

SOLID STATE

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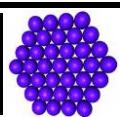
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JEE(Advanced) Syllabus

Classification of solids, crystalline state, seven crystal systems (cell parameters a , b , c , α , β , γ), close packed structure of solids (cubic), packing in fcc, bcc and hcp lattices; Nearest neighbours, ionic radii, simple ionic compounds, point defects.

JEE(Main) Syllabus

Classification of solids: molecular, ionic, covalent and metallic solids, amorphous and crystalline solids (elementary idea); Bragg's Law and its applications; Unit cell and lattices, packing in solids (fcc, bcc and hcp lattices), voids, calculations involving unit cell parameters, imperfection in solids; Electrical, magnetic and dielectric properties.



SOLID STATE

Section (A): Basics of solid state

State of matter depends on:

- (i) Tendency of relative motion at a particular temperature.
- (ii) Intermolecular forces.

Tab-1

Properties	Solid	Liquid	Gases
(i) Motion of particles	No free motion only vibration allow.	Random motion to a limited extent is allowed.	Totally random.
(ii) Inter molecular forces	Very strong	Intermediate strength	Very weak (\approx zero)
(iii) Average separation (volume)	Average separation is fixed so volume is fixed	Average separation is almost constant so almost fixed volume.	No fixed volume.
(iv) Shape	Definite shape as the location of particles are fixed.	Average separation is fixed but location of particle is not fixed so no definite shape.	No fixed shape.
(v) Effect of change in pressure & temperature.	Are incompressible.	Liquid are also almost incompressible.	Highly compressible.
(vi) Heat capacities	Heat capacity is almost independent of process.	Same as solid.	Heat capacity is dependent on process.

Types of Solid:

Tab-2 Classification on the basis of forces among constituting particles

Type of solid	Constituent partical	Force of interaction	Example	Physical state	Melting point
(i) Molecular solid (non conducting)	Molecules	(i) Non polar \rightarrow dispersion force. (ii) Polar \rightarrow dipole-dipole. (iii) Polar & H-bonding.	I ₂ , Xe(s), C ₆ H ₆ , CCl ₄ , H ₂ , HCl, SO ₂ , SF ₄ , H ₂ O(s), H ₃ BO ₃ (s)	Very soft Soft Hard	Very low Low Low
(ii) Ionic solid. solid \rightarrow insulator Molten & aqueous \rightarrow conducting.	Ions	Coulombic directional non long range.	NaCl, ZnS, CaF ₄ , CsCl	Very hard Brittle	Very high
(iii) Metallic solid good conductor in solid & molten state.	Metal ion at fixed locations in sea of delocalised electrons.	Metallic bond.	Cu, Al, Zn, Ag, etc.	Soft \rightarrow Hard depending on metallic bond.	Low \rightarrow High
(iv) Covalent or network. Insulator except C (graphite).	Atoms	Covalent bond.	C(diamond), SiC, SiO ₂ , AlN, graphite.	Very hard Graphite \rightarrow Soft only conducting.	Very high



Solved Examples

Ex-1 Identify molecular solid, covalent solid, ionic solid: $P_4(s)$, $S_8(s)$, $SiC(s)$, $Al_2O_3(s)$, $He(s)$, $Al_2Cl_6(s)$.

Sol. Molecular solid $\rightarrow P_4(s)$, $S_8(s)$, $He(s)$, $Al_2Cl_6(s)$

Covalent solid $\rightarrow SiC$

Ionic solid $\rightarrow Al_2O_3(s)$.

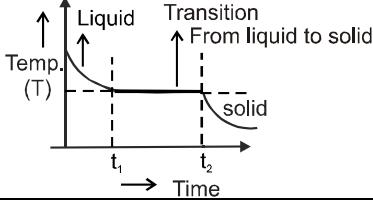
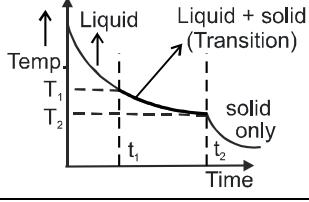
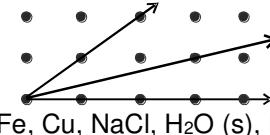
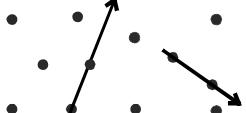
Th-1 General Characteristics of Solids:

- (i) Solids have definite mass, shape and volume.
- (ii) There are least intermolecular distances in solids as compared to liquids and gases.
- (iii) There are strong intermolecular forces of attraction between particles in solids.
- (iv) The particles of a substance cannot flow in their solid state but can flow in molten state.
- (v) The constituting particles (atoms/ions/ molecules) have fixed positions. They can oscillate only about their mean position, i.e., they have vibrational motions only.
- (vi) They are rigid and incompressible.

Th-2 Types of SOLIDS on the basis of arrangement of particles:

On the basis of arrangement of particle in the solid, these can be classified into crystalline & amorphous solids.

Tab-3

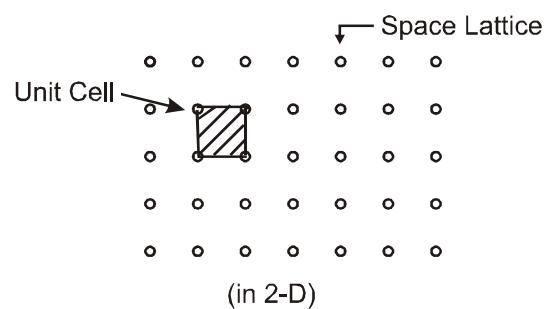
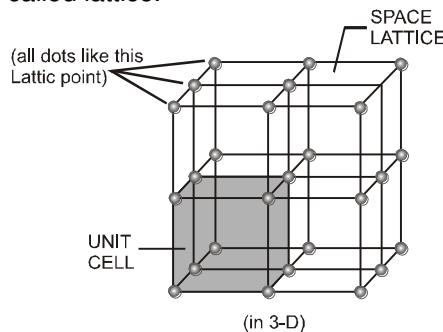
Crystalline solid		Amorphous solids
	True solid	Pseudo solids, super cooled liquid [In between solid & liquid]
1	The constituent practical (atoms, molecule, ion) follow a definite repeating arrangement.	1 No particular pattern is followed particle are random arranged.
2	These have long range order.	2 They have short range order no long range order are found.
3	These are produced by slow cooling under controlled condition of liquid. The crystalline structure is also dependent on conditions. Same substance can have different crystalline structure in different condition. Different crystalline structure of the same substance are called its polymorphic forms & this is known as polymorphism.	3 Rapid or suddenly cooling of the liquid generate the amorphous solid.
4	These have fixed or sharp melting point and enthalpy of fusion. Cooling Curve :  Ex. : Ag, Fe, Cu, NaCl, H ₂ O (s), Dimond, Quartz, Sucrose (Sugar)	4 These have a range of temperature in which they melts as. Their melting point and enthalpy of fusion is not fixed.  Ex. : Glass, Plastic, Amorphous silica, Rubber, Starch.
5	These are anisotropic: Physical properties will have different values in different direction.  Ex. : Ag, Fe, Cu, NaCl, H ₂ O (s), Dimond, Quartz, Sucrose (Sugar)	5 These are isotropic: All different physical properties are same in all different direction. Reason : Due to random arrangement of particles. 



Th-3 Internal arrangement of particle in crystalline solid:

Each constituent particle (Molecule of any shape, atom, and ions) will be represented by a dot (.) and this dot is called a **lattice point**.

- D-1 Lattice:** The 3-D regular and repeating arrangement of constituent particle represent by dots in solid is called lattice.



- D-2 Unit Cell:** *Unit cell is the smallest portion of a crystal lattice which, when repeated in different directions, generates the entire lattice.*

Th-4 Characteristics of a Unit Cell:

- (i) Its dimensional along the three edges, a , b and c . These edges may or may not be mutually perpendicular.
- (ii) Angles between the edges, α (between b and c) β (between a and c) and γ (between a and b).
- (iii) Each unit cell has characteristic relation between a , b and c or α , β , and γ to give rise different types of unit cell.

Thus, a unit cell is characterised by six parameters, a , b , c , α , β and γ . These parameters of a typical unit cell are shown in figure.

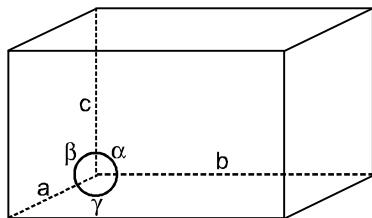
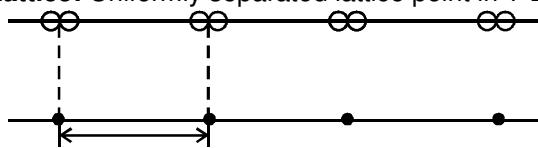


Illustration of parameters of a unit cell

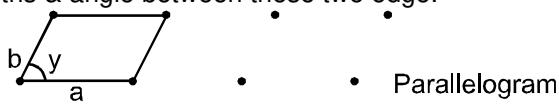
- Th-5** A unit cell may also be defined as a 1D, 2D, 3D three dimensional group of lattice points that generates the whole lattice by repetition or stacking.

- Generally most symmetrical and smallest volume unit cell is selected.

D-3 1-Dimensional Space Lattice: Uniformly separated lattice point in 1-D

only one parameter is required → distance between two lattice point.

- D-4 2-Dimensional Space Lattice:** Regular arrangement of point in plane 3 parameter required → Two edge lengths & angle between these two edge.



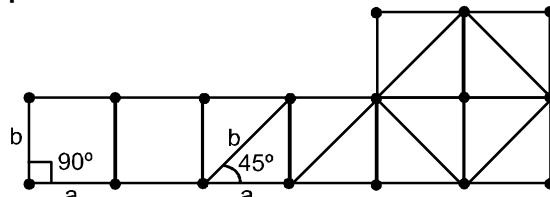
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Th-6 We can only shift the unit cell parallel not rotate it.

- (i) Square unit cell $\rightarrow a = b, \gamma = 90^\circ$
- (ii) Rectangle unit cell $\rightarrow a \neq b, \gamma = 90^\circ$
- (iii) Hexagonal unit cell $\rightarrow a = b, \gamma = 120^\circ$
- (iv) Rhombic unit cell $\rightarrow a = b, \gamma \neq 90^\circ, \gamma \neq 60^\circ \& \gamma \neq 120^\circ$
- (v) Parallelogram $\rightarrow a \neq b, \gamma \neq 90^\circ$

Most symmetrical \rightarrow square unit cell.

Square unit cell:

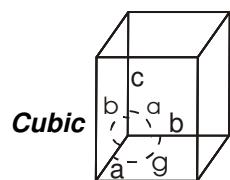


D-5 Primitive unit cell: Unit cell having lattice point only at the corner.

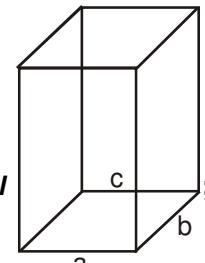
D-6 Non Primitive or centered unit cell: Unit cell having lattice point at corner as well as with in the unit cell.

3-Dimensional Space Lattice:

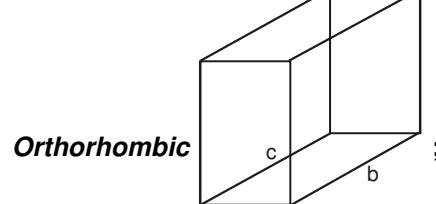
Seven Primitive unit cells in crystals



($a = b = c, \alpha = \beta = \gamma = 90^\circ$)

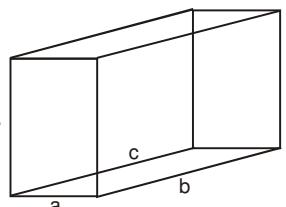


($a = b \neq c, \alpha = \beta = \gamma = 90^\circ$)



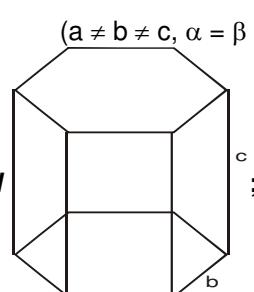
($a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$)

Monoclinic



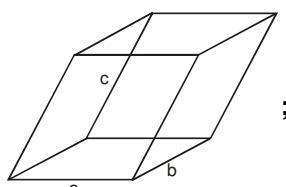
($a \neq b \neq c, \alpha = \gamma = 90^\circ, \beta \neq 120^\circ, \neq 90^\circ, \neq 60^\circ$)

Hexagonal



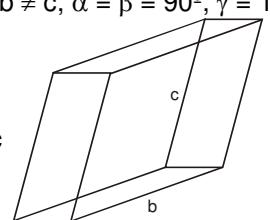
($a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$)

Rhombohedral



($a = b = c, \alpha = \beta = \gamma \neq 90^\circ$)

Triclinic

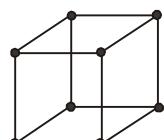


($a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$)

Th-7 The type of unit cells found in different types of crystals.

(Total number of atoms in unit cell)

1. **Primitive /simple unit cell:**



$$= 8 \times \frac{1}{8} = 1$$

2. Non primitive:



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



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

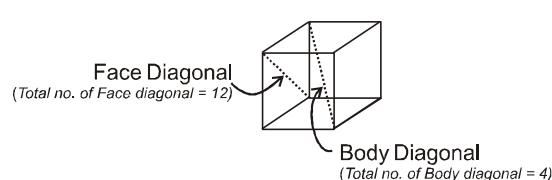
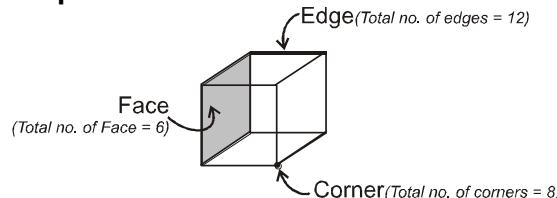


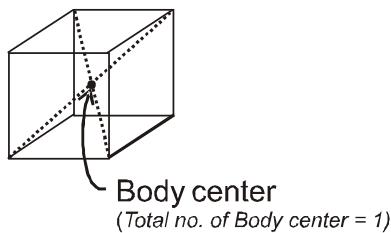
$$= 8 \times \frac{1}{8} + \frac{1}{2} \times 2 = 2$$

Note: (1) Which particular type of unit cell will be found in a particular crystal class is decided on the basis of "the surroundings of each & every lattice point in a particular lattice which is exactly identical.
(2) In 3-d to specify any unit cell 6 parameter are required.
→ **3-edge length (a, b, c) and 3-angle between these. (α, β, γ), [$a-b-\gamma$], [$b-c-\alpha$], [$c-a-\beta$].**

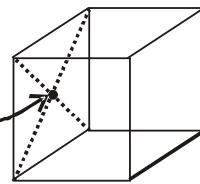
Tab-4 Seven Crystal System

S.No.	Crystal System	Edge length	Angles	Unit cell found	Examples
1	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	SC, BCC, FCC (3)	NaCl, ZnS, Fe, Al, Cu, C (diamond), CsCl, Na ₂ O, CaF ₂ , KCl, Pb, Alum.
2	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	SC, BC (2)	Sn (white tin), SnO ₂ , TiO ₂ , ZnO ₂ , NiSO ₄ , urea.
3	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	SC, BC, FC, EC (4)	Rhombic sulphur, BaSO ₄ , KNO ₃ , PbCO ₃ , CaCO ₃ (aragonite)
4	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ$ $\beta \neq 120^\circ, \neq 90^\circ, \neq 60^\circ$	SC, EC (2)	Monoclinic sulphur, PbCrO ₄ , Na ₂ SO ₄ , 10H ₂ O, Na ₂ B ₄ O ₇ .10H ₂ O
5	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ$ $\gamma \neq 120^\circ$	SC (1)	Graphite, ZnO, CdS, Mg, PbI ₂ , SiC.
6	Rhombohedral or Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	SC (1)	CaCO ₃ (Calcite), HgS (Cinnabar), NaNO ₃ , ICl.
7	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	SC (1)	K ₂ Cr ₂ O ₇ , CuSO ₄ .5H ₂ O, H ₃ BO ₃

Hint for memorise: CTOMHRT**Note:** In 3-D 14 different types of unit cell are found and these are also known as 14 **Bravais lattice**.**Th-8 Properties of a cube:**



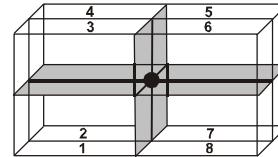
Face centre
(Total no. of Face center = 6)



Th-9 Contribution of different Lattice point in one Cubical unit cell:

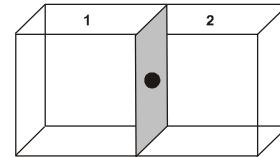
- (i) Contribution from **one corner lattice point** = $\frac{1}{8}$ th.

(shared in 8 identical cubes)



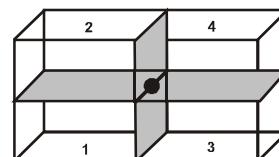
- (ii) Contribution from **one face centered lattice point** = $\frac{1}{2}$.

(shared in 2 identical cubes)



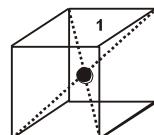
- (iii) Contribution from **edge centered lattice point** = $\frac{1}{4}$ th.

(shared in 4 identical cubes)



- (iv) Contribution from **body centered lattice point** = 1.

(it is present inside or at the centre of cube)



Solved Examples

Ex-2 The lattice parameters of a given crystal are $a = 5.62 \text{ \AA}$, $b = 7.41 \text{ \AA}$ and $c = 9.48 \text{ \AA}$. The three coordinate axes are mutually perpendicular to each other. The crystal is:

- (A) tetragonal (B) orthorhombic (C) monoclinic (D) trigonal.

Ans. (B)

Sol. $a \neq b \neq c$ & $\alpha = \beta = \gamma = 90^\circ$ the crystal system is orthorhombic.

Ex-3 Tetragonal crystal system has the following unit cell dimensions:

- | | |
|--|--|
| (A) $a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$ | (B) $a = b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$ |
| (C) $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$ | (D) $a = b \neq c$ and $\alpha = \beta = 90^\circ, \gamma = 120^\circ$ |

Ans. (B)

Ex-4 In a face centered cubic arrangement of A and B atoms whose A atoms are at the corner of the unit cell and B atoms at the face centres. One of the A atom is missing from one corner in unit cell. The simplest formula of the compound is:

- | | | | |
|--------------|------------|-----------------|--------------|
| (A) A_7B_3 | (B) AB_3 | (C) A_7B_{24} | (D) A_2B_3 |
|--------------|------------|-----------------|--------------|

Ans. (C)

Sol. $A = 7 \times \frac{1}{8} = \frac{1}{8}$; $B = 6 \times \frac{1}{2} = 3$

Formula = $A_{7/8}B_3$ or A_7B_{24}



Ex-5 A compound has cubical unit cell in which X atom are present at 6 corner, Y atom are at remaining corner & only at those face centers which are not opposite to each other & Z atoms are present at remaining face center & body center then find.

(i) Formula of compound (ii) Density if edge length = 2 Å.

Given: Atomic mass of X = 40 amu, Y = 60 amu, Z = 80 amu.

$$\text{Sol.} \quad (i) \quad X = \frac{1}{8} \times 6 = \frac{3}{4}$$

$$Y = \frac{1}{8} \times 2 + \frac{1}{2} \times 3 = \frac{7}{4}$$

$$Z = \frac{1}{2} \times 3 + 1 + 1 = \frac{5}{2} = \frac{10}{4}$$

For formula: $X_{\frac{3}{4}} Y_{\frac{7}{4}} Z_{\frac{10}{4}} = X_3 Y_7 Z_{10}$

$$(ii) \quad 1 \text{ amu} = 1.67 \times 10^{-24} \text{ gram}$$

$$1 \text{ amu} = \frac{1}{6.02 \times 10^{23}} \text{ gram.}$$

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{\frac{3}{4} \times 40 + \frac{7}{4} \times 60 + \frac{10}{4} \times 80}{(2 \times 10^{-8})^3} \text{ amu/cc} = \frac{335 \times 1.67 \times 10^{-24}}{8 \times 10^{-24}} = 69.8 \text{ gram/cc.}$$

Some Definitions

D-7 Coordination number: The number of nearest neighbours sphere in a packing is called coordination number.

D-8 Density of unit cell: It is the ratio of mass of the spheres present in unit cell and total volume of unit cell.

$$\text{Density of the unit cell} = \frac{\text{Mass of total atoms present in a unit cell}}{\text{Volume of that unit Cell}}$$

$$d = \frac{Z(M/N_A)}{a^3 \times 10^{-30}} \text{ gcm}^{-3} \Rightarrow d = \frac{ZM}{N_A (a^3 \times 10^{-30})} \text{ gcm}^{-3}$$

Where Z = no. of atoms in a unit cell

M/N_A = mass of a single atom in grams ($1 \text{ amu} = 1/N_A \text{ gram}$)

M = molar mass

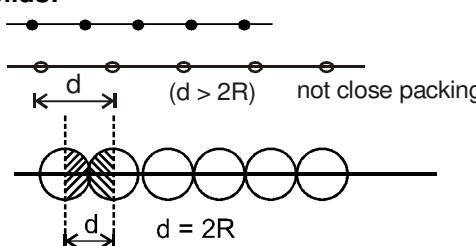
N_A = Avogadro number (6.023×10^{23})

D-9 Packing efficiency: The percentage of total space filled by the particles is called packing efficiency. Different types of packing arrangements have different packing efficiency.

$$\text{Packing efficiency} = \frac{\text{Volume of atoms in a unit cell}}{\text{Total volume of a unit cell}} \times 100\% \quad \text{For 3-D Crystal}$$

Th-10 Structure of Solids:

1-D Lattice:



→ Arrangement of maximum stability.

