(a) 2 (b) 4
(c) 6 (d) 8

27. In zinc blende structure the coordination number of Zn^{2+} ion is
(a) 2 (b) 4
(c) 6 (d) 8

28. Coordination number of Na^+ ion in rock salt is **[BVP 2004]**
(a) 12 (b) 4
(c) 8 (d) 6

29. The number of Cl^- ions around one Na^+ in $NaCl$ crystal lattice is **[MP PET 1996; BVP 2004]**
(a) 12 (b) 4
(c) 8 (d) 6

30. The number of atoms present in unit cell of a monoatomic substance of simple cubic lattice is **[Pb. PMT 2004]**
(a) 6 (b) 3
(c) 2 (d) 1

31. The coordination number of a metal crystallizing in a hexagonal close packed chep structure is **[MP PMT 2004]**
(a) 12 (b) 8
(c) 4 (d) 6

32. Which of the following statement(s) is(are) correct **[IIT 1998]**
(a) The coordination number of each type of ion in $CsCl$ crystal is 8
(b) A metal that crystallizes in *bcc* structure has a coordination number of 12
(c) A unit cell of an ionic crystal shares some of its ions with other unit cells
(d) The length of the unit cell in $NaCl$ is 552 pm $(r_{Na^+} = 95\ pm;\ r_{Cl^-} = 181\ pm)$

33. The co-ordination number of Na^+ in $NaCl$ is **[Orrisa JEE 2005]**
(a) 6 (b) 8
(c) 4 (d) 1

34. In the calcium fluoride structure the co-ordination number of the cation and anions are respectively **[J & K 2005]**
(a) 6, 6 (b) 8, 4
(c) 4, 4 (d) 4, 8

Defects in crystal

1. Certain crystals produce electric signals on application of pressure. This phenomenon is called **[BHU 2005]**
(a) Pyroelectricity (b) Ferroelectricity
(c) Peizoelectricity (d) Ferrielectricity

2. Which defect causes decrease in the density of crystal **[KCET 2000, 05]**
(a) Frenkel (b) Schottky
(c) Interstitial (d) F – centre

3. The correct statement regarding F – centre is
(a) Electron are held in the voids of crystals
(b) F – centre produces colour to the crystals
(c) Conductivity of the crystal increases due to F – centre
(d) All

4. Doping of silicon (Si) with boron (B) leads to **[UPSEAT 2004]**
(a) n -type semiconductor (b) p -type semiconductor
(c) Metal (d) Insulator

5. If $NaCl$ is doped with $10^{-3} mol\ \%\ SrCl_2$, then the concentration of cation vacancies will be
(a) $1 \times 10^{-3} mol\%$ (b) $2 \times 10^{-3} mol\%$
(c) $3 \times 10^{-3} mol\%$ (d) $4 \times 10^{-3} mol\%$

6. In the laboratory, sodium chloride is made by burning the sodium in the atmosphere of chlorine which is yellow in colour. The cause of yellow colour is
(a) Presence of Na^+ ions in the crystal lattice
(b) Presence of Cl^- ions in the crystal lattice
(c) Presence of electron in the crystal lattice
(d) Presence of face centered cubic crystal lattice

7. Frenkel defect is caused due to **[MP PET 1994]**
(a) An ion missing from the normal lattice site creating a vacancy
(b) An extra positive ion occupying an interstitial position in the lattice
(c) An extra negative ion occupying an interstitial position in the lattice
(d) The shift of a positive ion from its normal lattice site to an interstitial site

8. Which one of the following has Frenkel defect **[MP PMT 2000]**
(a) Sodium chloride (b) Graphite
(c) Silver bromide (d) Diamond

9. Schottky defect generally appears in **[DCE 2004]**
(a) $NaCl$ (b) KCl
(c) $CsCl$ (d) All of these

10. Schottky defect in crystals is observed when **[CBSE PMT 1998; KCET 2002]**
(a) Density of crystal is increased
(b) Unequal number of cations and anions are missing from the lattice
(c) An ion leaves its normal site and occupies an interstitial site
(d) Equal number of cations and anions are missing from the lattice

11. Ionic solids, with Schottky defects, contain in their structure **[CBSE PMT 1994]**
(a) Equal number of cation and anion vacancies
(b) Anion vacancies and interstitial anions
(c) Cation vacancies only
(d) Cation vacancies and interstitial cations

12. The following is not a function of an impurity present in a crystal **[MP PET 1995]**
(a) Establishing thermal equilibrium
(b) Having tendency to diffuse
(c) Contributing to scattering
(d) Introducing new electronic energy levels

13. Due to Frenkel defect, the density of ionic solids **[MP PET 1996; MP PMT 2002]**
(a) Increases (b) Decreases
(c) Does not change (d) Changes

14. Point defects are present in **[MP PMT 1997]**

(a) Ionic solids (b) Molecular solids
(c) Amorphous solids (d) Liquids

15. If a non-metal is added to the interstitial sites of a metal then the metal becomes **[DCE 2001]**

(a) Softer (b) Less tensile
(c) Less malleable (d) More ductile

16. In $AgBr$ crystal, the ion size lies in the order $Ag^+ << Br^-$. The $AgBr$ crystal should have the following characteristics

(a) Defectless (perfect) crystal
(b) Schottky defect only
(c) Frenkel defect only
(d) Both Schottky and Frenkel defects

17. Frenkel and Schottky defects are **[BHU 2003]**

(a) Nucleus defects (b) Non-crystal defects
(c) Crystal defects (d) None of these

18. Which one of the following is the most correct statement

(a) Brass is an interstitial alloy, while steel is a substitutional alloy
(b) Brass is a substitutional alloy, while steel is an interstitial alloy
(c) Brass and steel are both substitutional alloys
(d) Brass and steel are both interstitial alloys