→ Arrangement of close packing.

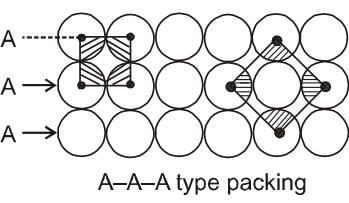
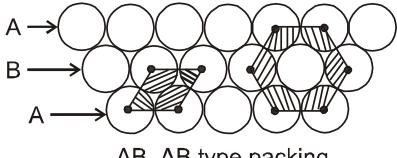
→ Arrangement of minimum P.E.

→ Arrangement of maximum efficiency (100%).

2-D Lattice:

Can be considered to be made up of one dimensional array or lines.

Tab-5

<p>(i) Square arrangement (poor arrangement) Atoms are arranged such that sphere of one array are exactly above the sphere of another array</p>  <p>Square packing in two dimension. Two type of unit cell : $=$ primitive & non-primitive (i) Effective no. of atom (Z) = 1 atom & 2 atoms. (ii) Edge length ($a = b$) = $2R$. (iii) Packing efficiency (Area wise) = $\frac{1 \times \pi R^2}{4R^2} = \frac{\pi}{4} = 78.5\%$ (iv) Co-ordination no. (CN) = 4.</p>	<p>Hexagonal Arrangement (Better arrangement) One dimensional array are arranged such that sphere of one array occupy the depression of other array.</p>  <p>Hexagonal close packing in two dimension. Two type of unit cell : $=$ primitive & non-primitive (i) Effective no. of atom (Z) = 1 atom & 3 atoms. (ii) Edge length ($a = b$) = $2R$. (iii) Packing efficiency (Area wise) = $\frac{3(\pi R^2)}{6 \times \frac{\sqrt{3}}{4}(2R)^2} = 90.6\%$ (iv) Co-ordination no. (CN) = 6.</p>
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Section (B): Simple Cubic Structure & BCC

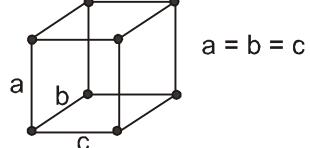
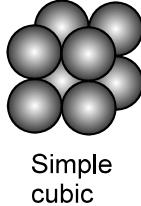
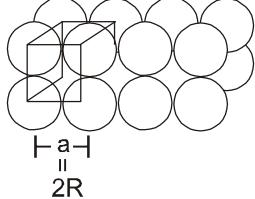
Th-11 3-D Lattice:

When 2-D close packed layers are kept on each other 3-D close packing will be generated.

(A) Square packed sheets:

- (1) Square packed sheets are kept on another such that -
atoms / spheres of one sheet are exactly above spheres of other sheet.
 $\rightarrow A A A A \dots \dots \dots$ Pattern repeated.

→ Simple cube can be taken as unit cell of this particular lattice:



(i) Relation between a & R .

Corner atoms are touching each other so, $a = 2R$.

(ii) Effective no. of atom (Z) (per unit cell).

$$Z = 8 \text{ [corner]} \times \frac{1}{8} = 1 \text{ atom.}$$

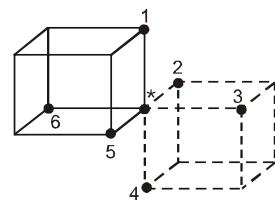
$$\text{(iii) Packing efficiency: } \frac{1 \times \frac{4}{3} \pi R^3}{(2R)^3} = \frac{\pi}{6} = 52.33\%.$$

$$\text{(iv) Density} = \frac{\text{Mass of unit cell}}{\text{volume of unit cell}} = \left(\frac{Z \times M}{N_A \times a^3} \right).$$

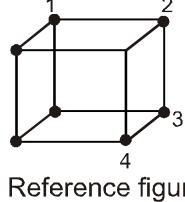
(v) Co-ordination number:

Number of nearest neighbour's or (no. of sphere which are touching any particular sphere). $CN = 6$.

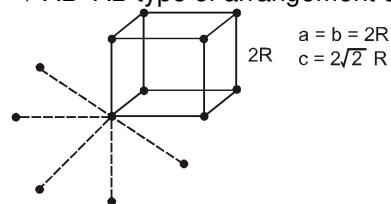
(The * marked atom touches atom number 1, 5, 6 in its own unit cell and 2, 3, 4 in other unit cells hence total number of nearest atom = 6)



Tab-6

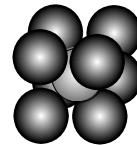
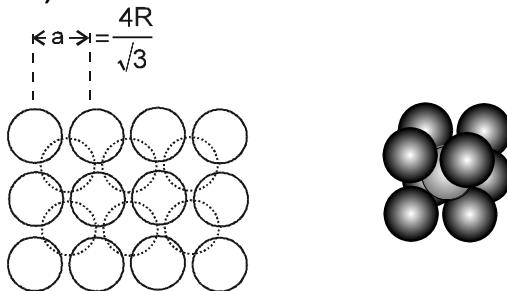
Type of neighbour	Distance	No. of neighbours	
(i) Nearest	a (distance b/w 1 & 2)	$\left\{ \frac{3 \times 8}{4} = 6 \right\} \Rightarrow 6$	
(ii) (next) ¹	$\sqrt{2} a$ (distance b/w 1 & 3)	$\left\{ \frac{3 \times 8}{2} = 12 \right\} \Rightarrow 12$	 Reference figure

(2) Square packed layer are placed such that sphere of one layer occupy the depression of other layer.
 → AB–AB type of arrangement of square sheet in 3-D.



a = edge length of cube; R = radius of sphere

Body centered cubic (BCC):



* Not so close pack arrangement.

* The lattice point in 2-D array do not touch each other. The sphere start touching each other only upon moving from 2-D to 3-D.

* 2-D array placed on top of each other such that sphere of next plane are into cavities of first plane of sphere.

(i) Relation between a & R :

Spheres are not touching along edge they touching along the body diagonal. So $\frac{\sqrt{3}}{2} a = 2 R$.

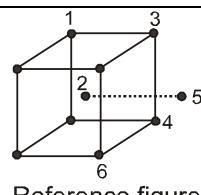
(ii) Effective no. of atom (Z) = $8 \times [\text{corner}] \times \frac{1}{8} + 1 = 2$

(iii) Packing fraction = $\frac{2 \times \frac{4}{3} \pi R^3}{\left(\frac{4R}{\sqrt{3}}\right)^3} = \frac{\sqrt{3}\pi}{8} = 68\%$.

(iv) Co-ordination No. (CN) = 8. (Body centered atom have only 8 nearest neighbouring atoms so CN = 8)

(v) Density = $\frac{Z \times M}{N_A(a)^3}$ where $Z = 2$.

Tab-7

Type of neighbour	Distance	No. of neighbours	
(i) Nearest	$\frac{\sqrt{3}a}{2}$ (distance b/w 1 & 2)	8	
(ii) (next) ¹	a (1 & 3)	6	 Reference figure



(Note: In bcc crystal structure, the co-ordination no. is 8 because each atom touches four atoms in the layer above it, four in the layer below it and none in its own layers.)

Solved Examples

- Ex-6** How many 'nearest' and 'next nearest' neighbours respectively does potassium have in b.c.c. lattice?
(A) 8, 8 (B) 8, 6 (C) 6, 8 (D) 8, 2

Ans. (B)

Ex-7 If a metal has a bcc crystal structure, the coordination number is 8, because:
(A) each atom touches four atoms in the layer above it, four in the layer below it and none in its own layer.
(B) each atom touches four atoms in the layer above it, four in the layer below it and one in its own layer.
(C) two atoms touch four atoms in the layer above them, four in the layer below them, and none in their own layer.
(D) each atom touches eight atoms in the layer above it, eight in the layer below it and none in its own layer.

Ans. (A)

- Ex-8** Potassium crystallizes in body centered cubic lattice with a unit cell length $a = 5.2 \text{ \AA}$

 - (A) What is the distance between nearest neighbours?
 - (B) What is the distance between next nearest neighbours?
 - (C) How many nearest neighbours does each K atom have?
 - (D) How many next nearest neighbours does each K has?
 - (E) What is calculated density of crystalline K.

Ans. (A) 4.5 Å, (B) 5.2, (C) 8, (D) 6 (E) 0.92 g/mL

Sol. (A) $2r = \frac{\sqrt{3}a}{2} = \frac{\sqrt{3} \times 5.2}{2} = 4.5 \text{ \AA}$ (B) distance = $a = 5.2 \text{ \AA}$
 (C) 8 (D) 6
 (E) $d = \frac{2 \times 39}{(5.2 \times 10^{-8})^3 \times 6.02 \times 10^{23}} = 0.92 \text{ g/ml}$

Section (C): HCP & CCP structures

Th-12 (B) Arrangement of hexagonal closed packed sheets:

- * To generate close packing two dimensions arrangement must be hexagonal.
 - * Sheet are arranged such that void or depressions of one sheet are occupied by sphere of other sheet.
 - * Only 50% void of one layer can be occupied by sphere of other layer (II layer).

* Now there will be two method to place in layer on the n layer.

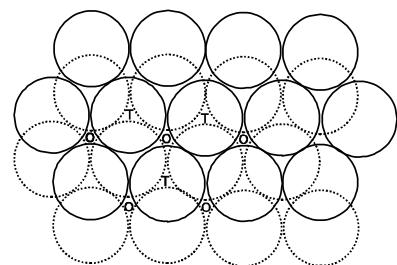
(1) Hexagonal close packing (HCP) AB-AB-AB-...-type:
 Spheres of III layer occupy these voids of II layer under

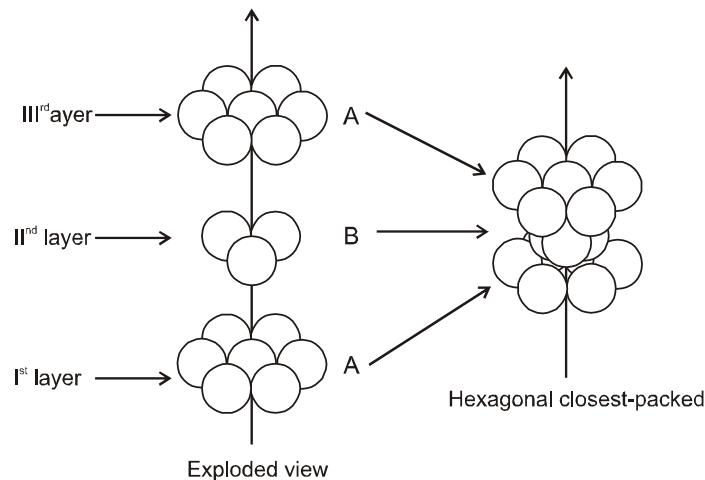
- * Sphere of III layer occupy those voids of II layer under which there are sphere of Ist layer. So third layer is exactly identical to Ist layer.

That's why this generate ABAB- - - -AB pattern.

One type of void always remain on occupied.

T = tetrahedral void
O = octahedral void

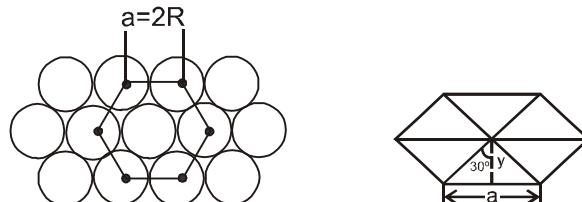




Unit cell: $a = 2r = b$; $\gamma = 120^\circ$

(i) Relation between a , b , c and R :

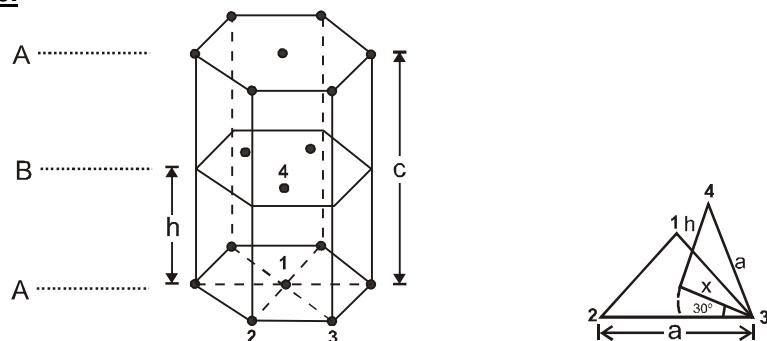
$$a = b = 2R$$



$$\tan 30^\circ = \frac{(a/2)}{y} \quad \text{So} \quad y = \frac{a \times \sqrt{3}}{2 \times 1} = \frac{\sqrt{3}}{2} a.$$

$$\text{Area} = 6 \left[\frac{1}{2} a \times \frac{\sqrt{3}}{2} a \right] = \frac{6\sqrt{3}a^2}{4}$$

calculation of c .



$$\cos 30^\circ = \frac{(a/2)}{x} \quad x = \frac{2a}{2 \times \sqrt{3}} = \frac{a}{\sqrt{3}}$$

Applying pythagoras theorem: $x^2 + h^2 = a^2$

$$\text{so} \quad h^2 = a^2 - x^2 = a^2 - \frac{a^2}{3} = \frac{2}{3} a^2$$

$$h = \sqrt{\frac{2}{3}} a \quad (\text{h = distance between two consecutive layers A-B})$$

$$\text{so} \quad c = 2h = 2\sqrt{\frac{2}{3}} a$$

c = height of hexagonal unit cell (Least distance between two same layers A-A or Ist and IIIrd).

So volume of hexagon = area of base × height

$$= \frac{6\sqrt{3}}{4} \times a^2 \times 2\sqrt{\frac{2}{3}} \quad a = \frac{6\sqrt{3}}{4} \times (2R)^2 + 2\sqrt{\frac{2}{3}} \times (2R) = 24\sqrt{2} R^3$$

(ii) Effective no. of atoms (Z) = $3 + 2 \times \frac{1}{2} + 12 \times \frac{1}{6} = 3 + 1 + 2 = 6$.

(iii) Packing efficiency = $\frac{6 \times \frac{4}{3}\pi R^3}{24\sqrt{2} R^3} = \frac{\pi}{3\sqrt{2}} = 74\%$.

(iv) Coordination number, (CN) = 12

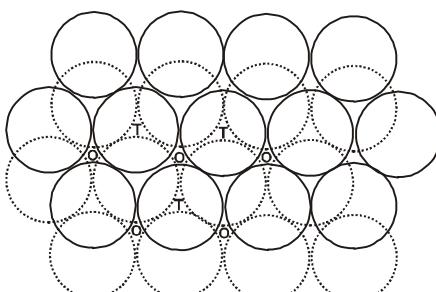
(Each sphere touch 6 sphere in its layer 3 above and 3 below)

(v) Density (d) = $\frac{\text{mass}}{\text{volume}} = \left[\frac{Z \times M}{N_A \times \text{volume}} \right] \quad (z = 6)$

Th-13 (2) ABC-ABC arrangement (Cubic close packing (CCP) or Face centred cube (FCC))

Third layer sphere are placed such that these occupy those 50% voids of II layer under which there are void of Ist layer.

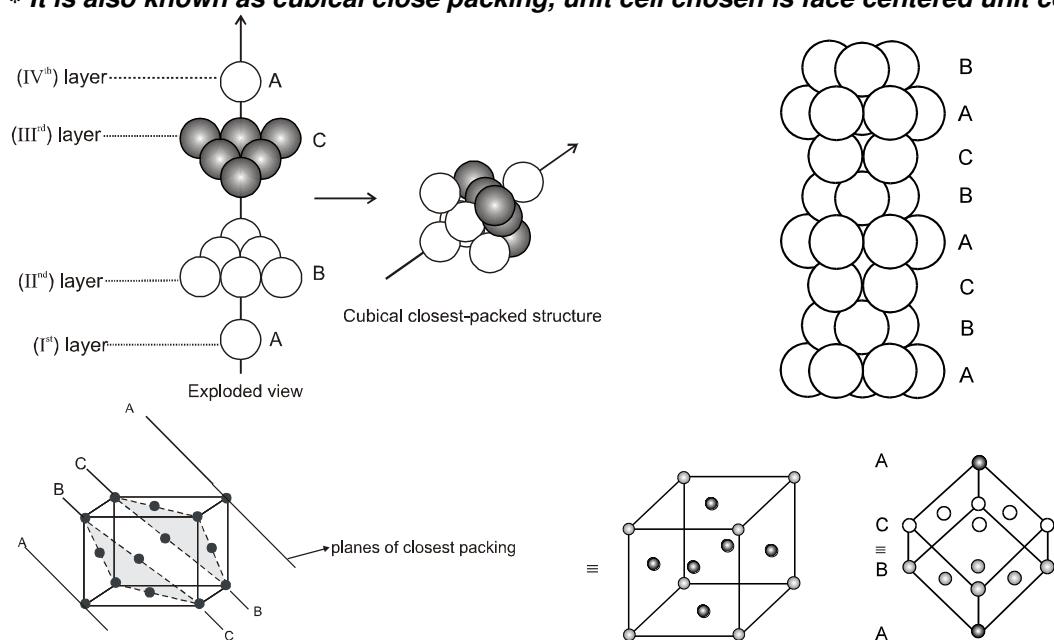
T = Tetrahedral void
O = Octahedral void



* IIIrd layer will be different from Ist layer as well as IInd layer.

* ABC-ABC type of arrangement.

* It is also known as cubical close packing, unit cell chosen is face centered unit cell (FCC).



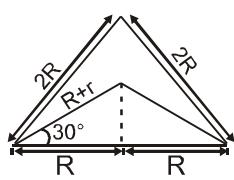
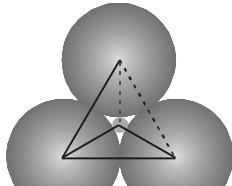
(i) Relation between 'a' and 'R':

$$a \neq 2R \quad \Rightarrow \quad \sqrt{2}a = 4R \quad (\text{sphere are touching along the face diagonal})$$

(ii) Effective no. of atoms per unit cell (Z) = $\frac{1}{8} \times 8 + \frac{1}{2} \times 6 = 4$

D-11 2-Dimensions void:**(i) Triangular void [2D-3 coordinate void]**

* This type of void found in close packed structure of plane when three sphere are in contact.

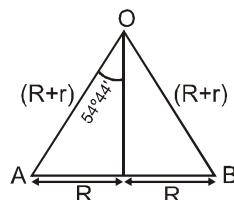
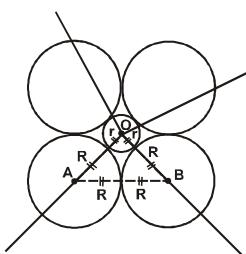
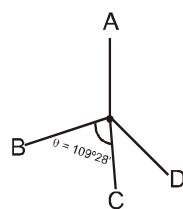
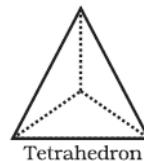
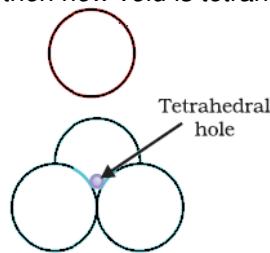
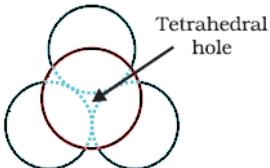
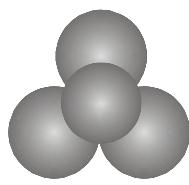


$$\cos 30^\circ = \left(\frac{R}{R+r} \right)$$

$$\left[\frac{R+r}{R} \right] = \frac{1}{\cos 30^\circ} \quad \frac{r}{R} = 0.155.$$

D-12 3-Dimensions void:**Tetrahedral void [3D-4 coordinate void]**

* If 2nd layer sphere are placed over a triangular void then new void is tetrahedral.

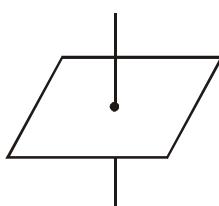
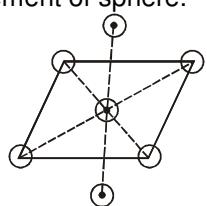


$$\sin 54^\circ 44' = \left(\frac{R}{R+r} \right)$$

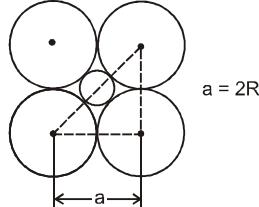
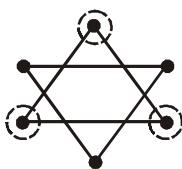
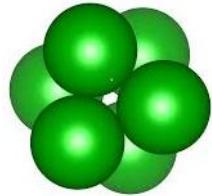
$$\frac{r}{R} = 0.225$$

D-13 3-Octahedral void: [3D-6 coordinate void]

Octahedral void is formed when ever two sphere are placed, one on top and the other below a square arrangement of sphere.



→ This can also be obtained by placing two three ball arrangement on the top of each other.



$$\sqrt{2} a = 2[R + r] ;$$

$$2\sqrt{2} R = 2[R + r].$$

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

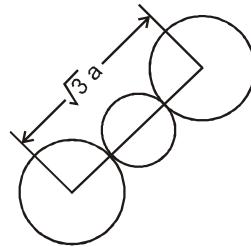
D-14 Cubical void (3D-8-coordinate void)

Sphere are touch along body diagonal:

$$\sqrt{3}a = 2[R + r]$$

$$2\sqrt{3}R = 2[R + r]$$

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

**Th-15 Location of void:****(i) FCC or CCP unit cell:****(a) Tetrahedral void:**

* FCC unit cell has **8 tetrahedral void** per unit cell.
Just below every corner of the unit cell.

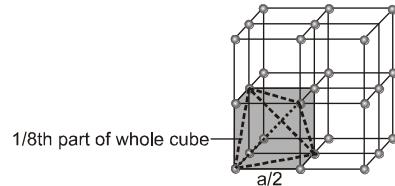
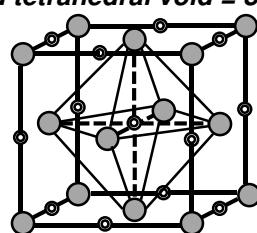
* As unit cell has **8 corner** that's why FCC unit cell has **8 tetrahedral void** per unit cell.

* Distance of tetrahedral void from corner is $\frac{\sqrt{3}a}{4}$ and distance between two tetrahedral void is $= \frac{\sqrt{3}a}{2}$.

* FCC unit cell has 4 body diagonal and each body diagonal contain **2 tetrahedral void** that's why total **tetrahedral void = 8**.

* If a large size cube is divided in 8 minicube than center of each minicube contain one tetrahedral void and distance of center of minicube from corner is $\frac{\sqrt{3}a}{4}$.

* For FCC unit cell $Z = 4$ and **tetrahedral void = 8 so tetrahedral void = 2 Z**.

**(b) Octahedral void (OV):**

(Circles labeled O represent centers of the octahedral interstices in the CCP arrangement of anions (FCC unit cell). The cell "owns" 4 octahedral sites.)

* Each edge center of FCC unit cell have one octahedral void and body center also contain 1 OV.

* Number of octahedral void per unit cell (Z) = $12[\text{Edge center}] \times \frac{1}{4} + 1[\text{Body center}] = 4$.

* For FCC unit cell (Z) = 4 and octahedral void = 4. So octahedral void = Z .

Th-16 Hexagonal close packing (HCP) unit cell:**(a) Tetrahedral void:**

* HCP unit cell have total 12 tetrahedral void per unit cell.

* Out of which 8 are completely inside the unit cell and 12 are shared. Which are present on edge center and contribution of each sphere present on edge center is $\frac{1}{3}$ so.

$$\text{Tetrahedral void (TV)} = 8[\text{Inside the body}] + 12[\text{at Edge center}] \times \frac{1}{3} = 12.$$

For HCP unit cell (Z) = 6. So tetrahedral void = $(Z \times 2) = 12$.

(b) Octahedral void:

* HCP unit cell have total 6 octahedral void, which are completely inside the unit cell.
So octahedral void = 6.

Note:

Tab-9

Unit cell	Z	Tetrahedral void = $Z \times 2$	Octahedral void = $Z \times 1$
CCP (FCC)	4	8	4
HCP	6	12	6



Solved Examples

Ex-13(a) In a face centred cubic arrangement of metallic atoms, what is the relative ratio of the sizes of tetrahedral and octahedral voids?

- (A) 0.543 (B) 0.732 (C) 0.414 (D) 0.637

Ans. (A)

Sol. $\frac{r_{\text{tetrahedral}}}{r_{\text{octahedral}}} = \frac{0.225R}{0.414R} = 0.543.$

- (b)** The numbers of tetrahedral and octahedral holes in a CCP array of 100 atoms are respectively
 (A) 200 and 100 (B) 100 and 200 (C) 200 and 200 (D) 100 and 100

Ans. (A)

Ex-14 Copper has a face-centred cubic structure with a unit-cell edge length of 3.61\AA .

What is the size of the largest atom which could fit into the interstices of the copper lattice without distorting it?

(Hint.: Calculate the radius of the smallest circle in the figure)

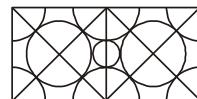
Ans. 0.53\AA

Sol. $r_{\text{octahedral}} = 0.414 R$

For FCC $4R = \sqrt{2} a$

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

$$r = \frac{0.414\sqrt{2} a}{4} = \frac{0.414\sqrt{2} \times 3.61}{4} = 0.53 \text{\AA}$$



Section (E): Radius ratio rule and Type of ionic structures

Th-17 Structure of ionic compounds

Structure of compounds containing two different types of atoms.

The bigger atom or ion will form the lattice & smaller atom / ion will occupy the voids. Generally, bigger ion is anion and smaller ion is cation. The type of void occupies by the cation is decided by radius ratio.

D-15 Radius Ratio Rule: Radius ratio = (r_+/r_-) , the ratio of radius of cation to the radius of anion is known as radius ratio of the ionic solid. This gives the idea about the type of void occupied.

Radius ratio = (r_+/r_-) , this gives the idea about the type of void occupied.

Tab-10

Radius ratio	Type of void occupied	Coordination No.	Ex. of ionic Compounds
$r_+/r_- < 0.155$	linear void	2	
$0.155 \leq r_+/r_- < 0.225$	triangular void	3	Boron oxide
$0.225 \leq r_+/r_- < 0.414$	tetrahedral void	4	Zinc sulphide
$0.414 \leq r_+/r_- < 0.732$	octahedral void	6	Sodium chloride
$0.732 \leq r_+/r_- < 1$	cubical void	8	Caesium chloride

NOTE: In ionic compounds for maximum stability.

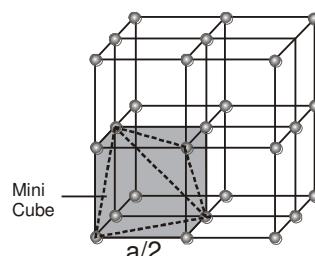
(1) A Cation must be surrounded by maximum number of anions and vice versa.

(2) Anion-anion and cation-cation contact should be avoided

⇒ There will 2 different kind of atoms, cation & anion, so there will be two different coordination number (C.N.). C.N. of cation = no. of anions surroundings any cation.

C.N. of anion = no. of cations surrounding any anion.

Considering a minicube



Cation will lie at the centre of the body diagonal of the mini cube of side $a/2$.

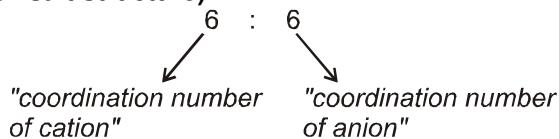
$$r_- + r_+ = \frac{1}{2} \times (\text{body diagonal of minicube})$$

$$r_+ + r_- = \frac{1}{2} \times \frac{a_{\text{fcc}}}{2} \sqrt{3}$$

$$a_{\text{fcc}} = \frac{4}{\sqrt{3}}(r_+ + r_-)$$

Th-18 Structure of some ionic compound:

(1) NaCl type of structure (Rock salt structure):



* Experimental $\frac{r_{\text{Na}^+}}{r_{\text{Cl}^-}} = 0.51 \quad (0.414 < \frac{r_{\text{Na}^+}}{r_{\text{Cl}^-}} < 0.732)$

(i) Cl^- ions form the FCC lattice while Na^+ ion occupy all the octahedral void.

(ii) Effective number of ion per unit cell

(iii) Effective number of Cl^- ion per unit cell = 4

Effective number of Na^+ ion per unit cell = 4

(iv) Formula of unit cell Na_4Cl_4

Formula of ionic compound = NaCl

Effective number of formula unit (Z) = 4

(v) Density (d) = $\frac{Z \times M}{N_A \times a^3}$

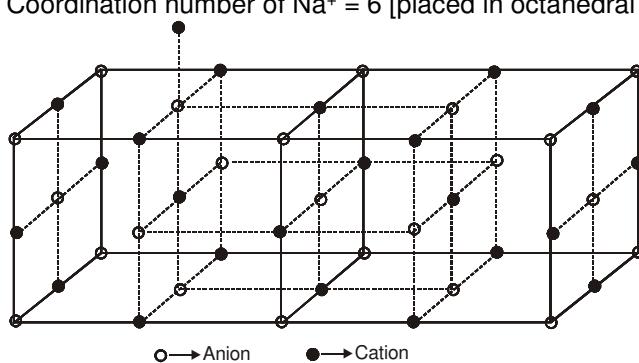
→ Here $\sqrt{2}a \neq 4R_{\text{Cl}^-}$ → **as anion-anion are not in contact.**

→ $[r_{\text{Cl}^-} + r_{\text{Na}^+}] = a/2$

(vi) **Coordination number:**

Coordination number of Cl^- = Number of Na^+ ion touching it = 6.

Coordination number of Na^+ = 6 [placed in octahedral void of Cl^- ions].



Tab-11

For Cl^- :

Type of neighbour	Distance	No. of neighbours
(i) Nearest	$\text{Na}^+, \frac{a}{2}$	6
(ii) (next) ¹	$\text{Cl}^-, \frac{a}{\sqrt{2}}$	12

Example: Halide of Li, Na, K and Rb, AgCl, AgBr, NH₄Cl.

Note: Lattice of NaCl is FCC of Cl⁻ in which all octahedral void are occupied by Na⁺. or → FCC of Na⁺ in which octahedral void are occupied by Cl⁻.

(2) ZnS type (Zinc blende) (AB type) (4: 4 coordination number compound):



Zinc blende type:

(i) S²⁻ ion form the FCC lattice.

* Zn²⁺ ion occupy alternate (non adjacent) four tetrahedral void. Given below a face-view.



(ii) Effective number of ion

* Effective number of S²⁻ ion per unit cell = 4.

* Effective number of Zn²⁺ ion per unit cell = 4.

(iii) Formula of unit cell = Zn₄S₄

Formula of ionic compound = ZnS

(iv) Experimental $\frac{r_{\text{Zn}^{2+}}}{r_{\text{S}^{2-}}} = 0.3 \quad (0.225 < \frac{r_{\text{Zn}^{2+}}}{r_{\text{S}^{2-}}} < 0.414)$

so anion-anion contact is not there.

$$\text{so } [r_{\text{Zn}^{2+}} + r_{\text{S}^{2-}}] = \frac{\sqrt{3}}{4} a_{\text{FCC}}$$

(v) Density (d) = $\left[\frac{Z \times M}{N_A \times a^3} \right]$ M = 97 gram/mole. (M_{Zn} = 65.3) + (M_S = 32)

(vi) Coordination number:

Coordination number of Zn²⁺ ions = 4.

Coordination number of S²⁻ ions = 4.

Ex: ZnS, CuCl, CuBr, Cul, AgI.

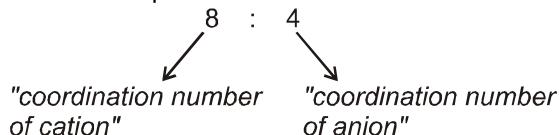
Tab-12

For S²⁻

Type of neighbour	Distance	No. of neighbours	Ions
(i) Nearest	$\frac{\sqrt{3}}{4} a_{\text{FCC}}$	4	Zn ²⁺
(ii) (next) ¹	$\frac{a}{\sqrt{2}}$	12	S ²⁻

(3) CaF₂ [Flourite structure] [AB₂ type] (It is a different case)

Coordination number of compound



(i) Ca²⁺ ion form the FCC lattice.

* F⁻ ion occupies all tetrahedral voids.

(ii) Coordination number of F⁻ ion = 4

∴ It occupies tetrahedral void.

* Coordination number of Ca²⁺ ion = 8

(iii) Effective number of Ca^{2+} ion = 4.

* **Effective number of F^- ion = 8.**

(iv) Formula of unit cell = Ca_4F_8

* **Formula of ionic compound = CaF_2 .**

(v) Effective number of formula unit cell (Z) = 4.

$$(vi) \text{Density} = \left[\frac{Z \times M}{N_A \times a^3} \right]$$

$$(vii) 0.225 < \frac{r_{\text{F}^-}}{r_{\text{Ca}^{2+}}} < 0.414 ; \quad [r_{\text{Ca}^{2+}} + r_{\text{F}^-}] = \frac{\sqrt{3}a}{4}$$

Other examples: CaF_2 , SrF_2 , BaF_2 , BaCl_2 .

Tab-13 For Ca^{2+}

Type of neighbour	Distance	No. of neighbours	Ions
(i) Nearest	$\frac{\sqrt{3}}{4}$	8	F^-
(ii) (next) ¹	$\frac{a}{\sqrt{2}}$	12	Ca^{2+}

Tab-14 For F^-

Type of neighbour	Distance	No. of neighbours	Ions
(i) Nearest	$\frac{\sqrt{3}}{4}$	4	Ca^{2+}
(ii) (next) ¹	$\frac{a}{2}$	6	F^-

(4) Na_2O [Sodium oxide] [A_2B type]

* **Anti-fluorite structure [4: 8 coordination compound]** \Rightarrow (O^{2-} ion at FCC lattice).
 Na^+ = All the tetrahedral void.

(5) **CsCl type of structure [8: 8 coordination compound]:** $\frac{r_{\text{Cs}^+}}{r_{\text{Cl}^-}} \approx 0.93$

(i) Cl^- form simple cubic lattice.

* **Cs^+ ion occupies cubical void.**

(ii) Effective number of ion:

* **Effective number of Cs^+ ion = 1. & Effective number of Cl^- ion = 1.**

(iii) Formula of ionic compound = CsCl . So $Z = 1$.

$$(iv) \text{Density (d)} = \left[\frac{Z \times M}{N_A \times a^3} \right]$$

* **anion-anion contact is not there so,**

$$[r_{\text{Cl}^-} + r_{\text{Cs}^+}] = \frac{\sqrt{3}a_{\text{SC}}}{2}$$

(v) Coordination number of Cs^+ ion = 8.

(vi) Coordination number of Cl^- ion = 8.

Other example: CsCl , CsBr , CsI .

Note: On increasing pressure \rightarrow Coordination number tends to increase.

On increasing temperature \rightarrow Coordination number tends to decrease.





STRUCTURES OF SOME CRYSTALS

S.No.	Crystal	C.N		Z	Structural arrangement	E.g.
		Cation	Anion	Total formula unit		
1	NaCl	6	6	$\text{Na}^+ = 4$ $\text{Cl}^- = 4$	Na^+ = at all octahedral voids $\text{Cl}^- \rightarrow \text{FCC}$	LiCl
2.	ZnS (wurtzite)	4	4	$\text{Zn}^{2+} = 6$ $\text{S}^{2-} = 6$	$\text{Zn}^{2+} = \text{At } 1/2 \text{ TV}$ $\text{S}^{2-} = \text{HCP}$	AgI
3.	ZnS (Blende)	4	4	$\text{Zn}^{2+} = 4$ $\text{S}^{2-} = 4$	$\text{Zn}^{2+} = \text{At } 1/2 \text{ of TV}$ $\text{S}^{2-} = \text{FCC}$	CuCl CuBr CuI, CdS
4.	CaF_2 (Fluorite)	8	4	$\text{Ca}^{2+} = 4$ $\text{F}^- = 8$	$\text{Ca}^{2+} = \text{FCC}$ $\text{F}^- = \text{All TV}$	BaF_2 SrF_2
5.	Na_2O	4	8	$\text{Na}^+ = 8$ $\text{O}^{2-} = 4$	$\text{Na}^+ = \text{All TV}$ $\text{O}^{2-} = \text{FCC}$	
6.	CsCl	8	8	$\text{Cs}^+ = 1$ $\text{Cl}^- = 1$	$\text{Cr}^+ = \text{Body centered void (Cubic void)}$ $\text{Cl}^- = \text{At corners}$	CsCN CsI CaS

# Rutile	(TiO ₂)	CN
Cation		6
Anion		3

# Perovskite	(CaTiO ₃)	CN
At Body centre	Ca ⁺⁺	12
At corner	Ti ⁴⁺	6
At Edge centre	O ²⁻	2

Th-19 Other important structure:

(1) Spinel structure [AB₂O₄]: Spinel is an oxide consisting of two type of metal ions with the oxides ion arranged in CCP layers in normal spinel one eighth of the tetrahedral holes occupied by one type of metal ion and one half of the octahedral holes occupied by another type of metal ion. eg: A spinel is formed by Zn²⁺, Al³⁺ and O²⁻ with Zn²⁺ ion in the tetrahedral holes. The formula of the spinel is ZnAl₂O₄.

(2) Perovskite structure [ABO₃]: This structure may be described as a cubic lattice, with barium ions occupying the corners of the unit cell, oxide ions occupying the face centers and titanium ions occupying the centres of the unit cells. eg: **BaTiO₃ or MgTiO₃**.

(3) Lattice of diamond: ZnS types in which all S^{2-} location and all Zn^{2+} location are occupied by C atoms.

So, $Z = 8$ atom per unit cell

$$d_{C-C} = \frac{\sqrt{3}}{4} a_{FCC}$$

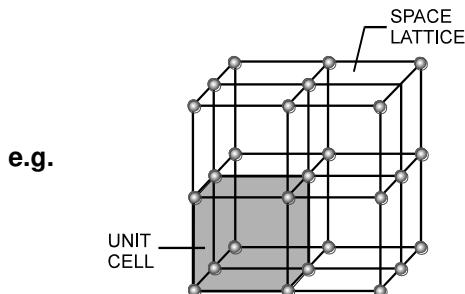
$d_{C-C} = 2r_{C-C}$ where r_{C-C} is radius of C-atom.

* **Packing efficiency = 34%.**

* In crystal lattice of diamond, carbon atoms adopt FCC arrangement with occupancy of 50% tetrahedral voids.

Note: (1) Distance between two plane in FCC or HCP arrangement is $\sqrt{\frac{2}{3}} a$ or $a = 2R = 2\sqrt{\frac{2}{3}} R$.

(2) If number of unit cell along one edge are 'x' then total number of unit cell in cube = x^3 .



Number of unit cell along one edge = 2, then total number of unit cell in cube = $2^3 = 8$.

Solved Examples

Ex-15 A mineral having formula AB_2 crystallize in the cubic close packed lattice, with the A atoms occupying the lattice points. What is the co-ordination no. of A atoms? of the B atoms? what fraction of tetrahedral sites is occupied by B atoms.

Ans. 8, 4, 100%. It has fluorite (CaF_2) structure.

Ex-16 CsBr has b.c.c. structure with edge length 4.3 Å. The shortest inter ionic distance in between Cs^+ and Br^- is:

(A) 3.72

(B) 1.86

(C) 7.44

(D) 4.3

Ans. (A)

$$\text{Sol. } r_+ + r_- = \frac{\sqrt{3}a}{2} = \frac{\sqrt{3} \times 4.3}{2} = 3.72 \text{ \AA}.$$

Section (F): Crystal defects and Properties of solids

Th-20 Crystal imperfections / defects

Imperfections can be because of:-

- Conditions under which crystals have been developed,
- Impurities,
- Temperature (because of thermal conductivity some atoms/ions can get displaced)

These imperfections can be

(a) **Point defects:** Defects will be only at certain lattice positions.

(b) **Line defects:** If atoms/ions are misplaced/missing/replaced by some other ions along a line.

(c) **Plane (screw) defects:** If atoms/ions are misplaced/missing/replaced by some other ions along a line in a plane.

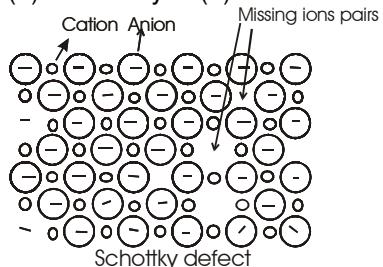
D-16 Point Defects:

1. Stoichiometric: The formula of compound remains same even after presence of these defects.

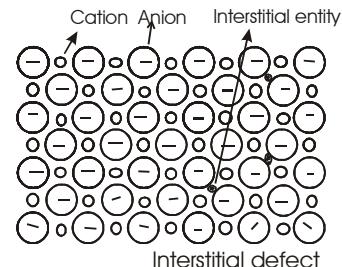
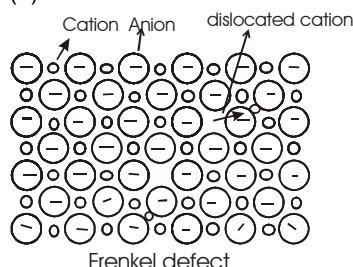
2. Non-stoichiometric: The formula of compound will get modified because of the presence of these defects.

(i) Stoichiometric defects:

(a) Schottkey (b) Frenkel



(c) Interstitial



D-17 Schottkey: When atoms/point are totally missing from the lattice.

Net density of crystal will get decreased

$$\rho_{\text{exp}} < \rho_{\text{theoretical}}$$

$$\% \text{ missing units} = \left(\frac{\rho_{\text{th}} - \rho_{\text{exp}}}{\rho_{\text{th}}} \right) \times 100\%$$



D-18 Frenkel: When atoms/ions displaced from normal lattice positions and are present in some interstitial voids. Density remains same

D-19 Interstitial: When some small foreign atoms are trapped in interstitial voids of the lattice without any chemical reaction. Formula remains the same $\rho_{\text{exp}} > \rho_{\text{theoretical}}$

Th-20 (ii) Non-stoichiometric defects:

D-20 (a) Metal excess or cation excess defect:

- If no. of missing anion is more than no. of missing cations.

- To maintain electrical neutrality some electron are trapped at anionic vacancies.

Because of these extra electrons the electrical and optical (colour) properties of the compound get modified.

So these locations of elecoron are also known as colour centres (F-centres).