19. The flame colours of metal ions are due to **[KCET 2003]**

(a) Frenkel defect (b) Schottky defect
(c) Metal deficiency defect (d) Metal excess defect

20. Which one of the following crystals does not exhibit Frenkel defect **[MP PET 2002]**

(a) $AgBr$ (b) $AgCl$
(c) KBr (d) ZnS

21. In a solid lattice the cation has left a lattice site and is located at an interstitial position, the lattice defect is **[AIIMS 1982, 1991; DCE 2002; J & K 2005]**

(a) Interstitial defect (b) Valency defect
(c) Frenkel defect (d) Schottky defect

22. When electrons are trapped into the crystal in anion vacancy, the defect is known as **[BHU 2005]**

(a) Schotky defect (b) Frenkel defect
(c) Stoichiometric defect (d) F-centres

23. Schottky defect defines imperfection in the lattice structure of a **[AIIMS 2002]**

(a) Solid (b) Liquid
(c) Gas (d) Plasma

Critical Thinking

Objective Questions

1. Amorphous solids are

(a) Solid substance in real sense
(b) Liquid in real sense
(c) Supercooled liquid
(d) Substance with definite melting point

2. Silicon is found in nature in the form of **[MH CET 2002]**

(a) Body centered cubic structure
(b) Hexagonal close-packed structure
(c) Network solid
(d) Face centered cubic structure

3. A match box exhibits **[MP PET 1993, 95]**

(a) Cubic geometry (b) Monoclinic geometry
(c) Orthorhombic geometry (d) Tetragonal geometry

4. Which has no rotation of symmetry **[Orrisa JEE 2004]**

(a) Hexagonal (b) Orthorhombic
(c) Cubic (d) Triclinic

5. Which of the following molecules has three-fold axis of symmetry **[UPSEAT 2004]**

(a) NH_3 (b) C_2H_4
(c) CO_2 (d) SO_2

6. Which one possess a antifluorite structure

(a) Na_2O (b) MgO
(c) Fe_2O_3 (d) Al_2O_3

7. Which one of the following is the biggest ion **[MP PET 1993]**

(a) Al^{+3} (b) Ba^{+2}
(c) Mg^{+2} (d) Na^+

8. The edge length of face centred unit cubic cell is $508\ pm$. If the radius of the cation is $110\ pm$, the radius of the anion is **[CBSE PMT 1998]**

(a) $285\ pm$ (b) $398\ pm$
(c) $144\ pm$ (d) $618\ pm$

9. An element (atomic mass $100\,g/mol$) having bcc structure has unit cell edge $400\ pm$. Then density of the element is **[CBSE PMT 1996; AIIMS 2002]**

(a) $10.376\ g/cm^3$ (b) $5.188\ g/cm^3$
(c) $7.289\ g/cm^3$ (d) $2.144\ g/cm^3$

10. If the pressure on a $NaCl$ structure is increased, then its coordination number will **[AFMC 2000]**

(a) Increase (b) Decrease
(c) Remain the same (d) Either (b) or (c)

11. The pyknometric density of sodium chloride crystal is $2.165 \times 10^3 kg\,m^{-3}$ while its X-rays density is $2.178 \times 10^3 kg\,m^{-3}$. The fraction of unoccupied sites in sodium chloride crystal is **[CBSE PMT 2003]**

(a) 5.96×10^{-3} (b) 5.96
(c) 5.96×10^{-2} (d) 5.96×10^{-1}

12. Which of the following statements is correct for $CsBr_3$ **[IIT 1996]**

(a) It is a covalent compound
(b) It contains Cs^{3+} and Br^- ions
(c) It contains Cs^+ and Br_3^- ions
(d) It contains Cs^+, Br^- and lattice Br_2 molecule

13. In which compound 8 : 8 coordination is found **[EAMCET 1984]**

(a) $CsCl$ (b) MgO
(c) Al_2O_3 (d) All of these

14. If the coordination of Ca^{2+} in CaF_2 is 8, then the coordination number of F^- ion would be

(a) 3 (b) 4
(c) 6 (d) 8

15. For some crystals, the radius ratio for cation and anion is 0.525, its coordination number will be

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

16. The basic building unit of all silicates is **[UPSEAT 2002]**

(a) SiO_4 square planar (b) $[SiO_4]^{4-}$ tetrahedron
(c) SiO_4 octahedron (d) SiO_4 linear

17. What type of crystal defect is indicated in the diagram below

[AIEEE 2004]

Na^+ Cl^- Na^+ Cl^- Na^+ Cl^-
Cl^- □ Cl^- Na^+ □ Na^+
Na^+ Cl^- □ Cl^- Na^+ Cl^-
Cl^- Na^+ Cl^- Na^+ □ Na^+

(a) Interstitial defect
(b) Schottky defect
(c) Frenkel defect
(d) Frenkel and Schottky defects

18. Which of the following is a three dimensional silicate **[MHCET 2003]**

(a) Mica
(b) Spodumene
(c) Zeolite
(d) None of these
(e) 12

Assertion & Reason

For AIIMS Aspirants

Read the assertion and reason carefully to mark the correct option out of the options given below :

(a) *If both assertion and reason are true and the reason is the correct explanation of the assertion.*
(b) *If both assertion and reason are true but reason is not the correct explanation of the assertion.*
(c) *If assertion is true but reason is false.*
(d) *If the assertion and reason both are false.*
(e) *If assertion is false but reason is true.*

1. Assertion : Diamond is a precious stone.
Reason : Carbon atoms are tetrahedrally arranged in diamond. **[AIIMS 1994]**

2. Assertion : In crystal lattice, the size of the cation is larger in a tetrahedral hole than in an octahedral hole.
Reason : The cations occupy more space than anions in crystal packing. **[AIIMS 1996]**

3. Assertion : Crystalline solids have short range order.
Reason : Amorphous solids have long range order.
[AIIMS 1999]

4. Assertion : In any ionic solid (MX) with Schottky defects, the number of positive and negative ions are same.
Reason : Equal number of cation and anion vacancies are present.
[IIT Screening 2001]

5. Assertion : Space or crystal lattice differ in symmetry of the arrangement of points.
Reason : $n\lambda = 2d \sin\theta$, is known as Bragg's equation.

6. Assertion : In close packing of spheres, a tetrahedral void is surrounded by four spheres whereas an octahedral void is surrounded by six spheres.
Reason : A tetrahedral void has a tetrahedral shape whereas an octahedral void has an octahedral shape.

7. Assertion : Cyclic silicates and chain silicates have the same general molecular formula.
Reason : In cyclic silicates, three corners of each SiO_4 tetrahedron are shared while in chain silicates only two are shared with other tetrahedra.

8. Assertion : The presence of a large number of Schottky defects in $NaCl$ lowers its density.
Reason : In $NaCl$, there are approximately 10^6 Schottky pairs per cm^3 at room temperature.

9. Assertion : Anion vacancies in alkali halides are produced by heating the alkali halide crystals with alkali metal vapour.
Reason : Electrons trapped in anion vacancies are referred to as F-centres.

10. Assertion : Electrical conductivity of semiconductors increases with increasing temperature.
Reason : With increase in temperature, large number of electrons from the valence band can jump to the conduction band.

11. Assertion : On heating ferromagnetic or ferrimagnetic substances, they become paramagnetic.
Reason : The electrons change their spin on heating.

12. Assertion : Lead zirconate is a piezoelectric crystal.
Reason : Lead zirconate crystals have no dipole moment.

Answers

Type of solid and Their properties

1	a	2	b	3	a	4	a	5	b
6	c	7	c	8	b	9	d	10	d
11	b	12	a	13	c	14	c	15	a
16	a	17	a	18	d	19	c	20	c
21	b	22	d	23	d	24	d	25	a
26	d	27	a	28	a	29	d	30	d
31	d	32	a	33	c	34	a	35	b
36	a	37	a	38	b	39	c	40	ac

Crystallography and Lattice

1	b	2	c	3	b	4	d	5	a
6	a	7	b	8	d	9	d	10	b
11	c	12	c	13	a	14	c	15	b
16	b	17	b	18	b	19	a	20	a
21	c	22	d	23	c	24	d	25	b
26	b	27	c	28	d				

Crystal packing

1	b	2	b	3	d	4	a	5	b
6	d	7	c	8	b	9	b	10	b

11	d	12	c	13	a	14	b	15	b
16	b	17	c	18	b	19	c	20	c
21	a	22	c	23	a	24	d	25	b
26	a								

Mathematical analysis of cubic system and Bragg's equation

1	b	2	b	3	a	4	b	5	b
6	a	7	b	8	c	9	b	10	a
11	c	12	c	13	a	14	b	15	d
16	c	17	a	18	b	19	d	20	c
21	c	22	b	23	d	24	a	25	c
26	b	27	b						

Crystal structure and Coordination number

1	b	2	d	3	b	4	a	5	d
6	b	7	d	8	a	9	b	10	b
11	d	12	a	13	b	14	a	15	b
16	c	17	d	18	d	19	b	20	d
21	c	22	b	23	b	24	c	25	a
26	c	27	b	28	d	29	d	30	d
31	a	32	acd	33	a	34	b		

Defects in crystal

1	c	2	b	3	d	4	d	5	a
6	c	7	d	8	c	9	d	10	d
11	a	12	a	13	c	14	a	15	b
16	c	17	c	18	c	19	d	20	c
21	c	22	d	23	a				

Critical Thinking Questions

1	c	2	c	3	c	4	d	5	a
6	a	7	b	8	c	9	b	10	a
11	a	12	c	13	a	14	b	15	c
16	b	17	b	18	c				

Assertion & Reason

1	b	2	d	3	d	4	a	5	b
6	c	7	c	8	b	9	b	10	a
11	a	12	c						

Answers and Solutions

Properties and Types of solids

1. (a) Both gases and liquids possess fluidity and hence viscosity molecules in the solid state do not have translational motion.

2. (b) It is a characteristic of liquid crystal.

3. (a) $BaTiO_3$ is a ferroelectric compound.

5. (b) The value of heat of fusion of $NaCl$ is very high due to *fcc* arrangement of its ions.

6. (c) Piezoelectric crystals are used in record player.

8. (b) $NaCl$ is a ionic solid in which constituent particles are positive (Na^+) and negative (Cl^-) ions.

9. (d) Amorphous solids have short range order but no sharp in melting point.

10. (d) Solids have definite shape, size and rigidity.

12. (a) In crystalline solid there is perfect arrangement of the constituent particles only at 0K. As the temperature increases the chance that a lattice site may be unoccupied by an ion increases. As the number of defects increases with temperature solid change in liquid.

13. (c) Diamond is a covalent solid in which constituent particles are atoms.

14. (c) Solid $NaCl$ is a bad conductor of electricity because ions are not free to move.

15. (a) The existence of a substance in more than one crystalline form is known as polymorphism.

16. (a) Solids are also non-crystalline in nature.

17. (a) Ice has the lowest melting point out of the given solids, hence it has the weakest intermolecular forces.

19. (c) All metals and some alloys are metallic crystal.

20. (c) Iodine crystals are molecular crystals, in which constituent particles are molecules having interparticle forces are Vander Waal's forces.

21. (b) Ionic solids have highest melting point due to strong electrostatic forces of attraction.

22. (d) For *n*-type, impurity added to silicon should have more than 4 valence electrons.

23. (d) Glass is an amorphous solid.

25. (a) Crystalline solids have regular arrangement of constituent particles, sharp melting points and are anisotropic.