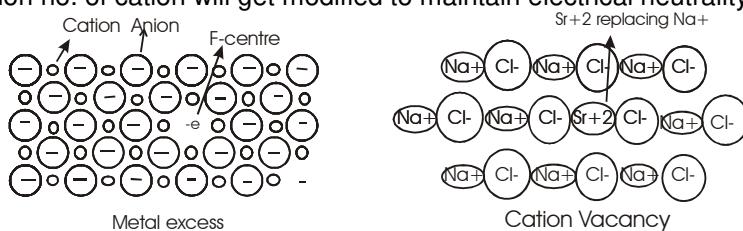
ZnO - white in colour at room temperature.

- On heating some O^{2-} ion get released in the form of O_2 and e^- are trapped at their locations. Because of this it because yellow in colour.

D-21 (b) Metal deficiency (cation deficiency) defects:

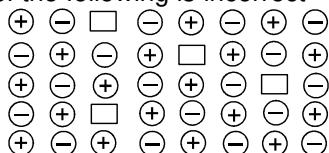
- no. of missing cations should be more than no. of missing anions.

- oxidation no. of cation will get modified to maintain electrical neutrality.



Solved Examples

Ex-17 Which of the following is incorrect



- (A) The defect is known as Schottky defect
- (B) Density of compound in the defect decreases
- (C) NaCl(s) is example which generally shows this defect
- (D) Stoichiometry of compound will change slightly.

Ans. (D)

Ex-18 Ferrous oxide (FeO) is experimentally found to have the formula $Fe_{0.93}O$. Find the %age of Fe ions in +3 state.



Some Fe atom are in +2 state Some Fe atom are in +3 state

Let there is x Fe atom in +3 state

$$3x + 2(93 - x) = 200 \Rightarrow x = 14 \Rightarrow \% Fe^{3+} = \frac{14}{93} \times 100\% = \frac{1400}{93}\% \approx 15.54\%$$

Th-21 Properties of Solids:

(i) Electrical Properties (ii) Magnetic Properties

(i) Electrical Properties: Solids exhibit an amazing range of electrical conductivities, the range of electrical conductivities from 10^{-20} to $10^7 \text{ ohm}^{-1} \text{ m}^{-1}$. Solids can be classified into three types on the basis of their conductivities.

D-22 (1) Conductors: Metals are goods condctors and have conductiveites in the order $10^7 (\Omega m^{-1})$.

D-23 (2) Insulators: Those solids which have very low conductivities ranging from 10^{-20} to $10^{-10} (\Omega m^{-1})$ are electrical insulators e.g.; MnO , CoO ; NiO , CuO , Fe_2O_3 , TiO_2 .

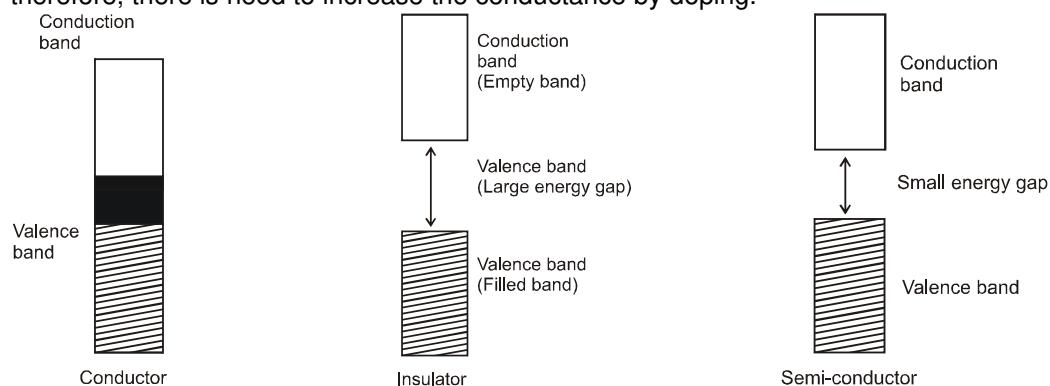


D-24 (3) Semiconductors: Those solids which have intermediate conductivities generally from 10^{-6} to $10^4 (\Omega m^{-1})$ are termed as semiconductors.

D-25 Intrinsic Semiconductors: The conduction by pure substances such as silicon and germanium is called intrinsic conduction and these pure substances exhibiting electrical conductivity are called intrinsic semiconductors.

Th-22 Causes of Conductance in Solids:

1. In most of the solids, conduction is through electron movement under an electric field.
2. In ionic solids conduction is by movement of ions in molten state.
3. The magnitude of electrical conductivity strongly depends upon the number of electrons available to take part in conduction process.
4. In metals, conductivity strongly depends upon the number of electrons available per atom. The atomic orbitals form molecular orbitals which are too close in energy to each other so as to form a band.
5. If conduction band is not completely filled or it lies very close to a higher unoccupied band, then electrons can flow easily under an electric field thereby showing conductivity.
6. In case of insulators, the gap between valence band and conduction band is too large, so electrons cannot jump from valence band to conduction band and very small conductivity is observed.
7. In case of semiconductors, the gap between valence band and conduction band is small and therefore some of the electrons may jump from valence band to conduction and some conductivity is observed.
8. Electrical conductivity of semiconductors increases, with increase in temperature. This is due to the fact that with increase in temperature, large number of valence electrons from the valence band can jump to conduction band. Pure substances like silicon and germanium that exhibit this type of conducting behaviour are called intrinsic semiconductors.
9. For particle purpose, the conductivity of pure silicon and germanium is too low at room temperature, therefore, there is need to increase the conductance by doping.



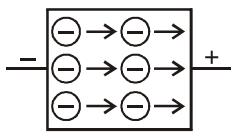
D-26 Doping: The conductivity of silicon and germanium can be increased by adding appropriate amount of suitable impurity. The process is called doping.

Th-23 Type of Semiconductors:

(1) n-Type Semiconductors: Metal excess compounds conduct electricity through normal electron conduction mechanism and are therefore n-type semiconductors.

Th-24 n-Type Semiconductor:

1. When silicon is doped with small amount of group -15 elements such as P, As or Sb, its electrical conductivity increases sharply.
2. In pure silicon each silicon atom uses its four valence electrons for the formation of four covalent bonds with the neighbouring silicon atoms.
3. When silicon is doped with some group-15 element, the some of the positions in the lattice are substituted by atoms of groups-15 elements have five valence electrons. After forming the four covalent bonds with silicon (or any other group-14 element such as germanium). One excess electron is left on them.
4. Since this electron is not involved in bonding it becomes delocalized and contribute to electrical conduction. Silicon doped with group 15 element behaves as a n-type semiconductor.

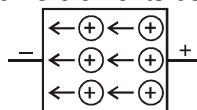


n-type semiconductor

(2) p-Type Semiconductors: Metal deficient compounds conduct electricity through positive hole conduction mechanism and are therefore p-type semiconductors.

Th-25 p-Type Semiconductor:

1. Electrical conductivity of silicon or germanium can also be increased by doping with some group-13 element such as B, Al or Ga.
2. Group-13 elements have only three valence electrons. They combine with group-14 elements to form an electron deficient bond or electron vacancy or a hole. These holes can move through the crystal like a positive charge giving rise to electrical conductivity.
3. Group-14 elements doped with group-13 elements behave as p-type semiconductors.



p-type semiconductor

In the presence of electrical field the holes move in direction opposite to that of electrons.

Th-26 Application of n-type and p-type semiconductors.

1. Diode is a combination of n-type and p-type semiconductors used as rectifier.
2. They are used for making transistors which contain n-p-n and p-n-p junctions to amplify radio and audio signals.
3. The solar cell is photo-diode used to convert light energy into electrical energy.

D-27 13-15 Compounds: The solid state materials are produced by combination of elements of groups 13 and 15 the compounds thus obtained are called 13-15 compounds e.g. InSb, AlP, GaAs.

D-28 12-16 Compounds: The solid state compounds are obtained by combination of elements of groups 12 and 16 the compounds are called 12-16 compounds e.g. ZnS, CdS, CdSe and HgTe.

D-29 Super Conductivity: The electrical resistance of metals is found to depend on temperature. Electrical resistance decreases with decrease in temperature and becomes almost zero near the absolute zero. Materials in this state are said to possess Superconductivity. The phenomenon of superconductivity was first discovered by Kammerlingh Onnes in 1913 when he found that mercury becomes superconducting at 4.0 K temperature.

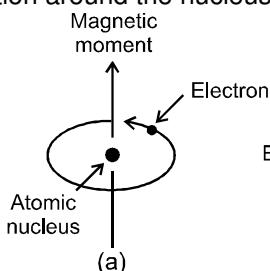
D-30 Transition Temperature: The temperature at which a substance starts behaving as super-conductor is called transition temperature.

Th-27 (ii) Magnetic Properties:

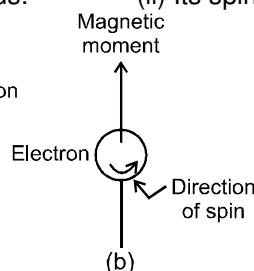
Every substance has some magnetic properties associated with it. The origin of these properties lies in the electrons. Each electron in an atom behaves like a tiny magnet.

Its magnetic moment originates from two types of motions.

(i) Its orbital motion around the nucleus.



(ii) Its spin around its own axis.



Demonstration of the magnetic moment associated with (a) an orbiting electron and (b) a spinning electron.

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

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

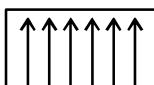
D-31 (1) Paramagnetic: When substances which are attracted by the external magnetic field are called paramagnetic substances and the phenomenon is called as paramagnetic. Atoms ion or molecules containing unpaired electron show this property, eg. O₂, Cu²⁺, Fe³⁺ etc. these substances lost their magnetism in the absence of magnetic field.



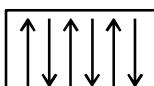
- D-32** (2) **Diamagnetic materials:** Those materials which are repelled by magnetic field are called diamagnetic materials e.g. Cu⁺, TiO₂, NaCl and C₆H₆. They do not have unpaired electrons.

D-33 (3) **Ferromagnetism:** When substances show permanent magnetism even in the absence of the magnetic field this phenomenon is called as Ferromagnetism and such substances are called as Ferromagnetic substances e.g. Fe Ni Co and CrO₂.

This type of magnetism arises due to the spontaneous alignment of magnetic moments due to unpaired electron in the same direction.



- D-34 (4) Anti Ferro Magnetism:** Substances which are expected to possess paramagnetism or ferromagnetism on the basis of unpaired electrons but actually they possess zero net magnetic moment are called Anti-ferromagnetic substances and the phenomenon is called as Anti-ferromagnetism. eg. MnO, Anti-ferromagnetism is due to the presence equal number of magnetic moments in the opposite direction.



- D-35** (5) **Ferrimagnetism:** Substances which are expected to possess large magnetism on the basis of unpaired electrons, but actually have small magnetic momentum are called ferrimagnetic substances eg. Fe_3O_4 , ferrites of the formula M^{2+} , Fe_2O_4 where $M = \text{Mg}, \text{Cu}, \text{Zn}$ etc. Ferrimagnetism arises due to the unequal moments in opposite direction resulting in same net magnetic moment. On heating these substance loss their magnetism and convert in to paramagnetic substance.



- D-36** **Curie Temperature:** The temperature at which a ferromagnetic substance loses its ferromagnetism and becomes only paramagnetic. For iron the curie temperature is 1033 K and for nickel 629 K, for Fe_3O_4 850 K. Below this temperature paramagnetic solid becomes ferromagnetic.

D-37 **Domain:** In solid state the metal ions of ferromagnetic substances are grouped together into small

regions called domains.

- Effect of Temperature on Metal (Conductor) Semiconductor or Insulator:**

Solved Examples

- Ex-19** What is a semiconductor? Name the two main types of semiconductors.

- Ans.** Substances whose conductance lies in between that of metals (conductors) and insulators are called semiconductors. Two main types of semiconductors are *n*-type and *p*-type.

- Ex-20** Explain the following with suitable examples:

- (iii) 12-16 and 13-15 group compounds

- Ans.** (i) **Ferromagnetism**: When substances show permanent magnetism even in the absence of the magnetic field this phenomenon is called as Ferromagnetism and such substances are called as Ferromagnetic substances e.g. Fe Ni Co and CrO_2 .

This type of magnetism arise due to the spontaneous alignment of magnetic moments due to unpaired electron in the same direction.

- (ii) Paramagnetism:** When substances which are attracted by the external magnetic field are called paramagnetic substances and the phenomenon is called as paramagnetism. Atoms ion or molecules containing unpaired electron show this property, eg. O_2 Cu^{2+} , Fe^{3+} etc. these substances lost their magnetism in the absence of magnetic field.

- (iii) 13-15 Compounds:** The solid state materials are produced by combination of elements of groups 13 and 15 the compounds thus obtained are called 13-15 compounds e.g. InSb, AlP GaAs.

- 12-16 Compounds:** The solid state compounds are obtained by combination of elements of groups 12 and 16 the compounds are called 12-16 compounds e.g. ZnS, CdS, CdSe and HgTe.



MISCELLANEOUS SOLVED PROBLEMS (MSPs)

1. Calculate the number of formula units in each of the following types of unit cells:
 - (a) MgO in a rock salt type unit cell
 - (b) ZnS in zinc blende structure
 - (c) platinum in a face-centred cubic unit cell.
- Sol.** (a) 4 (the same as in NaCl) (b) 4 (c) 4 (1 at the corner, 3 at the face-centres)
2. A mineral having the formula AB₂ crystallises in the cubic close-packed lattice, with the A atoms occupying the lattice points. What is the coordination number of the A atoms and B atoms? What percentage fraction of the tetrahedral sites is occupied by B atoms?
- Sol.** C.N. of A atom = 8; C.N. of B atom = 4
tetrahedral sites occupied by atoms B = 100% (all tetrahedral voids are occupied).
3. (a) What is the C.N. of Cr atom in bcc structure ?
(b) Cobalt metal crystallises in a hexagonal closest packed structure. What is the C.N. of cobalt atom ?
(c) Describe the crystal structure of Pt, which crystallises with four equivalent atoms in a cubic unit cell.
- Sol.** (a) 8, (b) 12, (c) fcc or cubic close packed.
4. Titanium metal has a density of 4.54 g/cm³ and an edge length of 412.6 pm. In what cubic unit cell does titanium crystallise? (Ti = 48)
- Sol.** Density $d = \frac{zM}{a^3 N_0}$
 $d = 4.54 \text{ g/cm}^3, M = 48 \text{ g mol}^{-1}, Z = ? \quad N_0 = 6.023 \times 10^{23} \text{ mol}^{-1}$
 If value of z is known, structure can be decided

$$z = \frac{dN_0 a^3}{M} = \frac{4.54 \times 6.023 \times 10^{23} \times (412.6 \times 10^{-10})^3}{48} = 4$$

 Thus, titanium has **face-centred cubic** structure.
5. MgO has a structure of NaCl and TiCl has the structure of CsCl. What are the coordination numbers of ions in each (MgO and TiCl)?
- Sol.** C.N. of Na⁺ in NaCl = 6
C.N. of Cl⁻ in NaCl = 6
Hence C.N. of Mg²⁺ is also = 6 and that of O²⁻ or O²⁻ = 6 in **MgO**
We know in CsCl
C.N. of Cs⁺ = 8
C.N. of Cl⁻ = 8
Hence, **Ti⁺ and Cl⁻, in TiCl, have also C.N. 8 each.**
6. A solid AB has the NaCl structure. If radius of cation A⁺ is 120 pm, calculate the maximum possible value of the radius of the anion B⁻.
- Sol.** We know for the NaCl structure, for maximum of radius of B⁻, the ratio r⁺ / r⁻ should be minimum for octahedral void i.e. 0.414.
Radius of cation/radius of anion = 0.414

$$\frac{r_{A^+}}{r_{B^-}} = 0.414 \Rightarrow r_{B^-} = \frac{r_{A^+}}{0.414} = \frac{120}{0.414} = 290 \text{ pm.}$$
7. The C.N. of the barium ion Ba²⁺, in BaF₂ is 8. What must be the C.N. of F⁻ ion ?
- Sol.** C.N. of barium ion tells us that it is surrounded by eight fluoride ions (charge $8 \times (-1) = -8$). In order to balance out the eight negative charges, we need four barium ion (charge $4 \times (+2) = +8$). Hence, the C.N. of F⁻ ions must be **4**.
8. The radius of calcium ion is 94 pm and of oxide ion is 146 pm. Predict the crystal structure of calcium oxide.
- Sol.** The ratio $\frac{r_+}{r_-} = \frac{94}{146} = 0.644$
The prediction is an octahedral arrangement of the oxide ions around the calcium. Because the ions have equal but opposite charges, there must also be an octahedral arrangement of calcium ions around oxide ions. Thus CaO structure is similar to Rock Salt (NaCl) structure.



9. Sodium metal crystallises in body centred cubic lattice with cell edge = 4.29 Å. What is radius of sodium atom?

Sol. In 'BCC' structure

$$\text{body diagonal} = 4 \times r_{\text{Na}} = \sqrt{3} \times a$$

$$\therefore 4 \times r_{\text{Na}} = \sqrt{3} \times 4.29 \quad \Rightarrow \quad r_{\text{Na}} = \frac{\sqrt{3}}{4} \times 4.29 = 1.86 \text{ \AA}$$

10. CsCl crystallises in a cubic that has a Cl⁻ at each corner and Cs⁺ at the centre of the unit cell. If $r_{\text{Cs}^+} = 1.69 \text{ \AA}$ and $r_{\text{Cl}^-} = 1.81 \text{ \AA}$, what is value of edge length a of the cube?

Sol. We assume that the closest Cs⁺ to Cl⁻ distance is the sum of the ionic radii of Cs⁺ and Cl⁻.
 $= 1.69 + 1.81 = 3.50 \text{ \AA}$

This distance is one-half of the cubic diagonal = $\frac{a\sqrt{3}}{2}$

$$\therefore \frac{a\sqrt{3}}{2} = 3.50 \text{ \AA} \quad \therefore \quad a = 4.04 \text{ \AA}$$

11. Platinum (atomic radius = 1.38 Å) crystallises in a cubic closest packed structure. Calculate the edge length of the face-centred cubic unit cell and the density of the platinum (Pt = 195).

Sol. $r = \frac{a}{2\sqrt{2}}$ (for fcc), $a = 2\sqrt{2}r = 3.9 \text{ \AA}$

$$\text{Density} = \frac{zM}{a^3 N_0} = \frac{4 \times 195}{(3.9 \times 10^{-8})^3 \times 6.023 \times 10^{23}} = 21.83 \text{ g/cm}^3.$$

12. Calculate the edge length of the unit cell of sodium chloride given density of NaCl is $2.17 \times 10^3 \text{ kg m}^{-3}$ and molecular weight $58.5 \times 10^{-3} \text{ kg mol}^{-1}$.

Sol. NaCl is face-centred cubic lattice so that number of NaCl molecules in a unit cell (z) = 4.

We know density $d = \frac{zM}{a^3 N_0}$

Where, a = length of the unit cell

$$\text{Volume} = a^3 = \frac{Mz}{dN_0} = \frac{4 \times 58.8 \times 10^{-3}}{2.17 \times 10^3 \times 6.02 \times 10^{23}} = 1.79 \times 10^{-28} \text{ m}^3$$

$$a = 5.64 \times 10^{-10} \text{ m} = 5.64 \text{ \AA} = 564 \text{ pm}.$$

13. The effective radius of an iron atom is 1.42 Å. It has a rock-salt structure. Calculate its density (Fe = 56).

Sol. Due to rock-salt (fcc) structure, number of atoms in a unit cell (z) = 4.

$$\text{Thus, } d \text{ (density)} = \frac{zM}{a^3 N_0} \quad a = 2\sqrt{2}r = 2\sqrt{2} \times 1.42 \times 10^{-8} \text{ cm}$$

$$\therefore d = \frac{4 \times 56}{6.02 \times 10^{23} \times (2\sqrt{2} \times 1.42 \times 10^{-8})^3} = 5.743 \text{ g/cm}^3$$

14. In a CPS (close packed structure) of mixed oxides, it is found that lattice has O²⁻ (oxide ions), and one-half of octahedral voids are occupied by trivalent cations (A³⁺) and one-eighth of tetrahedral voids are occupied by divalent cations (B²⁺). Derive formula of the mixed oxide.

Sol. Number of octahedral voids per ion in lattice = 1

$$\text{Hence, } \text{Number of trivalent cations (A}^{3+}\text{)} = 1 \times \frac{1}{2} = \frac{1}{2}$$

Number of tetrahedral voids per ion in lattice = 2

$$\text{Hence, } \text{Number of divalent cations (B}^{2+}\text{)} = 2 \times \frac{1}{8} = \frac{1}{4}$$

Thus, formula is A_{1/2}B_{1/4}O or A₂BO₄.

15. An element crystallises as face-centred cubic lattice with density as 5.20 g/cm³ and edge length of the side of unit cell as 300 pm. Calculate mass of the element which contains 3.01×10^{24} atoms.



Sol. $z = 4$ in fcc lattice $M = ?$, $d = 5.20 \text{ g/cm}^3$

$$a = 300 \text{ pm} = 3 \times 10^{-8} \text{ cm}$$

$$\therefore a^3 = 27 \times 10^{-24} \text{ cm}^3$$

$$N_0 = 6.02 \times 10^{23}$$

$$\therefore M = \frac{d N_0 a^3}{z} = \frac{5.20 \text{ g/cm}^3 \times 6.02 \times 10^{23} \text{ mol}^{-1} \times 27 \times 10^{-24} \text{ cm}^3}{4} = 21.13 \text{ g mol}^{-1}$$

Thus, 6.02×10^{23} atoms have = 21.13 g

$$\therefore 3.01 \times 10^{24} \text{ atoms have} = \frac{21.13}{6.02 \times 10^{23}} \times 3.01 \times 10^{24} \text{ g} = 105.65 \text{ g}$$

- 16.** Calcium crystallises in a face-centred cubic unit cell with $a = 0.556 \text{ nm}$. Calculate the density if it contained 0.1% vacancies defects.