26. (d) Sugar is a crystalline solid while glass, rubber and plastic are amorphous solids.

28. (a) MnO_2 is antiferromagnetic.

29. (d) Graphite is sp^2 hybridised and a covalent crystal.

30. (d) Ionic crystals exhibit non-directional properties of the bond.

31. (d) Ice is a molecular crystal in which the constituent units are molecules and the interparticle forces are hydrogen bonds.

32. (a) Quartz is a covalent crystal having a framework of silicates or silica, *i.e.* a three dimensional network when all the four oxygen atoms of each of SiO_4 tetrahedron are shared.

33. (c) Metallic crystals are good conductor of heat and current due to free electrons in them.

34. (a) Silicon is a covalent crystal in which constituent particles are atoms.

35. (b) *LiF* is an example of ionic crystal solid, in which constituent particles are positive (Li^+) and negative (F^-) ions.

36. (a) Amorphous solids neither have ordered arrangement (*i.e.* no definite shape) nor have sharp melting point like crystals, but when heated, they become pliable until they assume the properties usually related to liquids. It is therefore they are regarded as super-cooled liquids.

37. (a) Silicon is a semiconductor because it is a thermal active and its conductivity increased with increasing temperature.

38. (b) Amorphous solids are isotropic, because of these substances show same properties in all directions.

39. (c) Polymorphism is a ability of a substances which show two or more crystalline structure

40. (ac) Amorphous solids neither have ordered arrangement (*i.e.* no definite shape) nor have sharp melting point like crystals, but when heated, they become pliable until they assume the properties usually related to liquids. It is therefore they are regarded as super-cooled liquids.

Crystallography and Lattice

1. (b) A crystal system is hexagonal if its unit cell having $a = b \ne c$ axial ratio and $\alpha = \beta = 90°$, $\gamma = 120°$ axial angles.

2. (c) Rhombohedral crystal system

$a = b = c$, $\alpha = \beta = \gamma \ne 90^o$

ex – $NaNO_3$, $CaSO_4$, calcite $CaCO_3$, HgS

3. (b) Tetragonal system has the unit cell dimension $a = b \ne c, \alpha = \beta = \gamma = 90°$.

5. (a) Space lattice of CaF_2 is face centred cubic.

6. (a) For body centred cubic arrangement co-ordination number is 8 and radius ratio (r_+/r_-) is $0.732 - 1.000$.

7. (b) There are 14 Bravais lattices (space lattices).

8. (d) Monoclinic sulphur is an example of Monoclinic crystal system.

10. (b) $r = 0.414\,r$.

11. (c) Each unit cell of $NaCl$ contains $4\,NaCl$ units.

12. (c) For tetrahedral arrangement co-ordination number is 4 and radius ratio (r_+/r_-) is $0.225 - 0.414$.

13. (a) Face-centred cubic lattice found in KCl and $NaCl$.

14. (c) Definition of unit cell.

16. (b) In $NaCl$ (rock salt) : Number of Na^+ ions $= 12$ (at edge centers) $\times \frac{1}{4} + 1$ (at body centre) $\times 1 = 4$. Number of Cl^- ions $= 8$ (at corners) $\times \frac{1}{8} + 6$ (at face centre) $\times \frac{1}{2} = 4$. Thus 4 formula units per unit cell.

17. (b) Lowest potential energy level provides stable arrangement.

18. (b) The seven basic crystal lattice arrangements are :- Cubic, Tetragonal, Orthorhombic, Monoclinic, Hexagonal, Rhombohedral and Triclinic.

19. (a) The conditions for monoclinic crystal system.

20. (a) High lattice energy of $BaSO_4$ causes low solubility of $BaSO_4$ in water.

21. (c) 14 kinds of Bravais lattices (space lattices) are possible in a crystal.

22. (d) Radius ratio in $TlCl$ is 0.732 – 1.000 and co-ordination number is 8 and arrangement is body centred cubic.

23. (c) Zinc blende (ZnS) has *fcc* structure and is an ionic crystal having 4 : 4 co-ordination number.

24. (d) Na_2O has antifluorite (A_2B) type structure.

25. (b) Zinc blende (ZnS) has *fcc* structure and is an ionic crystal having 4 : 4 co-ordination number.

28. (d) $\frac{1}{8} \times 8$ (at corners) $= 1$

$\frac{1}{2} \times 6$ (at face centre) $= 3$

$Z = 1 + 3 = 4$ (total no. of atoms)

Crystal packing

1. (b) Number of tetrahedral voids in the unit cell = 2 × number of atoms = 2*Z*.

2. (b) The system *ABC ABC*...... is also referred to as face-centred cubic or *fcc*.

3. (d) It represents *ccp* arrangement.

4. (a) *BCC* has a coordination number of 8.

5. (b) In rock salt structure the co-ordination number of $Na^+ : Cl^-$ is $6 : 6$.

6. (d) The *bcc* cell consists of 8 atoms at the corners and one atom at centre.

$\therefore\ n = \left(8 \times \frac{1}{8}\right) + 1 = 2$.

The *fcc* cell consists of 8 atoms at the eight corners and one atom at each of the six faces. This atom at the face is shared by two unit cells.

$\therefore\ n = 8 \times \frac{1}{8} + \left(6 \times \frac{1}{2}\right) = 4$.

7. (c) AB_2 type of structure is present in CaF_2

$\therefore\ AB_2 \rightleftharpoons A^{2+} + 2B^-$; $\quad CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$

8. (b) Potassium (K) has *bcc* lattice.

9. (b) Number of atoms per unit cell in *bcc* system = 2.

10. (b) In body centred cubic, each atom/ion has a coordination number of 8.

11. (d) Number of octahedral sites = Number of sphere in the packing.

$\therefore$ Number of octahedral sites per sphere $= 1$.

12. (c) *ABAB* ...... is hexagonal close packing.

13. (a) Sodium (Na) is a body cube.

14. (b) SrF_2 has fluorite (CaF_2) type structure.

15. (b) In *ZnS* structure, sulphide ions occupy all *FCC* lattice points while Zn^{2+} ions are present in alternate tetrahedral voids.

16. (b) MgO contains rock salt $(NaCl)$ structure.

17. (c) CaF_2 (fluorite) has *fcc* structure with 8 : 4 coordination number.

18. (b) Every constituent has two tetrahedral voids. In *ccp* lattice atoms

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

$\therefore$ Tetrahedral void $= 4 \times 2 = 8$,

Thus ratio $= 4 : 8 :: 1 : 2$.

19. (c) Tetrahedral sites one double comparable to octahedral sites then ratio of X and Z respectively 2 : 1 since formula of the compound X_2Z.

20. (c) A atoms are at eight corners of the cube. Therefore, the no. of A atoms in the unit cell = $\frac{8}{8} = 1$. B atoms are at the face centre of six faces. Therefore, its share in the unit cell = $\frac{6}{2} = 3$. The formula is AB_3.

21. (a) In *bcc* structure 68% of the available volume is occupied by spheres. Thus vacant space is 32%.

22. (c) Number of atoms in the cubic close packed structure = 8.

Number of octahedral voids $= \frac{1}{2} \times 8 = 4$.

23. (a) Co-ordination number in *HCP* and *CCP* arrangement is 12 while in *bcc* arrangement is 8.

24. (d) In $NaCl$ (rock salt) : Number of Na^+ ions $= 12$ (at edge centers) $\times \frac{1}{4} + 1$ (at body centre) $\times 1 = 4$.

Number of Cl^- ions $= 8$ (at corners) $\times \frac{1}{8} + 6$ (at face centre) $\times \frac{1}{2} = 4$. Thus 4 formula units per unit cell.

25. (b) Co-ordination number in *HCP* =12
Co-ordination number in *Mg* is also = 12

26. (a) All are the iso-electronic species but Na^+ has low positive charge so have largest radius.

Mathematical analysis of cubic system and Bragg's equation

1. (b) Density of unit cell

$$= \frac{N \times \text{mol.wt.}(M)}{V(= a^3) \times \text{avogadro no.}(N_o)} g\,cm^{-3}$$

2. (b) Distance between K^+ and $F^- = \frac{1}{2} \times$ length of the edge

3. (a) There are two atoms in a *bcc* unit cell.

So, number of atoms in 12.08×10^{23} unit cells $= 2 \times 12.08 \times 10^{23} = 24.16 \times 10^{23}\, atom$.

4. (b) *bcc* structure has one atom shared by 1 unit cell.

5. (b) The structural arrangement of co-ordination number '6' is octahedral and its radius ratio is $0.414 - 0.732$. The example of octahedral is KCl and $NaCl$.

6. (a) The number of spheres in one body centred cubic and in one face centred cubic unit cell is 2 and 4 respectively.

7. (b) Closest approach in *bcc* lattice

$= \frac{1}{2}$ of body diagonal $= \frac{1}{2} \times \sqrt{3}a = \frac{\sqrt{3}}{2} \times 4.3 = 3.72\,Å$.

10. (a) $M = \frac{\rho \times a^3 \times N_0 \times 10^{-30}}{z}$

$$= \frac{10 \times (100)^3 \times (6.02 \times 10^{23}) \times 10^{-30}}{4} = 15.05$$

No. of atoms in 100 *g*

$$= \frac{6.02 \times 10^{23}}{15.05} \times 100 = 4 \times 10^{25}.$$

11. (c) Cs^+ and I^- have largest sizes.

12. (c) $58.5\,g\ NaCl = 1\,mole = 6.02 \times 10^{23}\ Na^+Cl^-\,units$.

One unit cell contains $4\,Na^+Cl^-$ units. Hence number of unit cell present

$$= \frac{6.02 \times 10^{23}}{4} = 1.5 \times 10^{23}.$$

13. (a) $\frac{1}{58.5} \times 6.023 \times 10^{23} = 1.029 \times 10^{22}$

A unit cell contains $4\,Na^+$ ion and $4\,Cl^-$ ions

$\therefore$ Unit cell $= \frac{1.029 \times 10^{22}}{4} = 2.57 \times 10^{21}$ unit cell.

14. (b) Bragg's equation is $n\lambda = 2d\sin\theta$
where *n* is an integer *i.e.* 1, 2, 3, 4 etc.

15. (d) Face centred cubic structure contribute of 1/8 by each atom present on the corner and 1/2 by each atom present on the face.

16. (c) As $CsCl$ is body-centred, $d = \sqrt{3}a/2$.

17. (a) Radius of Na (if *bcc* lattice) $= \frac{\sqrt{3}a}{4} = \frac{\sqrt{3} \times 4.29}{4}$

$= 1.8574\,Å = 1.8574 \times 10^{-8}\,cm$

18. (b) The crystals in which radius ratio value is found between $0.225 - 0.414$ shows tetrahedral crystal structure.

19. (d) For $bcc, d = \frac{\sqrt{3}}{2}a$ or

$$a = \frac{2d}{\sqrt{3}} = \frac{2 \times 4.52}{1.732} = 5.219\,Å = 522\,pm$$

$$\rho = \frac{Z \times M}{a^3 \times N_0 \times 10^{-30}} = \frac{2 \times 39}{(522)^3 \times (6.023 \times 10^{23}) \times 10^{-30}}$$

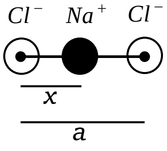
$= 0.91\,g/cm^3 = 910\,kg\,m^{-3}$

20. (c) The value of ionic radius ratio is 0.52 which is between $0.414 - 0.732$, then the geometrical arrangement of ions in crystal is octahedral.