Sol. Thus, density can be determined using $d = \frac{zM}{a^3 N_0}$

$$d(\text{with vacancy defect}) = \frac{3.996 \times 40}{(0.556 \times 10^{-7})^3 \times 6.02 \times 10^{23}} = 1.5448 \text{ g/cm}^3$$

CHECK LIST

Theories (Th)

- Th-1: General Characteristics of Solids
- Th-2: Types of SOLIDS on the basis of arrangement of particles
- Th-3: Internal arrangement of particle in crystalline solid
- Th-4: Characteristics of a Unit Cell
- Th-5: Unit cell
- Th-6: Types of unit cell
- Th-7: The type of unit cells found in different types of crystals
- Th-8: Properties of a cube
- Th-9: Contribution of different Lattice point in one cubical unit cell
- Th-10: Structure of Solids
- Th-11: 3-D Lattice
- Th-12: Arrangement of hexagonal closed packed sheets
- Th-13: ABC-ABC arrangement (Cubic close packing (CCP) or Face centred cube (FCC))
- Th-14: Types of voids found in close packings
- Th-15: Location of void
- Th-16: Hexagonal close packing (HCP) unit cell
- Th-17: Structure of ionic compounds
- Th-18: Structure of some ionic compound
- Th-19: Other important structure
- Th-20: Crystal imperfections/defects
- Th-21: Properties of Solids
- Th-22: Causes of Conductance in Solids
- Th-23: Type of Semiconductors
- Th-24: n-Type Semiconductor
- Th-25: p-Type Semiconductor
- Th-26: Application of n-type and p-type semiconductors
- Th-27: Magnetic Properties
- Th-28: Effect of Temperature of Metal (Conductor) Semiconductor or Insulator

- D-13: Octahedral Voids (3-Dimensional 6 coordinate void)
- D-14: Cubical void (eight coordinate void)
- D-15: Radius Ratio Rule
- D-16: Point defects
- D-17: Schottky Defects
- D-18: Frenkel Defects
- D-19: Interstitial Defects
- D-20: Metal excess defects due to interstitial cations
- D-21: Metal deficiency due to cation vacancies
- D-22: Conductors
- D-23: Insulators
- D-24: Semiconductors
- D-25: Intrinsic Semiconductors
- D-26: Doping
- D-27: 13-15 Compounds
- D-28: 12-16 Compounds
- D-29: Super Conductivity
- D-30: Transition Temperature
- D-31: Paramagnetism
- D-32: Diamagnetic materials
- D-33: Ferromagnetism
- D-34: Anti Ferro Magnetism
- D-35: Ferrimagnetism
- D-36: Curie temperature
- D-37: Domain

Table (Tab)

- Tab-1 : Properties of solid, liquid and gas.
- Tab-2 : Types of solid
- Tab-3 : Crystalline and amorphous solid
- Tab-4 : Seven Crystal system
- Tab-5 : Close Packing in 2-Dimension
- Tab-6 : Nearest neighbour in SC
- Tab-7 : Nearest neighbour in BCC
- Tab-8 : Nearest neighbour in FCC
- Tab-9 : Relation between tetrahedral void and octahedral void
- Tab-10 : Ratio of voids.
- Tab-11 : Nearest neighbour in NaCl.
- Tab-12 : Nearest neighbour in S²⁻
- Tab-13 : Nearest neighbour in Ca²⁺
- Tab-14 : Nearest neighbour in F⁻

Definitions (D)

- D-1: Lattice
- D-2: Unit cell
- D-3: 1-Dimensional Space Lattice
- D-4: 2-Dimensional Space Lattice
- D-5: 3-Dimensional Space Lattice
- D-6: Non Primitive or centered unit cell
- D-7: Coordination number
- D-8: Density of unit cell
- D-9: Packing efficiency
- D-10: Voids (Interstitial Voids)
- D-11: Triangular void (2-Dimensional 3-coordinate void)
- D-12: Tetrahedral Voids (3-Dimensional 4-coordinate)



Exercise-1

Marked Questions may have for Revision Questions.

PART - I : SUBJECTIVE QUESTIONS

Section (A) : Basics of solid state

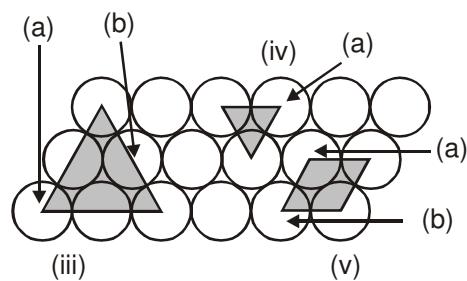
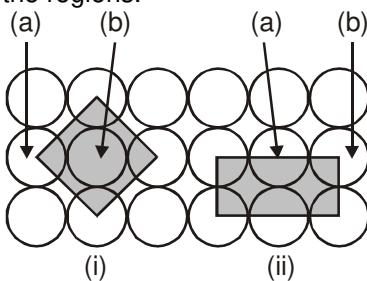
Commit to memory :

$$\text{Contribution of a particle} = \frac{\text{angle}}{360^\circ} \quad (\text{for 2D unit cell}).$$

A-1. Classify each of the following solids.

- | | |
|---|--|
| (a) Tetra phosphorus decoxide (P_4O_{10}) | (b) Graphite |
| (c) Brass | (d) Ammonium phosphate $[(NH_4)_3 PO_4]$ |
| (e) SiC | (f) Rb |
| (g) I_2 | (h) LiBr |
| (i) P_4 | (j) Si |
| (k) Plastic. | |

A-2. Given below are two dimension lattices with nicely shaded regions. You just have to find the contributions (in fractions) of particles marked to the shaded regions and the total number of particles in the regions.



Figure

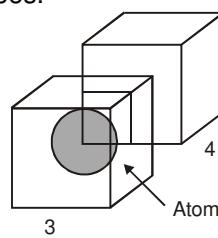
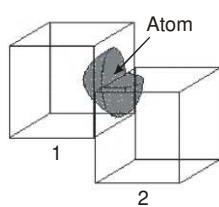
A-3. What are the crystallographic parameter of hexagonal, monoclinic and triclinic unit cell respectively.

Section (B) : Simple Cubic Structure & BCC

Commit to memory :

$$\text{Density} = \frac{Z \times M}{N_A \times a^3}$$

B-1. Following diagrams show identical cubes such that edge of cube2 lies exactly in the middle of one of the faces of Cube1 and Cube 4 has a corner at the body center of the Cube3. Find the contributions (in fraction) of the spheres shown to each of the cubes.



B-2. The inter metallic compound Li Ag crystallizes in a cubic lattice in which both lithium and silver atoms have coordination no. of 8. To what crystal class does the unit cell belong?

B-3. Chromium metal crystallizes with a body centered cubic lattice. The length of the unit cell is found to be 287 pm. Calculate the atomic radius. What would be the density of chromium in g/cm³. [JEE 1997]



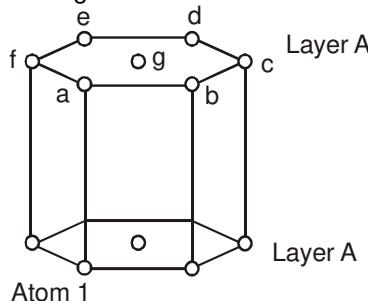
Section (C) : HCP & CCP structures

Commit to memory :

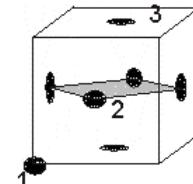
For CCP : $a = b = c = 2\sqrt{2} R$, $Z = 4$, Coordination number = 12

For HCP : $a = 2R$, $b = 2R$, $c = 2h$ and $h = \frac{8}{3} R$, $Z = 6$, Coordination number = 12

- C-1.** In which type of 3D arrangement have Ist and IV layer's of sphere are identical.
- C-2.** Metallic magnesium has a hexagonal close-packed structure and a density of 1.74 g/cm³. Assume magnesium atoms to be spheres of radius r. 74.1% of the space is occupied by atoms. Calculate the volume of each atom and the atomic radius r. (Mg = 24.31)
- C-3.** Consider a corner atom of Ist layer of an HCP unit cell showing alternate AA layers. Find
 (i) Find identical atoms (III layer) with respect to the distances from the atom 1.
 (ii) Arrange the distances in ascending order.



- Following figure shows an FCC unit cell with atoms of radius r marked 1(corner), 2(face center), 3(face center). A quadrilateral is also shown by joining the centers of 4 face centered atoms.
- C-4.** joining the centers of 4 face centered atoms.



- C-5.** Aluminium metal (atomic weight = 27 g) crystallises in the cubic system with edge length 4.0 Å. The density of metal is 27/16 amu/Å³. Determine the unit cell type and calculate the radius of the Aluminium metal.
- C-6.** "Tom" cat arranges the glass balls, in a particular 3D array; that two (I and II) continuous layer are not identical, but all (I and III) alternative layers are identical, this type of arrangement is known as :

Section (D) : Voids

Commit to memory :

Radius ratio = 0.155, 0.225, 0.414, 0.732 for triangular, tetrahedral, octahedral, cubic void respectively.

- D-1.** A student wants to arrange 4 identical spheres (of radius R) on a two dimensional floor as close as possible. Finally he could arrange them. Identify the type and dimensions of the figure obtained by joining their centers. Could he occupy the whole available space, if not, then what type of voids were generated. Calculate their number and radius of small ball that can be fitted in them.
- D-2.** Illustrate an octahedral void in the close packing of spheres. Why is it so called ?
- D-3.** The number of tetrahedral and octahedral voids in hexagonal primitive unit cell are _____ and _____.
- D-4.** What is the number and closest distance between two octahedral voids and two tetrahedral voids in fcc unit cell ?

Section (E) : Radius ratio rule and Type of ionic structures

Commit to memory :

Radius ratio = 0.155, 0.225, 0.414, 0.732 for triangular, tetrahedral, octahedral, cubic void respectively.



E-1. Suggest the probable structures of the unit cells of following each compound with the help of given data

		Cationic radius	Anionic radius
(a)	RbBr	1.48 Å	1.95 Å
(b)	MeTe	0.65 Å	2.21 Å
(c)	MgO	0.65 Å	1.40 Å
(d)	BaO	1.35 Å	1.40 Å

E-2. Why does ZnS not crystallize in the NaCl structure?

E-3. Try to answer the following:

- (i) In Zinc Blende structure there is one Zn^{+2} ion per S^{2-} ion. But the radius ratio lies in the range of Tetrahedral void and there are two tetrahedral voids available per S^{2-} . Can you give the idea about the arrangement of the lattice.
- (ii) What is the striking difference between the Fluorite and the Anti-fluorite structures.

E-4. KBr crystallizes in NaCl type of unit cell. K^+ radius = 1.33 Å, Br^- radius = 1.95 Å

- (a) How many K^+ ions and how many Br^- ions are in each unit cell?
- (b) Assuming the additivity of ionic radii, what is a ?
- (c) Calculate the density of a perfect KBr crystal.
- (d) What minimum value of r_+/r_- is needed to prevent anion-anion contact in this structure.

Section (F) : Crystal defects and Properties of solids

Commit to memory :

Stoichiometric - The formula of compound remains same even after presence of these defects.

Non-stoichiometric - The formula of compound will get modified because of the presence of these defects.

$$\% \text{ missing units} = \left(\frac{\rho_{\text{th}} - \rho_{\text{exp}}}{\rho_{\text{th}}} \right) \times 100\% \quad (\text{Schottky Defects})$$

Locations of electrons in metal excess defect are also known as color centres (F-centres).

F-1. What do you understand by imperfections in ionic crystals ? Name the types of imperfections which generally occur in ionic crystals.

F-2. How would you explain that (i) non-stoichiometric NaCl is yellow ; (ii) non-stoichiometric ZnO is yellow ?

F-3. Account the following: Silicon is an insulator but silicon doped with phosphorus acts as a semiconductor.

F-4. How does the conductivity of a semiconductor change if its temperature is raised?

PART - II : ONLY ONE OPTION CORRECT TYPE

Section (A) : Basics of solid state

A-1. Which of the following is/are pseudo solids ?

- | | |
|-------------|--|
| I. KCl | II. Barium chloride dihydrate |
| III. Rubber | IV. Solid cake left after distillation of coal tar |
| (A) I, III | (B) II, III |
| | (C) III, IV |
| | (D) only III |

A-2. The smallest repeating pattern which when repeated in three dimensions results in the crystal of the substance is called

- (A) Space lattice
- (B) Crystal lattice
- (C) Unit cell
- (D) coordination number

A-3. The crystal system for which $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$ is said to be :

- (A) triclinic
- (B) tetragonal
- (C) cubic
- (D) orthorhombic

A-4. Which of the following are the correct axial distance and axial angles for rhombohedral system?

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

A-5. Choose the correct statements

- (A) equivalent points in unit cells of a periodic lattice lie on a Bravais lattice
- (B) equivalent points in unit cells of a periodic lattice do not lie on a Bravais lattice
- (C) There are four Bravais lattices in two dimensions
- (D) There are five Bravais lattices in three dimensions

A-6. The crystal system of a compound with unit cell dimensions, $a = 0.387$ and $b = 0.387$ and $c = 0.504\text{nm}$ and $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$ is :

- (A) Cubic
- (B) Hexagonal
- (C) Orthorhombic
- (D) Rhombohedral

Section (B) : Simple Cubic Structure & BCC

B-1. Body centred cubic lattice has co-ordination number of :

- (A) 8
- (B) 12
- (C) 6
- (D) 4

B-2. Iron has body centred cubic lattice structure. The edge length of the unit cell is found to be 286 pm . What is the radius of an iron atom?

- (A) $r = 124\text{ pm}$
- (B) $r = 128\text{ pm}$
- (C) $r = 124\text{ \AA}$
- (D) $r = 128\text{ \AA}$

B-3. A metal crystallizes in a body centered cubic lattice (bcc) with the edge of the unit cell 5.2\AA . The distance between the two nearest neighbour is

- (A) 10.4 \AA
- (B) 4.5 \AA
- (C) 5.2\AA
- (D) 9.0\AA

B-4. At room temperature, Polonium cryatllises in Cubic primitive cell. If edge length is 3.0 \AA , calculate the theoretical density of Po. (Atomic wt of Po = 207g)

- (A) $25/3\text{ amu/ \AA}^3$
- (B) $23/3\text{ amu/ \AA}^3$
- (C) $21/3\text{ amu/ \AA}^3$
- (D) $27/3\text{ amu/ \AA}^3$

B-5. Lithium crystallizes in a body centered cubic lattice. How many next-nearest neighbors does each Li have?

- (A) 6
- (B) 8
- (C) 12
- (D) 4

B-6. Consider a Body Centered Cubic(bcc) arrangement, let d_e , d_{fd} , d_{bd} be the distances between successive atoms located along the edge, the face-diagonal, the body diagonal respectively in a unit cell. Their order is given by:

- (A) $d_e < d_{fd} < d_{bd}$
- (B) $d_{fd} > d_{bd} > d_e$
- (C) $d_{fd} > d_e > d_{bd}$
- (D) $d_{bd} > d_e > d_{fd}$

Section (C) : HCP & CCP structures

C-1. How many number of atoms are completely inside the HCP unit cell ?

- (A) Exactly 6
- (B) > 6
- (C) < 6
- (D) 12

C-2. The shortest distance between Ist and Vth layer of HCP arrangement is :

- (A) $8\sqrt{\frac{2}{3}}r$
- (B) $4\sqrt{\frac{3}{2}}r$
- (C) $16\frac{\sqrt{2}}{3}r$
- (D) $8\sqrt{\frac{3}{2}}r$

C-3. Volume of HCP unit cell is :

- (A) $24\sqrt{2}r^3$
- (B) $8\sqrt{2}r^3$
- (C) $16\sqrt{2}r^3$
- (D) $24\sqrt{3}r^3$

C-4. Fraction of empty space in ABAB type arrangement in 3D :

- (A) 0.74
- (B) 0.26
- (C) 0.68
- (D) 0.32

C-5. What is the height of an HCP unit cell ?

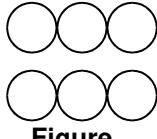
- (A) $\frac{\sqrt{3}}{2}a$
- (B) $\sqrt{\frac{3}{2}}a$
- (C) $\sqrt{\frac{2}{3}} \times 2a$
- (D) $\frac{\sqrt{2}}{3}a$

C-6. What is the number of atoms in a unit cell of face-centred cubic crystal?

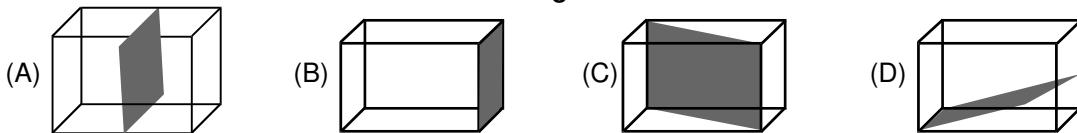
- (A) 4
- (B) 6
- (C) 2
- (D) 1



C-7. Which of the following shaded plane in fcc lattice contains arrangement of atoms as shown by circles :



Figure



C-8. Copper crystallises in a structure of face centered cubic unit cell. The atomic radius of copper is 1.28 Å. What is axial length on an edge of copper?

- (A) 2.16 Å (B) 3.62 Å (C) 3.94 Å (D) 4.15 Å

C-9. The maximum percentage of available volume that can be filled in a face centred cubic system by atoms is-

- (A) 74% (B) 68% (C) 34% (D) 26%

C-10. In a face centred cubic lattice the number of nearest neighbours for a given lattice point are :

- (A) 6 (B) 8 (C) 12 (D) 14

C-11. Which one of the following schemes of ordering closed packed sheets of equal sized spheres does not generate close packed lattice.

- (A) ABCABC (B) ABACABAC (C) ABBAABBA (D) ABCBCABCBC

Section (D) : Voids

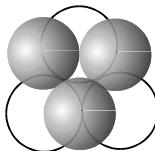
D-1. If the anions (A) form hexagonal closest packing and cations (C) occupy only 2/3 octahedral voids in it, then the general formula of the compound is

- (A) CA (B) CA₂ (C) C₂A₃ (D) C₃A₂

D-2. You are given 4 identical balls. What is the maximum number of square voids and triangular voids (in separate arrangements) that can be created ?

- (A) 1, 2 (B) 2, 1 (C) 3, 1 (D) 1, 3

D-3. The empty space between the shaded balls and hollow balls as shown in the diagram is called

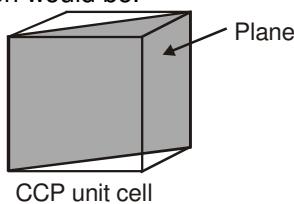


- (A) hexagonal void (B) octahedral void (C) tetrahedral void (D) double triangular void

D-4. In the close packed structure of AB type solid have cation radius of 75 pm, what would be the maximum and minimum sizes of the anions which formed voids in unit cell ?

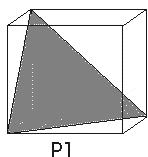
- (A) r_{min} = 101.45, r_{max} = 303.3 pm
 (B) r_{min} = 105.45, r_{max} = 300.3 pm
 (C) r_{min} = 102.45, r_{max} = 333.3 pm
 (D) r_{min} = 98.4, r_{max} = 333.3 pm

D-5. In a hypothetical solid C atoms form CCP lattice with A atoms occupying all the Tetrahedral Voids and B atoms occupying all the octahedral voids. A and B atoms are of the appropriate size such that there is no distortion in the CCP lattice. Now if a plane is cut (as shown) then type of voids and their numbers which are present at the cross section would be.

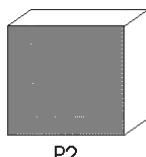


- (A) O.V. = 3, T.V. = 4 (B) O.V. = 2, T.V. = 4 (C) O.V. = 1, T.V. = 2 (D) O.V. = 0, T.V. = 4

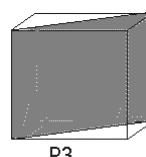
D-6. Following three planes (P_1 , P_2 , P_3) in an FCC unit cell are shown:



P1



P2

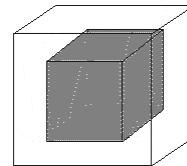


P3

Consider the following statements and choose the correct option that follow:

D-7. In an FCC unit cell a cube is formed by joining the centers of all the tetrahedral voids to generate a new cube. Then the new cube would contain voids as :

- (A) 1 full tetrahedral void, 1 full octahedral void
(B) 1 full tetrahedral void only
(C) 8 full tetrahedral voids and 1 full octahedral void
(D) 1 full Octahedral void only



Section (E) : Radius ratio rule and Type of ionic structures

E-3. Antifluorite structure is derived from fluorite structure by:

- Antimonite structure is derived from fluorite structure by :

 - (A) heating fluorite crystal lattice
 - (B) subjecting fluorite structure to high pressure
 - (C) Inter changing the positions of positive and negative ions in the lattice
 - (D) none of these

E-4. In zinc blende structure the coordination number of Zn^{2+} ion is

E-5. Strontium chloride has a fluorite structure, which of the following statement is true for the structure of strontium chloride?