21. (c) The number of atoms present in *sc, fcc* and *bcc* unit cell are 1, 4, 2 respectively.

22. (b) The number of atoms present in *sc, fcc* and *bcc* unit cell are 1, 4, 2 respectively.

23. (d)



a = 2x

24. (a) $r = \frac{a}{2\sqrt{2}}$; $r = \frac{620}{2\sqrt{2}} = 219.25\,Pm$

25. (c) $Z = \frac{V \times N_0 \times d}{M}$

$$= \frac{4.2 \times 8.6 \times 8.3 \times 10^{-24} \times 6.023 \times 10^{23} \times 3.3}{155} = 3.84 = 4$$

26. (b) Volume of unit cell $= a^3$

$= (3.04 \times 10^{-8}\,cm)^3 = 2.81 \times 10^{-23}\,cm^3$

27. (b) In *FCC*

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

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

Crystal structure and Coordination number

1. (b) In a unit cell, W atoms at the corner $= \frac{1}{8} \times 8 = 1$

O atoms at the centre of edges $= \frac{1}{4} \times 12 = 3$

Na atoms at the centre of the cube = 1

$W : O : Na = 1 : 3 : 1$, hence formula $= NaWO_3$

2. (d) For *bcc* lattice, co-ordination number is 8.

3. (b) Body centered cubic lattice has a co-ordination number 8.

4. (a) A atoms are at eight corners of the cube. Therefore, the number of A atoms in the unit cell $= \frac{8}{8} = 1$, atoms B per unit cell = 1. Hence the formula is *AB*.

5. (d) Co-ordination number for *Cu* is 12.

6. (b) Each Cs^+ in $CsCl$ is surrounded by eight Cl^- and each Cl^- in $CsCl$ is surrounded by eight Cs^+.

7. (d) X atoms are at eight corners of the cube. Therefore, the number of X atoms in the unit cell $= \frac{8}{8} = 1$.

Y atoms are at the face centre of six faces. Therefore, its share in the unit cell $= \frac{6}{2} = 3$.

The formula is XY_3.

8. (a) Let the units of ferrous oxide in a unit cell $= n$, molecular weight of ferrous oxide $(FeO) = 56 + 16 = 72\, g\, mol^{-1}$,

weight of n units $= \frac{72 \times n}{6.023 \times 10^{23}}$

Volume of one unit $= (\text{length of corner})^3$

$$= (5\mathring{A})^3 = 125 \times 10^{-24}\, cm^3$$

$$\text{Density} = \frac{\text{wt.of cell}}{\text{volume}},$$

$$4.09 = \frac{72 \times n}{6.023 \times 10^{23} \times 125 \times 10^{-24}}$$

$$n = \frac{3079.2 \times 10^{-1}}{72} = 42.7 \times 10^{-1} = 4.27 \approx 4$$

9. (b) In $NaCl$ crystal Na^+ ions has coordination number 6.

10. (b) Cl^- ions in $CsCl$ adopt *BCC* type of packing.

11. (d) There were 6 A atoms on the face-centres removing face-centred atoms along one of the axes means removal of 2 A atoms.

Now, number of A atoms per unit cell

$$= \underset{\text{(corners)}}{8 \times \frac{1}{8}} + \underset{\text{(face–centred)}}{4 \times \frac{1}{2}} = 3$$

Number of B atoms per unit cell

$$= \underset{\text{(edge centred)}}{12 \times \frac{1}{4}} + \underset{\text{(body centred)}}{1} = 4$$

Hence the resultant stoichiometry is A_3B_4

12. (a) In Cs^+Cl^- crystal co-ordination number of each ion is 8.

13. (b) $r_+ / r_- = \frac{180}{187} = 0.962$ which lies in the range of $0.732 - 1.000$, hence co-ordination number = 8 *i.e.* the structure is $CsCl$ type.

14. (a) In diamond, C-atoms are arranged in a regular tetrahedral structure.

15. (b) In *hcp*, co-ordination no. is 12.

16. (c) Mg has 6 co-ordination number (*fcc* structure).

17. (d) In $NaCl$ crystal every Na^+ ion is surrounded by $6\,Cl^-$ ion and every chloride ion is surrounded by $6\,Na^+$ ion.

18. (d) Crystals show good cleavage because their constituent particles are arranged in planes.

19. (b) Fe_3O_4 is a non-stoichiometric compound because in it the ratio of the cations to the anions becomes different from that indicated by the chemical formula.

20. (d) The radius ratio for co-ordination number 4, 6 and 8 lies in between the ranges $[0.225 - 0.414]$, $[0.414 - 0.732]$ and $[0.732 - 1]$ respectively.

21. (c) The radius ratio for co-ordination number 4, 6 and 8 lies in between the ranges $[0.225 - 0.414]$, $[0.414 - 0.732]$ and $[0.732 - 1]$ respectively.

22. (b) In Na_2O, each oxide ions (O^{2-}) is co-ordinated to $8\,Na^+$ ions and each Na^+ ion to 4 oxide ions. Hence it has 4 : 8 co-ordination.

23. (b) When radius ratio between $0.732 - 1$, then co-ordination number is 8 and structural arrangement is body-centred cubic.

24. (c) Each Cs^+ is surrounded by eight Cl^- ions in $CsCl$ crystal lattice because its co-ordination number is 8 : 8.

25. (a) $NaCl$ has *fcc* arrangement of ions.

26. (c) Each Na^+ is surrounded by six Cl^- ions in $NaCl$ crystal lattice because its co-ordination number is 6 : 6.

27. (b) Zinc blende (ZnS) has *fcc* structure and is an ionic crystal having 4 : 4 co-ordination number.

30. (d) In a simple cubic structure

$z = \frac{1}{8} \times 8$ (atoms one at a corners)

$z = 1$

31. (a) Co-ordination number in hcp structure is 12.