- (A) the strontium ions are in a body-centered cubic arrangement
(B) the strontium ions are in a face-centered cubic arrangement
(C) each chloride ion is at the center of a cube of 8 strontium ions
(D) each strontium ion is at the center of a tetrahedron of 4 chloride ions

E-6. The spinal structure (AB_2O_4) consists of an fcc array of O^{2-} ions in which the A and B ions are located at the centers of the faces of the unit cell.

- (A) A cation occupies one-eighth of the tetrahedral holes and B cation occupies one-half of octahedral holes
(B) A cation occupies one-fourth of the tetrahedral holes and the B cations the octahedral holes
(C) A cation occupies one-eighth of the octahedral hole and the B cation the tetrahedral holes
(D) A cation occupies one-fourth of the octahedral holes and the B cations the tetrahedral holes

E-7. In the crystal lattice of diamond, carbon atoms adopt :

- (A) fcc arrangement along with occupancy of 50% tetrahedral holes
 - (B) fcc arrangement along with occupancy of 25% tetrahedral holes
 - (C) fcc arrangement along with occupancy of 25% octahedral hole
 - (D) bcc arrangement

E-8. Cesium chloride on heating to 760 K changes into

- (A) CsCl(g) (B) NaCl structure
(C) antifluorite structure (D) ZnS structure

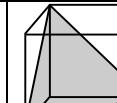
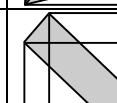
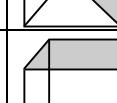
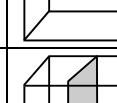
Section (F) : Crystal defects and Properties of solids

PART - III : MATCH THE COLUMN

1. We are good at matching things let us try our hand on the following columns:

Solid	Constituent particle	Binding force
(a) Diamond	(e) Ion	(i) Metallic
(b) Sodium Chloride	(f) Atom	(j) Dipole dipole
(c) HCl	(g) Kernel	(k) Ionic
(d) Aluminium	(h) Molecule	(l) Covalent

- 2. Match the column :**

	Column I (Arrangement of the atoms/ions)		Column II (Planes in fcc lattice)
(A)		(p)	
(B)		(q)	
(C)		(r)	
(D)	 	(s)	

- ### **3. Match the column :**

	Column-I		Column-II
(A)	ZnS crystal	(p)	fcc
(B)	CaF ₂ crystal	(q)	hcp
(C)	NaCl crystal	(r)	Distance between closest particles is $\frac{\sqrt{3}}{4} a$.
(D)	Diamond crystal	(s)	Only one type of voids are occupied

Exercise-2

Marked Questions may have for Revision Questions.

PART - I : ONLY ONE OPTION CORRECT TYPE

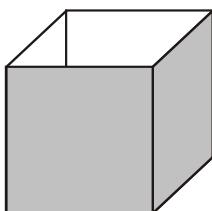
1. Which of the following solids are not correctly matched with the bonds found between the constituent particles:
 (A) Solid CO₂ : Vanderwaal's
 (B) Graphite : Covalent and Vanderwaal
 (C) Grey Cast Iron : Ionic
 (D) Metal alloys : Ions-delocalised electrons
2. Which of the following is not correct for ionic crystals :
 (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
3. An element (atomic mass = 100 g/mole) having bcc structure has unit cell edge 400 pm. The density of the element is (no. of atoms in bcc(Z) = 2).
 (A) 2.144 g/cm³ (B) 5.2 g/cm³ (C) 7.289 g/cm³ (D) 10.376 g/cm³
4. What is the nearest distance between two different layers in ABAB arrangement ($a = 2 \times$ radius of the particle).
 (A) $\sqrt{\frac{8}{3}} a$ (B) $\sqrt{\frac{4}{3}} a$ (C) $\frac{1}{\sqrt{6}} a$ (D) $\sqrt{\frac{2}{3}} a$
5. In a CCP lattice of X and Y, X atoms are present at the corners while Y atoms are at face centers. Then the formula of the compound would be if one of the X atoms from a corner is replaced by Z atoms (also monovalent)?
 (A) X₇Y₂₄Z₂ (B) X₇Y₂₄Z (C) X₂₄Y₇Z (D) XY₂₄Z
6. You are given 6 identical balls. What is the maximum number of square voids and triangular voids (in separate arrangements) that can be created?
 (A) 2, 4 (B) 4, 2 (C) 4, 3 (D) 3, 4
7. In a simple cubic lattice of anions, the side length of the unit cell is 2.88 Å. The diameter of the void in the body centre is
 (A) 1.934 Å (B) 0.461 Å (C) 2.108 Å (D) 4.988 Å
8. In a multi layered close-packed structure
 (A) there are twice as many tetrahedral holes as many close-packed atoms
 (B) there are as many tetrahedral holes as many closed packed atoms
 (C) there are twice as many octahedral holes as many close-packed atoms
 (D) there are as many tetrahedral holes as many octahedral holes
9. In a compound, oxide ions are arranged in cubic close packing arrangement. Cations A occupy one-sixth of the tetrahedral voids and cations B occupy one-third of the octahedral voids. The formula of the compound is
 (A) A₂BO₃ (B) AB₂O₃ (C) A₂B₂O₂ (D) ABO₃
10. Platinum crystallizes in a face-centered cubic crystal with a unit cell length 'a'. The distance between nearest neighbors is :
 (A) a (B) $a \frac{\sqrt{3}}{2}$ (C) $a \frac{\sqrt{2}}{2}$ (D) $a \frac{\sqrt{2}}{4}$
11. Platinum crystallises in a face centered cube crystal with a unit cell length of 3.9231 Å. The density and atomic radius of platinum are respectively. [Atomic mass of Pt = 195]
 (A) 45.25 g. cm⁻³, 2.516 Å (B) 21.86 g. cm⁻³, 1.387 Å
 (C) 29.46 g. cm⁻³, 1.48 Å (D) None of these



12. Metallic gold crystallises in face centered cubic. Lattice with edge-length 4.070 Å. Closest distance between gold atoms is :
 (A) 2.035 Å (B) 8.140 Å (C) 2.878 Å (D) 1.357 Å
13. Which of the following statements is correct in the rock-salt structure of ionic compounds?
 (A) Co-ordination number of cation is four whereas that of anion is six.
 (B) Co-ordination number of cation is six whereas that of anion is four.
 (C) Co-ordination number of each cation and anion is four.
 (D) Co-ordination number of each cation and anion is six.
14. The compound AB crystallizes in a cubic lattice in which both A and B atoms have coordination numbers of 8. To what crystal class does the unit cell belong ?
 (A) CsCl structure (B) NaCl structure (C) ZnS structure (D) Al₂O₃ structure
15. BaO has a rock-salt type structure. When subjected to high pressure, the ratio of the coordination number of Ba⁺ ion to O⁻ changes to
 (A) 4 : 8 (B) 8 : 4 (C) 8 : 8 (D) 4 : 4
16. A crystal of NaCl, which has sodium ions and chloride ions missing from the lattice point, is said to exhibit
 (A) Surface defect (B) Lattice defect (C) Frenkel defect (D) Schottky defect
17. In the Schootky defect :
 (A) cations are missing from the lattice sites and occupy the interstitial sites
 (B) equal number of cations and anions are missing
 (C) anion are missing and electrons are present in their place
 (D) equal number of extra cations and electrons are present in the interstitial sites
18. NaCl shows Schottky defects and AgCl Frenkel defects. Their electrical conductivity is due to:
 (A) motion of ions and not the motion of electrons
 (B) motion of electrons and not the motion of ions
 (C) lower co-ordination number of NaCl
 (D) higher co-ordination number of AgCl
19. Zinc Oxide, white in colour at room temperature, acquires yellow colour on heating due to:
 (A) Zn being a transition element.
 (B) paramagnetic nature of the compound.
 (C) trapping of electrons at the site vacated by Oxide ions.
 (D) Both (A) & (B).

PART - II : NUMERICAL VALUE QUESTIONS

1. How many of the following are Covalent network solids?
 S₈, Bronze, SiO₂, Diamond, ZnSO₄, Si, AlN, SiC, CO₂.
2. How many number of atom effectively present in a cubic unit formed by arrangement of eight B.C.C unit cell.
3. How many spherical balls of radii 2 cm can be placed completely inside a cubical box of edge = 8 cm ?



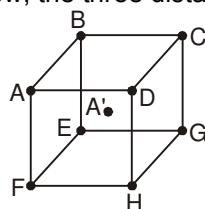
4. What is the co-ordination number of an atom in its own layer in ABAB type arrangement.
5. In ABAB arrangement if an atom is placed in A layer then calculate the number of atoms touching in its adjacent B layers ?
6. How many number octahedral voids are effectively inside an HCP unit cell.

7. In a compound, oxide ions are arranged in cubic close packing arrangement. Cations A occupy one-sixth of the tetrahedral voids and cations B occupy one-third of the octahedral voids. The formula of the compound is $A_xB_yO_z$, then find the value of $x + y + z$.

8. The coordination number of cation and anion in Fluorite CaF_2 and Zinc blende ZnS are respectively $x : y$ and $a : b$. Find $(x + y + a + b)$.

9. In a crystalline solid having molecular formula A_2B anion (B) are arranged in cubic close packed lattice and cations (A) are equally distributed between octahedral and tetrahedral voids.
(i) What percentage of octahedral voids is occupied?
(ii) What percentage of tetrahedral voids is occupied?
Report your answer ((i) – (ii)).

PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE



- (A) $AB = a$ (B) $AC = \sqrt{2}a$ (C) $AA' = \frac{\sqrt{3}a}{2}$ (D) $AA' = \sqrt{3}a$

4. A metal crystallises in bcc. Find the % fraction of edge length not covered and also % fraction of edge length covered by atom is :
 (A) 10.4% (B) 13.4% (C) 86.6% (D) 11.4%

5. Select the correct statements about three dimensional HCP system.
 (A) Number of atoms in HCP unit cell is six. (B) The volume of HCP unit cell is $24\sqrt{2} r^3$.
 (C) The empty space in HCP unit cell is 26%. (D) The base area of HCP unit cell is $6\sqrt{3} r^2$.

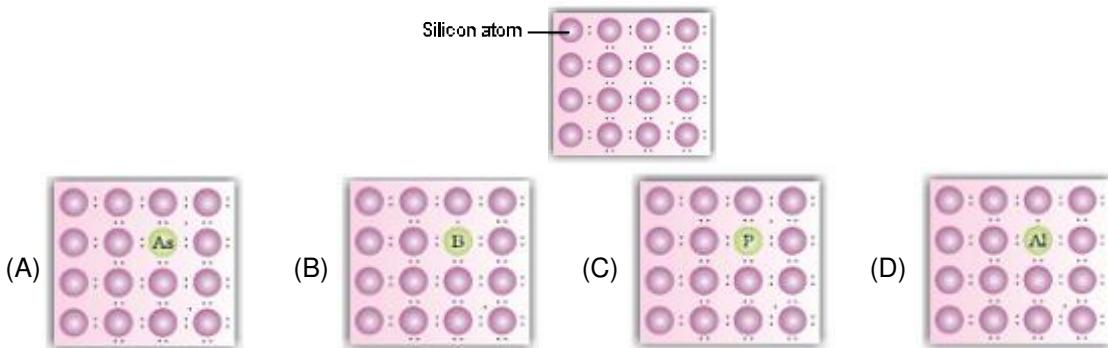
6. Which statements is/are true about HCP and CCP lattice
 (A) Number of tetrahedral voids are twice of octahedral holes
 (B) 12 tetrahedral and 6 octahedral voids are present in one HCP unit cell
 (C) C.N. of HCP unit cell is 12
 (D) If atom of tetrahedral voids displace into octahedral voids then it is Schootky defect.

7. In which of the following arrangements octahedral voids are formed?
 (A) hcp (B) bcc (C) simple cubic (D) fcc

8. The number of tetrahedral voids per unit cell in NaCl crystal is _____.
 (A) 4 (B) 8
 (C) twice the number of octahedral voids. (D) four times the number of octahedral voids.

9. Which of the following statements are correct :
 (A) The coordination number of each type of ion in CsCl crystal is 8.
 (B) A metal that crystallises in bcc structure has a coordination number of 12.
 (C) A unit cell of ionic crystal shares some of its ion with other unit cells.
 (D) The length of the unit cell in NaCl is 552 pm. ($\gamma_{Na^+} = 95$ pm, $\gamma_{Cl^-} = 181$ pm)

10. Which of the following is/are correct ?
 (A) Schottky defect lowers the density
 (B) Frenkel defect increases the dielectric constant of the crystals
 (C) Stoichiometric defects make the crystals electrical conductors
 (D) In the Schottky defect, equal number of extra cations and electrons are present in the interstitial sites
11. A perfect crystal of silicon (Fig) is doped with some elements as given in the options. Which of these options show n-type semiconductors?



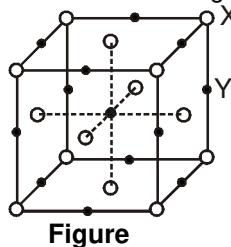
12. Which of the following statements are true about semiconductors?
 (A) Silicon doped with electron rich impurity is a p-type semiconductor.
 (B) Silicon doped with an electron rich impurity is an n-type semiconductor.
 (C) Delocalised electrons increase the conductivity of doped silicon.
 (D) An electron vacancy increases the conductivity of n-type semiconductor.

PART - IV : COMPREHENSION

Read the following comprehension carefully and answer the questions.

Comprehension # 1

Consider the figure given for solid XY. Answer the following questions



1. The site Y represents
 (A) tetrahedral void (B) Octahedral void (C) triangular void (D) cubical void.
2. The number of XY units per unit cell is
 (A) 4 (B) 3 (C) 3 (D) 8
3. Co-ordination number of Y is
 (A) 3 (B) 4 (C) 6 (D) 8

Comprehension # 2

When an atom or an ion is missing from its normal lattice site, a lattice vacancy (Schottky defect) is created. In stoichiometric ionic crystals, a vacancy of one ion has to be accompanied by the vacancy of the oppositely charged ion in order to maintain electrical neutrality.

In a Frenkel defect an ion leaves its position in the lattice and occupies an interstitial void. This is the Frenkel defect commonly found along with the Schottky defects and interstitials. In pure alkali halides, Frenkel defects are not found since the ions cannot get into the interstitial sites. Frenkel defects are found in silver halides because of the small size of the Ag^+ ion. Unlike Schottky defects, Frenkel defects do not change the density of the solids. In certain ionic solids (e.g. AgBr) both Schottky and Frenkel defects occur.



The defects discussed above do not disturb the stoichiometry of the crystalline material. There is large variety of non-stoichiometric inorganic solids which contain an excess or deficiency of one of the elements. Such solids showing deviations from the ideal stoichiometric composition form an important group of solids. For example in the vanadium oxide, VO_x , x can be anywhere between 0.6 and 1.3. There are solids which are difficult to prepare in the stoichiometric composition. Thus, the ideal composition in compounds such as FeO is difficult to obtain (normally we get a composition of $\text{Fe}_{0.95}\text{O}$ but it may range from $\text{Fe}_{0.93}\text{O}$ to $\text{Fe}_{0.96}\text{O}$). Non-stoichiometric behaviour is most commonly found for transition metal compounds though is also known for some lanthanoids and actinoids.

Zinc oxide loses oxygen reversibly at high temperatures and turns yellow in colour. The excess metal is accommodated interstitially, giving rise to electrons trapped in the neighbourhood. The enhanced electrical conductivity of the non-stoichiometric ZnO arises from these electrons.

Anion vacancies in alkali halides are produced by heating the alkali halide crystals in an atmosphere of the alkali metal vapour. When the metal atoms deposit on the surface they diffuse into the crystal and after ionisation the alkali metal ion occupies cationic vacancy whereas electron occupies anionic vacancy. Electrons trapped in anion vacancies are referred to as F-centers (from Farbe the German word for colour) that gives rise to interesting colour in alkali halides. Thus, the excess of potassium in KCl makes the crystal appear violet and the excess of lithium in LiCl makes it pink.

4. When LiCl is heated into the vapour of lithium, the crystal acquires pink colour. This is due to
 - (A) Schottky defects
 - (B) Frenkel defects
 - (C) Metal excess defect leading to F-centers
 - (D) Electronic defect
5. Strongly heated ZnO crystal can conduct electricity. This is due to
 - (A) Movement of extra Zn^{2+} ions present in the interstitial sites
 - (B) Movement of electrons in the anion vacancies
 - (C) Movement of both Zn^{2+} ions and electrons
 - (D) None of these
6. AgCl is crystallized from molten AgCl containing a little CdCl_2 . The solid obtained will have
 - (A) cationic vacancies equal to number of Cd^{2+} ions incorporated
 - (B) cationic vacancies equal to double the number of Cd^{2+} ions
 - (C) anionic vacancies
 - (D) neither cationic nor anionic vacancies
7. Which of the following is most appropriate crystal to show Frenkel defect.

(A) CsCl	(B) NaCl	(C) AgBr	(D) CaCl_2
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Comprehension # 3

Answer Question no. 8, 9 and 10 by appropriately matching the information given in the three columns of the following table. (Z = effective number of atoms)

Column 1	Column 2	Column 3
(I) Square 2D packing	(i) $Z = 1$ in smallest unit cell	(P) edge length = $2R$ in smallest unit cell
(II) Hexagonal 2D packing of circles	(ii) $Z \geq 3$ in smallest unit cell	(Q) close packing in 3D
(III) CCP	(iii) Coordination Number = 6	(R) packing efficiency > 50%
(IV) Simple cubic	(iv) Primitive unit cell possible	(S) can be made by 2D hexagonal layers of spheres

8. Identify the true combination:

(A) (I) (i) P	(B) (II) (i) Q	(C) (III) (iii) R	(D) (IV) (ii) S
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9. For packing with minimum void space the true combination is:
(Consider 2D & 3D arrangements separately)

(A) (I) (i) P	(B) (II) (i) P	(C) (III) (iv) S	(D) (IV) (iii) R
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10. For the arrangement classified as ABAB type the correct combination is:

(A) (I) (ii) P	(B) (III) (i) Q	(C) (II) (iii) R	(D) (IV) (iv) S
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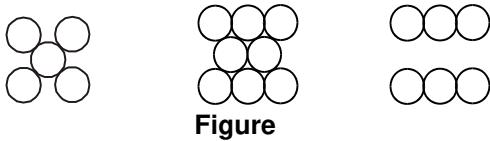
Exercise-3

* Marked Questions may have more than one correct option.

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

1. In the figures given below show the location of atoms in three crystallographic planes in a fcc lattice. Draw the unit cell of the corresponding structure and identify these planes in your diagram.

[JEE-2000, 3/100]



2. 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:

[JEE-2001, 1/35]

- (A) AB_2 (B) A_2B (C) A_4B_3 (D) A_3B_4

3. A substance $A_x B_y$ crystallizes in a face centered cubic lattice in which atoms 'A' occupy each corner of the cube and atoms 'B' occupy the centers of each face of the cube. Identify the correct composition of the substance $A_x B_y$.

[JEE-2002, 3/90]

- (A) AB_3 (B) $A_4 B_3$
(C) $A_3 B$ (D) composition cannot be specified

4. Marbles of diameter 10 mm each are to be arranged on a flat surface so that their centers lie within the area enclosed by four lines of length each 40 mm. Sketch the arrangement that will give the maximum number of marbles per unit area, that can be enclosed in this manner and deduce the expression to calculate it.

[JEE-2003, 2/60]

5. A binary salt AB (formula weight = 6.023 Y amu, where Y is an arbitrary number) has rock salt structure with 1 : 1 ratio of A to B. The shortest A—B distance in the unit cell is $Y^{1/3}$ nm.

[JEE-2004, 4/60]

- (a) Calculate the density of the salt in kg m^{-3} .
(b) Given that the measured density of the salt is 20 kg m^{-3} , specify the type of point defect present in the crystal.

6. In which of the following compounds the cations are present in alternate tetrahedral voids:

[JEE-2005, 3/84]

- (A) NaCl (B) ZnS (C) CaF_2 (D) Na_2O

7. In a FCC lattice of a metal edge length is 400 pm. Find the maximum diameter of an atom which can be accommodated in an interstitial gap in this lattice without causing any distortion.

[JEE-2005, 2/60]

8. For a unit cell edge length = 5\AA , the element is of atomic mass 75, has density of 2gm/cc. Calculate atomic radius of the element.

[JEE-2006, 6/184]

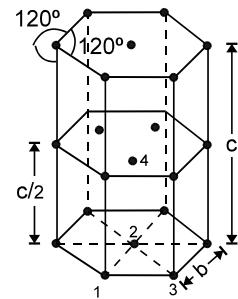
9. Match the crystal system/unit cells mentioned in **Column I** with their characteristic features mentioned in **Column II**.

[JEE-2007, 6/162]

	Column I		Column II
(A)	simple cubic and face-centered cubic	(p)	have these cell parameters $a = b = c$ and $\alpha = \beta = \gamma$
(B)	cubic and rhombohedral	(q)	are two crystal systems
(C)	cubic and tetragonal	(r)	have only two crystallographic angles of 90°
(D)	hexagonal and monoclinic	(s)	belong to same crystal system

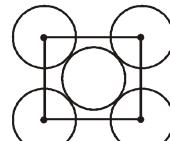
**Comprehension :**

In hexagonal systems of crystals, a frequently encountered arrangement of atoms is described as a hexagonal prism. Here, the top and bottom of the cell are regular hexagons and three atoms are sandwiched in between them. A space-filling model of this structure, called hexagonal close-packed (HCP), is constituted of a sphere on a flat surface surrounded in the same plane by six identical spheres as closely as possible. There spheres are then placed over the first layer so that they touch each other and represent the second layer. Each one of these three spheres touches three spheres of the bottom layer. Finally, the second layer is covered with third layer that is identical to the bottom layer in relative position. Assume radius of every sphere to be 'r'.