32. (acd) A metal that crystallizes in *bcc* structure has a co-ordination number of 8.

33. (a) In sodium chloride, each Na^+ ion is surrounded by six Cl^- ions and each Cl^- ion is surrounded by six Na^+ ions. Thus, both the ions have coordination number six.

34. (b) The Ca^{2+} ions are arranged in (ccp) arrangement, i.e. Ca^{2+} ions are present at all corners and tat the centre of each face of the cube. the fluoride ions occupy all the tetrahedral sites. This is 8 : 4 arrangement i.e., each Ca^{2+} ion is surrounded by $8F^-$ ions and each F^- ion by four Ca^{2+} ions.

Defects in crystal

1. (c) When polar crystal is subjected to a mechanical stress, electricity is produced – a case of piezoelectricity. Reversely, if electric field is applied, mechanical stress is developed. Piezoelectric crystal acts as a mechanical electrical transductor.

2. (b) More is the Schottky defect in crystal more is the decrease in density.

3. (d) All the given statements are correct about *F*-centres.

5. (a) As each Sr^{2+} ion introduces one cation vacancy, therefore concentration of cation vacancies = mol % of $SrCl_2$ added.

6. (c) Yellow colour on heating $NaCl$ in presence of Na is due to presence of electrons in anion vacancies (*F*-centres).

7. (d) Frenkel's defect is due to shift of an ion from the normal lattice site (Creating a vacancy) and occupy interstitial spaces.

8. (c) $AgBr$ exhibits Frenkel defect due to large difference in the size of Ag^+ and Br^- ions.

9. (d) Schottky defects occurs in highly ionic compounds which have high co-ordination number ex. $NaCl, KCl, CsCl$.

10. (d) Schottky defect is due to missing of equal number of cations and anions.

11. (a) Schottky defect is due to missing of equal number of cations and anions.

12. (a) Impurity present in a crystal does not establish thermal equilibrium.

13. (c) Since no ions are missing from the crystal as a whole, there is no effect on density.

15. (b) On adding non-metal in metal the metal becomes less tensile.

16. (c) $AgBr$ exhibits Frenkel defect due to large difference in the size of Ag^+ and Br^- ions.

17. (c) Both are stoichiometric crystalline defects.

18. (c) Brass, $Cu = 80\%, Zn = 20\%$ substitutional alloy.

Steel is an interstitial alloy because it is an alloy of *Fe* with *C*, *C* atoms occupy the interstitial voids of *Fe* crystal.

19. (d) In metal excess defect when holes created by missing of anions are occupied by electrons, there sites are called *F*-centres and are responsible for colour in the crystal.

20. (c) KBr exhibits Schottky defect and not Frenkel defect.

21. (c) When cation shifts from lattice to interstitial site, the defect is called Frenkel defect.

22. (d) F-centres are the sites where anions are missing and instead electrons are present. they are responsible for colour.

Critical Thinking Questions

1. (c) Amorphous solids neither have ordered arrangement (*i.e.* no definite shape) nor have sharp melting point like crystals, but when heated, they become pliable until they assume the properties usually related to liquids. It is therefore they are regarded as super-cooled liquids.

2. (c) Silicon due to its catenation property form network solid.

3. (c) Orthorhombic geometry has $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90°$. The shape of match box obey this geometry.

4. (d) In a triclinic crystal has no notation of symmetry.

5. (a) In NH_3 molecule, the original appearance is repeated as a result of rotation through 120^o. Such as axis is said to be an axis of three-fold symmetry or a triad axis.

6. (a) Na_2O has antifluorite (A_2B) type structure.

7. (b) Cationic radius increases down the group and decreases along the period.

8. (c) Distance between centres of cation and anion

$$= \frac{d}{2} = \frac{508}{2} = 254\ pm$$

$r_c + r_a = 254\ pm$ or $110 + r_a = 254$ or $r_a = 144\ pm$

9. (b) $\rho = \dfrac{n \times M}{a^3 \times N_0 \times 10^{-30}}$

$$= \frac{2 \times 100}{(400)^3 \times (6.02 \times 10^{23}) \times 10^{-30}} = 5.188\ g/cm^3$$

10. (a) $\underset{(6:6\ \text{co.–ord.})}{NaCl\ \text{structure}} \underset{760\ K}{\overset{\text{High}}{\rightleftharpoons}} \underset{(8:8\ \text{co.–ord.})}{CsCl\ \text{structure}}$

11. (a) Difference $= 2.178 \times 10^3 - 2.165 \times 10^3 = 0.013 \times 10^3$

Fraction unoccupied $= \dfrac{0.013 \times 10^3}{2.178 \times 10^3} = 5.96 \times 10^{-3}$

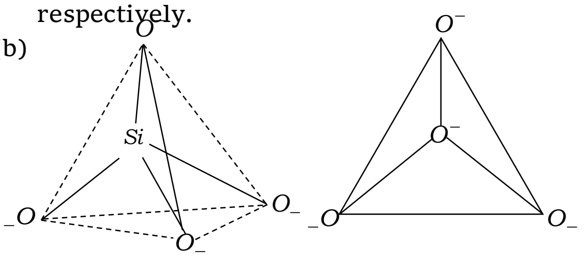
12. (c) $CsBr_3$ consist of Cs^+ and Br_3^- ions.

13. (a) Each Cs^+ is surrounded by eight Cl^- ions in $CsCl$ crystal lattice because its co-ordination number is $8:8$.

14. (b) In each CaF_2 each calcium cation is surrounded by eight fluoride anions in a body centred cubic arrangement. Each fluoride ion is in contact with four calcium ions. Thus CaF_2 has 8 : 4 co-ordination number.

15. (c) The radius ratio for co-ordination number 4, 6 and 8 lies in between the ranges $[0.225-0.414]$, $[0.414-0.732]$ and $[0.732-1]$ respectively.