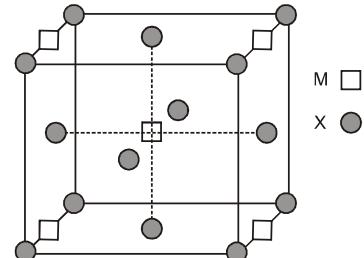


10. The number of atoms in the HCP unit cell is [JEE-2008, 4/163]
 (A) 4 (B) 6 (C) 12 (D) 17
11. The volume of this HCP unit cell is [JEE-2008, 4/163]
 (A) $24\sqrt{2} r^3$ (B) $16\sqrt{2} r^3$ (C) $12\sqrt{2} r^3$ (D) $\frac{64}{3\sqrt{3}} r^3$
12. The empty space in this HCP unit cell is [JEE-2008, 4/163]
 (A) 74% (B) 47.6% (C) 32% (D) 26%
- 13.* The correct statement(s) regarding defects in solids is(are) : [JEE-2009, 4/160]
 (A) Frenkel defect is usually favoured by a very small difference in the sizes of cation and anion.
 (B) Frenkel defect is a dislocation defect.
 (C) Trapping of an electron in the lattice leads to the formation of F-center.
 (D) Schottky defects have no effect on the physical properties of solids.

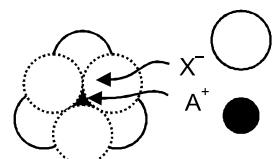
14. The packing efficiency of the two dimensional square unit cell shown below is: [JEE-2010, 5/163]
 (A) 39.27%
 (B) 68.02%
 (C) 74.05%
 (D) 78.54%

**Figure**

15. The number of hexagonal faces that are present in a truncated octahedron is [JEE-2011, 3/160]
16. A compound $M_P X_q$ has cubic close packing (ccp) arrangement of X. Its unit cell structure is shown below. The empirical formula of the compound is : [JEE, 2012, 3/136]



17. The arrangement of X^- ions around A^+ ion in solid AX is given in the figure (not drawn to scale). If the radius of X^- is 250 pm, the radius of A^+ is : [JEE(Advanced) 2013, 2/120]
 (A) 104 pm (B) 125 pm
 (C) 183 pm (D) 57 pm



18. If the unit cell of a mineral has cubic close packed (ccp) array of oxygen atoms with m fraction of octahedral holes occupied by aluminium ions and n fraction of tetrahedral holes occupied by magnesium ions, m and n, respectively, are [JEE(Advanced) 2015, 4/168]
 (A) $\frac{1}{2}, \frac{1}{8}$ (B) $1, \frac{1}{4}$ (C) $\frac{1}{2}, \frac{1}{2}$ (D) $\frac{1}{4}, \frac{1}{8}$



- 19.* The **CORRECT** statement(s) for cubic close packed (ccp) three dimensional structure is(are)
[JEE(Advanced) 2016, 4/124]
- (A) The number of the neighbours of an atom present in the topmost layer is 12
(B) The efficiency of atom packing is 74%
(C) The number of octahedral and tetrahedral voids per atom are 1 and 2, respectively
(D) The unit cell edge length is $2\sqrt{2}$ times the radius of the atom
20. A crystalline solid of a pure substance has a face-centred cubic structure with a cell edge of 400 pm. If the density of the substance in the crystal is 8 g cm^{-3} , then the number of atoms present in 256 g of the crystal is $N \times 10^{24}$. The value of N is
[JEE(Advanced) 2017, 2/122]
21. Consider an ionic solid **MX** with NaCl structure. Construct a new structure (**Z**) whose unit cell is constructed from the unit cell of **MX** following the sequential instructions given below. Neglect the charge balance.
- (i) Remove all the anions (**X**) except the central one
 - (ii) Replace all the face centered cations (**M**) by anions (**X**)
 - (iii) Remove all the corner cations (**M**)
 - (iv) Replace the central anion (**X**) with cation (**M**)
- The value of $\left(\frac{\text{number of anions}}{\text{number of catons}} \right)$ in **Z** is _____.
[JEE(Advanced) 2018, 3/120]

PART - II : JEE (MAIN) ONLINE PROBLEMS (PREVIOUS YEARS)

1. In a face centered cubic lattice atoms A are at the corner points and atoms B at the face centered points. If atom B is missing from one of the face centered points, the formula of the ionic compound is :
[JEE(Main) 2014 (09-04-14), 4/120]
- (1) AB_2 (2) A_5B_2 (3) A_2B_3 (4) A_2B_5
2. The appearance of colour in solid alkali metal halides is generally due to :
[JEE(Main) 2014 (11-04-14), 4/120]
- (1) Schottky defect (2) Frenkel defect (3) Interstitial position (4) F-centres
3. In a monoclinic unit cell the relation of sides and angles are respectively :
[JEE(Main) 2014 (12-04-14), 4/120]
- (1) $a = b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$ (2) $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$
(3) $a \neq b \neq c$ and $\alpha = \gamma = 90^\circ \neq \beta$ (4) $a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma \neq 90^\circ$
4. The total number of octahedral void (s) per atom present in a cubic close packed structure is :
[JEE(Main) 2014 (19-04-14), 4/120]
- (1) 2 (2) 4 (3) 1 (4) 3
5. Which of the following arrangements shows the schematic alignment of magnetic moments of antiferromagnetic substance ?
[JEE(Main) 2018 (15-04-18), 4/120]
- | | |
|-----|-----|
| (1) | (2) |
| (3) | (4) |
6. All of the following share the same crystal structure except :
[JEE(Main) 2018 (15-04-18), 4/120]
- (1) LiCl (2) NaCl (3) RbCl (4) CsCl
7. The one that is extensively used as a piezoelectric material is :
[JEE(Main) 2019 (09-01-19), 4/120]
- (1) tridymite (2) amorphous silica (3) quartz (4) mica
8. At 100°C , copper (Cu) has FCC unit cell structure with cell edge length of $x \text{ \AA}$. What is the approximate density of Cu (in g cm^{-3}) at this temperature? [Atomic mass of Cu = 63.55 u]
[JEE(Main) 2019 (09-01-19), 4/120]
- (1) $\frac{205}{x^3}$ (2) $\frac{105}{x^3}$ (3) $\frac{422}{x^3}$ (4) $\frac{211}{x^3}$



9. Which primitive unit cell has unequal edge lengths ($a \neq b \neq c$) and all axial angles different from 90° ? [JEE(Main) 2019 (10-01-19), 4/120]
 (1) Monoclinic (2) Triclinic (3) Hexagonal (4) Tetragonal
10. A compound of formula A_2B_3 has the hcp lattice. Which atom forms the hcp lattice and what fraction of tetrahedral voids is occupied by the other atoms; [JEE(Main) 2019 (10-01-19), 4/120]
 (1) hcp lattice -A, $\frac{2}{3}$ Tetrahedral voids-B (2) hcp lattice -B, $\frac{1}{3}$ Tetrahedral voids-A
 (3) hcp lattice -B, $\frac{2}{3}$ Tetrahedral voids-A (4) hcp lattice -A, $\frac{1}{3}$ Tetrahedral voids-B
11. A solid having density of $9 \times 10^3 \text{ kg m}^{-3}$ forms face centred cubic crystals of edge length $200\sqrt{2} \text{ pm}$. What is the molar mass of the solid? [Avogadro constant $\approx 6 \times 10^{23} \text{ mol}^{-1}$, $\pi \approx 3$] [JEE(Main) 2019 (11-01-19), 4/120]
 (1) $0.0432 \text{ kg mol}^{-1}$ (2) $0.0305 \text{ kg mol}^{-1}$ (3) $0.4320 \text{ kg mol}^{-1}$ (4) $0.0216 \text{ kg mol}^{-1}$
12. The radius of the largest sphere which fits properly at the centre of the edge of a body centred cubic unit cell is : (Edge length is represented by 'a') [JEE(Main) 2019 (11-01-19), 4/120]
 (1) $0.047 a$ (2) $0.027 a$ (3) $0.134 a$ (4) $0.067 a$
13. Element 'B' forms ccp structure and 'A' occupies half of the octahedral voids, while oxygen atoms occupy all the tetrahedral voids. The structure of bimetallic oxide is : [JEE(Main) 2019 (08-04-19)S1, 4/120]
 (1) A_2BO_4 (2) A_2B_2O (3) AB_2O_4 (4) A_4B_2O
14. Consider the bcc unit cells of the solid 1 and 2 with the position of atoms as shown below. The radius of atoms as shown below. The radius of atom B is twice that of atom A. The unit cell edge length is 50% more in solid 2 than in 1. What is the approximate packing efficiency in solid 2? [JEE(Main) 2019 (08-04-19)S2, 4/120]
- Solid 1

Solid 2
- (1) 65% (2) 45% (3) 90% (4) 75%
15. An element has a face-centred cubic (fcc) structure with a cell edge of a . The distance between the centres of two nearest tetrahedral voids in the lattice is: [JEE(Main) 2019 (12-04-19)S1, 4/120]
 (1) $\sqrt{2}a$ (2) a (3) $\frac{3}{2}a$ (4) $\frac{a}{2}$
16. The ratio of number of atoms present in a simple cubic, body centered cubic and face centered cubic structure are respectively : [JEE(Main) 2019 (12-04-19)S2, 4/120]
 (1) $4 : 2 : 1$ (2) $8 : 1 : 6$ (3) $4 : 2 : 3$ (4) $1 : 2 : 4$
17. Which of the following compounds is likely to show both Frenkel and Schottky defects in its crystalline form? [JEE(Main) 2020, (08-01-20)S2, 4/100]
 (1) CsCl (2) KBr (3) AgBr (4) ZnS
18. 'X' melts at low temperature and is a bad conductor of electricity in both liquid and solid state. X is : [JEE(Main) 2020, (09-01-20)S1, 4/100]
 (1) Carbon tetrachloride (2) Zinc sulphide
 (3) Silicon carbide (4) Mercury

Answers**EXERCISE - 1****PART - I**

- A-1.** Ionic – LiBr , $(\text{NH}_4)_3\text{PO}_4$; Metallic – Brass, Rb; Molecular – P_4O_{10} , I_2 , P_4
Network – SiC, Graphite, Si, Amorphous – Plastic

A-2.	Ques.	(a)	(b)	Total particles
	(i)	1/4	1	2
	(ii)	1/2	1/4	2
	(iii)	1/6	1/2	2
	(iv)	1/6	–	1/2
	(v)	1/3	1/6	1

A-3.

Crystal System	Features	Unit cell found	Examples
Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ$; $\beta \neq 120^\circ, \neq 90^\circ, \neq 60^\circ$	S, EC	Monoclinic sulphur, PbCrO_4 , $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$.
Hexagonal	$a = b \neq c$ $\alpha = \beta = 90^\circ, \gamma = 120^\circ$	S	Graphite, ZnO , CdS , Mg , PbI_2 , SiC .
Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	S	$\text{K}_2\text{Cr}_2\text{O}_7$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, H_3BO_3 .

- B-1.** Cube1 - 1/2 ; Cube2 - 1/4 ; Cube3 - 1 ; Cube4 - 1/8 **B-2.** BCC

- B-3.** 124.27 pm, density = 7.30 g cm⁻³

- C-1.** ABC-ABC-Arrangement (CCP unit cell).

- C-2.** $1.72 \times 10^{-23} \text{ cm}^3$, 1.60 Å

- C-3.** (i) b, f, g are identical; c, e are identical. (ii) $d_a < [d_b = d_f = d_g] < [d_c = d_e] < d_d$

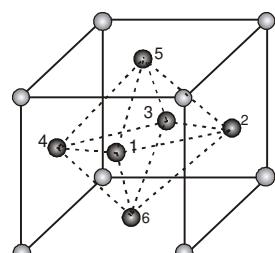
- C-4.** (i) $2r$, $2r$, $2\sqrt{3}r$; (ii) Square, side = $2r$.

- C-5.** FCC, $\sqrt{2}$ Å

- C-6.** ABAB.....type arrangement (unit cell = HCP).

- D-1.** No, Rhombous: $2R$, 60° , 120° ; Triangular voids; 2 voids, 0.155 R.

- D-2.** Octahedral void is present at the body center, which is formed by six face centered atoms and it consist at triangle faces.



- D-3.** 12 and 6

- D-4.** 4, 8, $\frac{a}{\sqrt{2}}$, $\frac{a}{2}$

- E-1.** (a) CsCl type (b) ZnS type (c) NaCl type (d) CsCl type



- E-2.** In case of ZnS radius ratio is $\frac{r_{\text{Zn}^{2+}}}{r_{\text{S}^{2-}}} = 0.402$.

That's why Zn^{2+} ion is present in tetrahedral void. If Zn^{2+} ion is present in octahedral void [For NaCl type structure] then anion-anion contact is there and compound become unstable. That's why. ZnS not crystallize in the NaCl structure.

- E-3.** (i) Zn²⁺ ions occupy alternate Tetrahedral holes; (ii) Anti-Flourite: Anions in FCC and Cations in Tetrahedral holes, Fluorite: Cations in FCC and Anions in Tetrahedral holes

- F-1.** **Imperfections in solids :** Any deviation from the perfectly ordered arrangement constitutes a defect or imperfection. These defects are sometimes called thermodynamic defects because the number of these defects depends on the temperature.

(i) Stoichiometric point defects : Schottky Defects, Interstitial Defects, Frenkel Defects.

(ii) Non-Stoichiometric defects : Metal excess defects, Metal deficiency defects.

- F-2.** The reason of both is the presence of electron in anionic vacancies which is known as F- center.

- F-3.** Silicon doped with phosphorus forms n - type of semiconductor. Phosphorus contains one extra electron than silicon which can move easily through the crystal and is responsible for semiconductor properties.

- F-4.** In semiconductor fairly small band gap is present between valence band (filled with electrons) and conduction band (lowest unoccupied energy band). Increase in temperature gives thermal energy to some of the electrons and they move to conduction band and change the conductivity of semiconductor (Increase).

PART - II

- | | | | | | | | | | |
|-------------|-----|--------------|-----|--------------|-----|-------------|-----|-------------|-----|
| A-1. | (C) | A-2. | (C) | A-3. | (D) | A-4. | (A) | A-5. | (A) |
| A-6. | (B) | B-1. | (A) | B-2. | (A) | B-3. | (B) | B-4. | (B) |
| B-5. | (A) | B-6. | (C) | C-1. | (C) | C-2. | (A) | C-3. | (A) |
| C-4. | (B) | C-5. | (C) | C-6. | (A) | C-7. | (C) | C-8. | (B) |
| C-9. | (A) | C-10. | (C) | C-11. | (C) | D-1. | (C) | D-2. | (A) |
| D-3. | (B) | D-4. | (C) | D-5. | (A) | D-6. | (A) | D-7. | (A) |
| E-1. | (C) | E-2. | (D) | E-3. | (C) | E-4. | (B) | E-5. | (B) |
| E-6. | (A) | E-7. | (A) | E-8. | (B) | F-1. | (C) | F-2. | (B) |
| F-3. | (A) | F-4. | (B) | | | | | | |

PART - III

- 1.** (a - f,l); (b - e,k); (c - h,j); (d - g,i) **2.** (A - r,s); (B - r,s); (C - p); (D - q)
3. (A - p,q,r,s); (B - p,r,s); (C - p,s); (D - p,r,s)

EXERCISE - 2

PART - I

- | | | | | | | | | | |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1. | (C) | 2. | (D) | 3. | (B) | 4. | (D) | 5. | (B) |
| 6. | (A) | 7. | (C) | 8. | (A) | 9. | (D) | 10. | (C) |
| 11. | (B) | 12. | (C) | 13. | (D) | 14. | (A) | 15. | (C) |
| 16. | (D) | 17. | (B) | 18. | (A) | 19. | (C) | | |

PART - II

- | | | | | |
|----------------------|----------------------|------|---------------------------|------|
| 1. 5 | 2. 16 | 3. 8 | 4. 6 | 5. 6 |
| 6. 6 | 7. $5 = (1 + 1 + 3)$ | | 8. $20 = (8 + 4 + 4 + 4)$ | |
| 9. $50 = (100 - 50)$ | | | | |

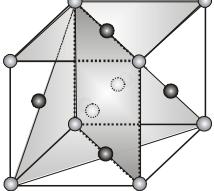
PART - III

- | | | | | |
|----------|----------|----------|----------|-----------|
| 1. (ABC) | 2. (AC) | 3. (ABC) | 4. (BC) | 5. (ABCD) |
| 6. (ABC) | 7. (AD) | 8. (BC) | 9. (ACD) | 10. (ABC) |
| 11. (AC) | 12. (BC) | | | |

PART - IV

- | | | | | |
|--------|--------|--------|--------|---------|
| 1. (B) | 2. (A) | 3. (C) | 4. (C) | 5. (B) |
| 6. (A) | 7. (C) | 8. (A) | 9. (B) | 10. (C) |

EXERCISE - 3**PART - I**

1. 
- | | |
|--|--|
| 2. (D) | 3. (A) |
| 4. 25, 1.804 marbles/cm ² | 5. (a) 5 kg m ⁻³ (b) Cancelled (Full marks given in part a) |
| 6. (B) | 7. 117.08 pm |
| 9. (A – p,s); (B–q, p); (C–q); (D–q, r). | 10. (B) |
| 13. (BC) | 14. (D) |
| 18. (A) | 19. (BCD) |
| 20. 2 | 21. 3 |

PART - II

- | | | | | |
|---------|---------|---------|---------|---------|
| 1. (4) | 2. (4) | 3. (3) | 4. (3) | 5. (4) |
| 6. (4) | 7. (3) | 8. (3) | 9. (2) | 10. (2) |
| 11. (2) | 12. (4) | 13. (3) | 14. (3) | 15. (4) |
| 16. (4) | 17. (1) | 18. (1) | | |



Additional Problems for Self Practice (APSP)

 Marked questions are recommended for Revision.

This Section is not meant for classroom discussion. It is being given to promote self-study and self testing amongst the Resonance students.

PART - I : PRACTICE TEST-1 (IIT-JEE (MAIN Pattern))

Max. Marks: 100

Max. Time : 1 Hour

Important Instructions:

A. General :

1. The test paper is of **1** hour duration.
 2. The Test Paper consists of **25** questions and each question carries **4** Marks. Test Paper consists of **Two Sections**.

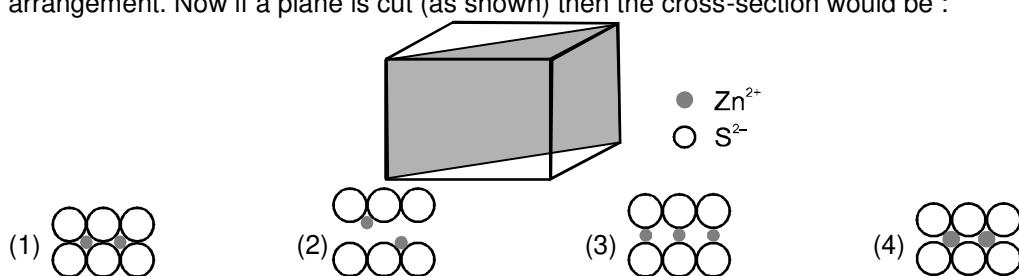
B. Test Paper Format and its Marking Scheme:

- Section-1 contains **20** multiple choice questions. Each question has four choices (1), (2), (3) and (4) out of which **ONE** is correct. For each question in Section-1, you will be awarded 4 marks if you give the corresponding to the correct answer and zero mark if no given answers. In all other cases, minus one (**-1**) mark will be awarded.
 - Section-2 contains **5** questions. The answer to each of the question is a **Numerical Value**. For each question in Section-2, you will be awarded 4 marks if you give the corresponding to the correct answer and zero mark if no given answers. No negative marks will be answered for incorrect answer in this section. In this section answer to each question is **NUMERICAL VALUE** with two digit integer and decimal upto two digit. If the numerical value has more than two decimal places **truncate/round-off** the value to **TWO** decimal placed.

SECTION-1

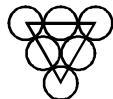
This section contains **20** multiple choice questions. Each question has four choices (1), (2), (3) and (4) out of which Only **ONE** option is correct.