16. (b)



17. (b) In this diagram, equal number of cations (Na^+) and anions (Cl^-) are missing, so it, shows schottky defect.

18. (c) Zeolite is a three dimensional silicate because of in the silicates all the four oxygen atoms at $(SiO_4)^{-4}$ tetrahedra are shared with other tetrahedra, vesulting in a three dimensional network.

Assertion & Reason

1. (b) It is true that in the dimond structure, carbon atoms are arranged in tetrahedrally (sp^3 hybridized) but it is not the correct explanation of assertion.

2. (d) Tetrahedral holes are smaller in size than octahedral holes. Cations usually occupy less space than anions.

3. (d) Crystalline solids have regular arrangement of constituent particles and are anisotropic whereas amorphous solids have no regular arrangement and are isotropic.

4. (a) Schottky defect is due to missing of equal number of cations and anions.

5. (b) Space or crystal lattice is a regular repeating arrangement of points in space and forms the basis of classification of all structures.

6. (c) Tetrahedral void is so called because it is surrounded by four spheres tetrahedrally while octahedral void is so called because it is surrounded by six spheres octahedrally.

7. (c) Two corners per tetrahedron one shared in both the cases.

8. (b) When an atom or an ion is missing from its normal lattice site, a lattice vacancy or defect is created, which is called schottky defect. Due to missing density of crystal will be lowered.

9. (b) On heating, the metal atoms deposit on the surface and finally they deffuse into the crystal and after ionisation the alkali metal ion occupies cationic vacancy where as electron occupies anionic vacancy.

10. (a) In case of semiconductors, the gap between valence band and the conduction band is small and there fore some of the electrons may jump from valence band to conduction band and thus on increasing temperature conductivity is also increased.

11. (a) All magnetically ordered solids (ferromagnetic and antiferromagnetic solids) transform to the paramagnetic state at high temperature due to the randomisation of spins.

12. (c) In piezoelectric crystals, the dipoles may align them selves in an ordered manner such that there is a net dipole moment in the crystal.

Solid State

SET Self Evaluation Test -5

1. Particles of quartz are packed by

(a) Electrical attraction forces

(b) Vander Waal's forces

(c) Covalent bond forces

(d) Strong electrostatic attraction forces

2. Crystals of covalent compounds always have **[BHU 1984]**

(a) Atoms as their structural units

(b) Molecules as structural units

(c) Ions held together by electrostatic forces

(d) High melting points

3. Wax is an example of

(a) Ionic crystal (b) Covalent crystal

(c) Metallic crystal (d) Molecular crystal

4. Among the following which crystal will be soft and have low melting point

(a) Covalent (b) Ionic

(c) Metallic (d) Molecular

5. In zinc blende structure, zinc atom fill up

(a) All octahedral holes

(b) All tetrahedral holes

(c) Half number of octahedral holes

(d) Half number of tetrahedral holes

6. Which ion has the lowest radius from the following ions

[Kurukshetra CEE 1998]

(a) Na^+ (b) Mg^{2+}

(c) Al^{3+} (d) Si^{4+}

7. The second order Bragg's diffraction of $X-$rays with $\lambda = 1\ \AA$ from a set of parallel planes in a metal occurs at an angle of 60^o. The distance between the scattering planes in the crystal is **[CBSE PMT 1**

(a) $0.575\ \AA$ (b) $1.00\ \AA$

(c) $2.00\ \AA$ (d) $1.15\ \AA$

8. The edge length of the unit cell of $NaCl$ crystal lattice is $552\ pm$. If ionic radius of sodium ion is $95\ pm$, what is the ionic radius of chloride ion **[KCET 1998]**

(a) $190\ pm$ (b) $368\ pm$

(c) $181\ pm$ (d) $276\ pm$

9. The ionic radii of Rb^+ and I^- are 1.46 Å and 2.16Å. the most probable type of structure exhibited by it is

[UPSEAT 2004]

(a) $CsCl$ type (b) ZnS type

(c) $NaCl$ type (d) CaF_2 type

10. The coordination number of a cation occupying a tetrahedral hole is

(a) 6 (b) 8

(c) 12 (d) 4

11. If a electron is present in place of anion in a crystal lattice, then it is called

(a) Frenkel defect

(b) Schottky defect

(c) Interstitial defects

(d) $F-$centre

Answers and Solutions

(SET -5)

1. (c) Quartz is a covalent solid in which constituent particles are atoms which are held together by covalent bond forces.

2. (a) Constituent particles of covalent compounds are atoms.

3. (d) Iodine crystals are molecular crystals, in which constituent particles are molecules having interparticle forces are Vander Waal's forces.

4. (d) Molecular crystals are soft and have low melting point.

5. (d) In zinc blende (ZnS) half number of tetrahedral holes are filled by zinc atoms.

6. (d) All are the iso-electronic species but Si^{4+} has high positive charge so have lowest radius.

7. (d) $2d\sin\theta = n\lambda$ or $2 \times d \times \sin 60° = 2 \times 1 Å$

or $2 \times d \times 0.8660 = 2$

or $d = 1.15 Å$ $(\sin 60° = \sqrt{3}/2$ or $0.8660)$.

8. (c) Distance between centres of Na^+ and Cl^-

$r_{Na^+} + r_{Cl^-} = 276\ pm$ or $95 + r_{Cl^-} = 276\ pm$

or $r_{Cl^-} = 276 - 95 = 181\ pm$

9. (c) $\frac{r_{c^+}}{r_{a^-}} = \frac{1.46}{2.16} = 0.676$

It permits co-ordination number 6 and octahedral structure of type $NaCl$.

10. (d) The co-ordination number of a cation occupying a tetrahedral hole is 4.

11. (d) When electrons are trapped in anion vacancies, these are called *F*-centres.

***