7. Schottky defect occurs mainly in electrovalent compounds where :
 (1) positive ions and negative ions are of different size
 (2) positive ions and negative ions are of same size
 (3) positive ions are small and negative ions are big
 (4) positive ions are big and negative ions are small.
8. An ionic compound is expected to have tetrahedral structure if r_+/r_- lies in the range of :
 (1) 0.155 to 0.225 (2) 0.732 to 0.414 (3) 0.414 to 0.732 (4) 0.225 to 0.414
9. Malleability and ductility of metals can be accounted due to :
 (1) the capacity of layers of metal ions to slide over the other
 (2) the interaction of electrons with metal ions in the other
 (3) the presence of electrostatic forces
 (4) the crystalline structure of metal
10. A solid compound contains X, Y and Z atoms in a cubic lattice with X atom occupying the corners, Y atoms in the body centred positions and Z atoms at the centres of faces of the unit cell. What is the empirical formula of the compound :
 (1) XY_2Z_3 (2) XYZ_3 (3) $X_2Y_2Z_3$ (4) X_8YZ_6
11. In AgBr, there can occur
 (1) only schottky defect (2) only Frenkel defect (3) both (1) and (2) (4) None of these
12. In face-centred cubic unit cell, edge length is :
 (1) $\frac{4}{\sqrt{3}} r$ (2) $\frac{4}{\sqrt{2}} r$ (3) $2r$ (4) $\frac{\sqrt{3}}{2} r$
13. In an antifluorite structure, cations occupy :
 (1) octahedral voids (2) centre of the cube (3) tetrahedral voids (4) corners of the cube
14. The interionic distance for cesium chloride crystal will be :
 (1) a (2) $a/2$ (3) $\sqrt{3} a/2$ (4) $2a/\sqrt{3}$
15. A substance A_xB_y crystallizes in a face centred cubic (FCC) lattice in which atoms 'A' occupy each corner of the cube and atoms 'B' occupy the centres of each face of the cube. Identify the correct composition of the substance A_xB_y .
 (1) AB_3 (2) A_4B_3
 (3) A_3B (4) Composition cannot be specified
16. The number of atoms in 100 g of a fcc crystal with density = 10.0 g/cm³ and cell edge equal to 200 pm is equal to :
 (1) 5×10^{24} (2) 5×10^{25} (3) 6×10^{23} (4) 2×10^{25}
17. In the sphalerite (ZnS) structure, S^{2-} ions form a face-centred cubic lattice. Then Zn^{2+} ions are present on the body diagonals at
 (1) $\frac{1}{3}$ rd of the distance (2) $\frac{1}{4}$ th of the distance
 (3) $\frac{1}{6}$ th of the distance (4) $\frac{1}{8}$ th of the distance
18. In a solid, S^{2-} ions are packed in fcc lattice. Zn^{2+} occupy half of the tetrahedral voids in an alternating arrangement. Now if a plane is cut (as shown) then the cross-section would be :



19. **S₁** : Cubic system have four possible type of unit cells.
S₂ : H₂O is diamagnetic substance and it is weakly attracted in magnetic field.
S₃ : Graphite is a covalent solid with vanderwaal's forces as well.
- (1) F F T (2) F T F (3) T F F (4) F F F

20. **S₁** : Distance between Na⁺ & Cl⁻ in NaCl crystal is more than half of edge length.
S₂ : The no. of triangular voids in the given arrangement in the enclosed region is 3.



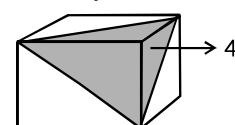
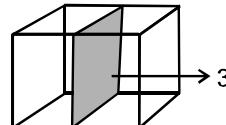
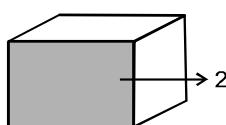
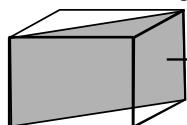
S₃ : In ZnS structure, 2Zn²⁺ & 2S²⁻ ions are present in each unit cell.

- (1) F F T (2) F T F (3) T F F (4) F F F

SECTION-2

This section contains 5 questions. Each question, when worked out will result in **Numerical Value**.

21. The vacant space in B.C.C. unit cell is :
22. In 3D close packed structures, for every 100 atoms, number of octahedral voids will be:
23. The co-ordination number of calcium fluoride (CaF₂) type structure is a : b. Find a + b
24. KCl crystallises in the same type of lattice as does NaCl. Given that $r_{\text{Na}^+}/r_{\text{Cl}^-} = 0.55$ and $r_{\text{K}^+}/r_{\text{Cl}^-} = 0.72$. Calculate the ratio of the side of the unit cell of KCl to that of NaCl :
25. In a bcc- arrangement which of the marked planes have maximum spatial density of atoms ?



Practice Test-1 (IIT-JEE (Main Pattern))

OBJECTIVE RESPONSE SHEET (ORS)

Que.	1	2	3	4	5	6	7	8	9	10	
Ans.											
Que.	11	12	13	14	15	16	17	18	19	20	
Ans.											
Que.	21	22	23	24	25						
Ans.											

PART - II : JEE (MAIN) OFFLINE PROBLEMS (PREVIOUS YEARS)

1. 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, 3/225]
(1) 4 and 2 (2) 9 and 14 (3) 14 and 9 (4) 2 and 4
2. How many unit cells are present in a cube-shaped ideal crystal of NaCl of mass 1.00g?
[Atomic masses : Na = 23, Cl = 35.5] [AIEEE-2003, 3/225]
(1) 2.57×10^{21} (2) 5.14×10^{21} (3) 1.28×10^{21} (4) 1.71×10^{21} .
3. What type of crystal defect is indicated in the diagram below? [AIEEE-2004, 3/225]
- | | | | | | |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Na ⁺ | Cl ⁻ | Na ⁺ | Cl ⁻ | Na ⁺ | Cl ⁻ |
| Cl ⁻ | □ | Cl ⁻ | Na ⁺ | □ | Na ⁺ |
| Na ⁺ | Cl ⁻ | □ | Cl ⁻ | Na ⁺ | Cl ⁻ |
| Cl ⁻ | Na ⁺ | Cl ⁻ | Na ⁺ | □ | Na ⁺ |
- (1) Frenkel defect
(2) Schottky defect
(3) interstitial defect
(4) Frenkel and Schottky defects





PART - III : NATIONAL STANDARD EXAMINATION IN CHEMISTRY (NSEC) STAGE-I

1. Number of atoms per unit cell for Body Centered Cubic system is : [NSEC-2001]
 (A) six (B) four (C) two (D) one

2. Co-ordination number for sodium metal is : [NSEC-2001]
 (A) 11 (B) 12 (C) 8 (D) 10

3. Sodium chloride crystallises in a face centred cubic lattice in which each [NSEC-2003]
 (A) sodium ion is tetrahedrally surrounded by 4 chloride ions and each chloride ion is tetrahedrally
 surrounded by 4 sodium ions
 (B) sodium ion is tetrahedrally surrounded by 4 chloride ions and each chloride ion is octahedrally surrounded by 6
 sodium ions
 (C) sodium ion is octahedrally surrounded by 6 chloride ions and each chloride ion is surrounded by 4
 sodium ions
 (D) sodium ion is octahedrally surrounded by 6 chloride ions and each chloride ion is octahedrally
 surrounded by 6 sodium ions.

4. An element crystallises in a face centered cubic lattice. Hence, its unit cell contains [NSEC-2004]
 (A) 14 atoms of the element and 8 of them belong to the unit cell
 (B) 14 atoms of the element and 4 of them belong to the unit cell
 (C) 8 atoms of the unit cell and only 1 of them belongs to the cell
 (D) 8 atoms of the unit cell and only 2 of them belong to the cell

5. Arsenic is used to dope germanium to obtain [NSEC-2005]
 (A) intrinsic semiconductors (B) p-type semiconductors
 (C) n-type semiconductors (D) non-conducting germanium.

6. Carborundum is a [NSEC-2005]
 (A) molecular solid (B) covalent solid (C) ionic solid (D) amorphous solid.

7. If $a \neq b \neq c$ and $\alpha = \beta = 90^\circ$, $\gamma \neq 90^\circ$, the crystal system is called [NSEC-2005]
 (A) monoclinic (B) triclinic (C) hexagonal (D) orthorhombic.

8. The number of units cells in 117.0 grams of NaCl is approximately [NSEC-2006]
 (A) 12×10^{20} (B) 3×10^{23} (C) 6×10^{23} (D) 1×10^{24}

9. In the unit cell of the crystal formed by the ionic compound of X and Y, the corners are occupied by X [NSEC-2007] and the centers of the faces by Y. The empirical formula of the compound is :
 (A) XY (B) X_2Y (C) XY_3 (D) X_8Y_6

10. How many nearest neighbours surround each ion in a face-centered cubic lattice of an ionic crystal ? [NSEC-2008]
 (A) 4 (B) 6 (C) 8 (D) 12

11. A match box exhibits [NSEC-2008]
 (A) Cubic geometry (B) Monoclinic geometry
 (C) Tetragonal geometry (D) Orthorhombic geometry

12. For a face centered cubic lattice, the unit cell content is – [NSEC-2009]
 (A) 1 (B) 2 (C) 3 (D) 4

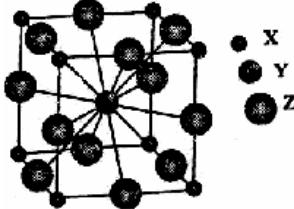
13. Body-centred cubic lattice has a coordination number of : [NSEC-2010]
 (A) 8 (B) 10 (C) 6 (D) 4

14. If $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$, the crystal system is [NSEC-2011]
 (A) monoclinic (B) triclinic (C) hexagonal (D) orthorhombic

15. The number of atoms per unit cell and number of the nearest neighbour in a body centred cubic [NSEC-2011]
 structure are :
 (A) 4, 12 (B) 2, 6 (C) 9, 6 (D) 2, 8

16. Ionic salt AX grows in face centered cubic lattice with cell length ‘a’. The ratio r_{A^+} / r_{X^-} for this salt will be [NSEC-2014]
 (A) 0.155 (B) 0.225 (C) 0.414 (D) 0.732

17. The unit cell of a compound made up of the three elements X, Y and Z is given below.



The formula of this compound is :

- (A) X_2YZ_3 (B) XY_3Z (C) XYZ_3 (D) X_3YZ_2

[NSEC-2014]

18. The metal M crystallizes in a body centered lattice with cell edge 400 pm. The atomic radius of M is. [NSEC-2015]

- (A) 200pm (B) 100pm (C) 173pm (D) 141pm

19. Ice crystallizes in a hexagonal lattice. At ascertain low temperature, the lattice constants are $a = 4.53 \text{ \AA}$ and $c = 7.41 \text{ \AA}$. The number of H_2O molecules contained in a unit cell ($d \approx 0.92 \text{ g cm}^{-3}$ at the given temperature) is [NSEC-2015]

- (A) 4 (B) 8 (C) 12 (D) 24

20. One mole crystal of a metal halide of the type MX with molecular weight 119 g having face centered cubic structure with unit cell length 6.58 \AA was recrystallized. The density of the recrystallized crystal was found to be 2.44 g cm^{-3} . The type of defect introduced during the recrystallization is [NSEC-2015]

- (A) a ditional M^+ and X^- ions at interstitial sites (B) Schottky defect
(C) F-centre (D) Frenkel defect

21. An ionic solid LaI_2 shows electrical conduction due to presence of : [NSEC-2016]

- (A) La^{2+} and 2I^- (B) La^{3+} , 2I^- and e^- (C) La^{2+} , I_2 and $2e^-$ (D) La^{3+} , I_2 and $3e^-$

22. In a cubic crystal structure, divalent metal-ion is located at the body-centered position, the smaller tetravalent metal ions are located at each corner and the O^{2-} ions are located half way along each of the edges of the cube. The number of nearest neighbour for oxygen is : [NSEC-2016]

- (A) 4 (B) 6 (C) 2 (D) 8

23. HgO is prepared by two different methods: one shows yellow colour while the other shows red colour. The difference in colour is due to difference in [NSEC-2016]

- (A) electronic d-d transitions (B) particle size
(C) Frenkel defect (D) Schottkey defect

24. When NiO is doped with a small quantity of Li_2O [NSEC-2017]

- (A) both cation and anion vacancies are generated
(B) Shottky defects are generated
(C) NiO becomes an n-type semiconductor
(D) NiO becomes a p-type semiconductor

25. A crystal of KCl containing a small amount of CaCl_2 will have [NSEC-2018]

- (A) vacant Cl^- sites
(B) vacant K^+ sites and a higher density as compared to pure KCl
(C) vacant K^+ sites and a lower density as compared to pure KCl
(D) K^+ ions in the interstitial sites

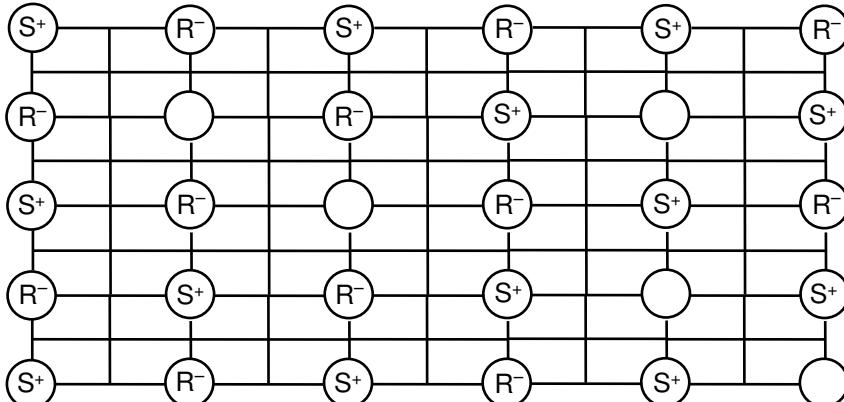
26. A scientist attempts to replace a few carbon atoms in 1.0 g of diamond with boron atoms or nitrogen atoms in separate experiments. Which of the following is correct ? [NSEC-2018]

- (A) The resulting material with B doping will be an n-type semiconductor
(B) The resulting material with B doping will be an p-type semiconductor
(C) B doping is NOT possible as B cannot form multiple bonds
(D) The resulting material with N doping will be a p-type semiconductor

27. A solid comprises of three types of elements, 'P', 'Q' and 'R'. 'P' forms an FCC lattice in which 'Q' and 'R' occupy all the tetrahedral voids and half the octahedral voids respectively. The molecular formula of the solid is [NSEC-2019]

- (A) $\text{P}_2\text{Q}_2\text{R}$ (B) PQ_2R_4 (C) $\text{P}_4\text{Q}_2\text{R}$ (D) P_4QR

28. The crystal defect indicated in the diagram below is



(A) Frenkel defect
(C) Frenkel and Schottky defects

(B) Schottky defect
(D) Interstitial defect

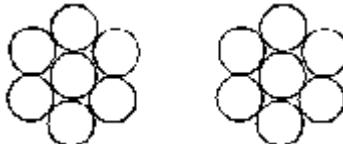
PART - IV : HIGH LEVEL PROBLEMS (HLP)

ONLY ONE OPTION CORRECT TYPE

1. Consider a cube 1 of Body Centered Cubic unit cell of edge length a now atom at the body center can be viewed to be lying on the corner of another cube 2. Find the volume common to cube 1 and cube 2.
 (A) $\frac{a^3}{27}$ (B) $\frac{a^3}{64}$ (C) $\frac{a^3}{2\sqrt{2}}$ (D) $\frac{a^3}{8}$
2. In an arrangement of type ABABA... (HCP), identical atoms of I layer A and III layer A are joined by a line passing through their centers. Suggest the correct statement.
 (A) No void is found on the line
 (B) Only Tetrahedral voids are found on the line
 (C) Only octahedral voids are found on the line
 (D) Equal number of tetrahedral and octahedral voids are found on the line
3. Square packed sheets are arranged on the top of other such that a sphere in the next layer rests on the center of a square in the previous layer. Identify the type of arrangement and find the coordination number.
 (A) Simple Cubic, 6 (B) Face Centered Cubic, 8
 (C) Face Centered Cubic, 12 (D) Body Centered Cubic, 8
4. Given an alloy of Cu, Ag and Au in which Cu atoms constitute the CCP arrangement. If the hypothetical formula of the alloy is Cu_4Ag_3Au . What are the probable locations of Ag and Au atoms.
 (A) Ag - All tetrahedral voids; Au - all octahedral voids
 (B) Ag - 3/8th tetrahedral voids; Au - 1/4th octahedral voids
 (C) Ag - 1/2 octahedral voids; Au - 1/2 tetrahedral voids
 (D) Ag - all octahedral voids; Au - all tetrahedral voids
5. The distance between adjacent, oppositely charged ions in rubidium chloride is 3.285 Å; in potassium chloride is 3.139 Å; in sodium bromide is 2.981 Å and in potassium bromide is 3.293 Å. The distance between adjacent oppositely charged ions in rubidium bromide is :
 (A) 3.147 Å (B) 3.385 Å (C) 3.393 Å (D) 3.439 Å
6. Zinc sulphide exists in two different forms-zinc blende and wurtzite. Both occur as 4:4 co-ordination compounds. Choose the correct option from among the following :
 (A) zinc blende has a bcc structure and wurtzite an fcc structure
 (B) zinc blende has an fcc structure and wurtzite an hcp structure
 (C) zinc blende as well as wurtzite have a hcp structure
 (D) zinc blende as well as wurtzite have a ccp structure

SINGLE AND DOUBLE VALUE INTEGER TYPE

7. The 2 D unit cell of an element is shown. The two layers are placed one over the other and touching each other. Find the effective number of atoms in the unit cell :



8. The density of solid argon is 1.65 g/mL at -233°C . If the argon atom is assumed to be sphere of radius $1.54 \times 10^{-8} \text{ cm}$, what percentage of solid argon is apparently empty space ? (At. wt. of Ar = 40)
9. How many number of tetrahedral voids are completely inside the HCP unit cell.
10. How many number of atoms present in half of HCP unit cell.
11. Let MgTiO_3 exists in perovskite structure. In this lattice, all the atoms of one of the face diagonals are removed. Calculate the density of unit cell if the radius of Mg^{2+} is 0.7 \AA and the corner ions are touching each other. [Given atomic mass of Mg = 24, Ti = 48]
12. A mineral having the formula AB_2 , crystallises in the cubic close - packed lattice, with the A atoms occupying the lattice points. The co-ordination number of the A atoms is x, that of B atoms is y. Report your answer ($x - y$).

ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

13. Which of the following is not true about the voids formed in 3 dimensional hexagonal close packed structure?
- (A) A tetrahedral void is formed when a sphere of the second layer is present above triangular void in the first layer.
 (B) All the triangular voids are not covered by the spheres of the second layer.
 (C) Tetrahedral voids are formed when the triangular voids in the second layer lie above the triangular voids in the first layer and the triangular shapes of these voids do not overlap.
 (D) Octahedral voids are formed when the triangular voids in the second layer exactly overlap with similar voids in the first layer.
14. The co-ordination number of FCC structure for metals is 12, since
 (A) each atom touches 4 others in same layer, 3 in layer above and 3 in layer below.
 (B) each atom touches 4 others in same layer, 4 in layer above and 4 in layer below.
 (C) each atom touches 6 others in same layer, 3 in layer above and 3 in layer below.
 (D) each atom touches 3 others in same layer, 6 in layer above and 6 in layer below.
15. Three lines are drawn from a single corner of an FCC unit cell to meet the other corner such that they are found to pass through exactly only 1 octahedral void, no voids of any type and exactly 2 tetrahedral voids with 1 octahedral void. Identify the line?
 (A) Edge length (B) Body diagonal (C) Face diagonal
 (D) A line which passes through only two face centres of opposite faces

PART - V : PRACTICE TEST-2 (IIT-JEE (ADVANCED Pattern))

Max. Time : 1 Hr.

Max. Marks : 66

Important Instructions

A. General :

1. The test is of 1 hour duration.
2. The Test Booklet consists of 22 questions. The maximum marks are 66.

B. Question Paper Format :

3. Each part consists of five sections.
4. Section-1 contains 7 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE is correct.

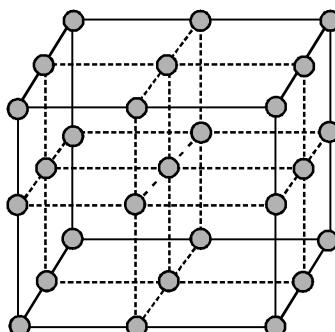
5. Section-2 contains 5 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE OR MORE THAN ONE are correct.
 6. Section-3 contains 6 questions. The answer to each of the questions is a single-digit integer, ranging from 0 to 9 (both inclusive).
 7. Section-4 contains 1 paragraphs each describing theory, experiment and data etc. 3 questions relate to paragraph. Each question pertaining to a particular passage should have only one correct answer among the four given choices (A), (B), (C) and (D).
 8. Section-5 contains 1 multiple choice questions. Question has two lists (list-1 : P, Q, R and S; List-2 : 1, 2, 3 and 4). The options for the correct match are provided as (A), (B), (C) and (D) out of which ONLY ONE is correct.

C. Marking Scheme :

9. For each question in Section 1, 4 and 5 you will be awarded 3 marks if you darken the bubble corresponding to the correct answer and zero mark if no bubble is darkened. In all other cases, minus one (-1) mark will be awarded.
 10. For each question in Section 2, you will be awarded 3 marks. If you darken all the bubble(s) corresponding to the correct answer(s) and zero mark. If no bubbles are darkened. No negative marks will be answered for incorrect answer in this section.
 11. For each question in Section 3, you will be awarded 3 marks if you darken only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. No negative marks will be awarded for incorrect answer in this section.

SECTION-1 : (Only One option correct Type)

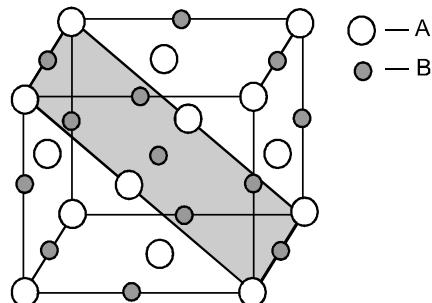
This section contains 7 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which Only ONE option is correct.



- (A) The arrangement is SC with each lattice point surrounded by 6 nearest neighbours.
 - (B) The arrangement is SC with each lattice point surrounded by 8 nearest neighbours.
 - (C) The arrangement is FCC with each lattice point surrounded by 12 nearest neighbours.
 - (D) The arrangement is BCC with each lattice point surrounded by 8 nearest neighbours



5. A crystal is made of particles A and B. A forms FCC packing and B occupies all the octahedral voids. If all the particles along the plane as shown in figure are removed, then, the formula of the crystal would be :

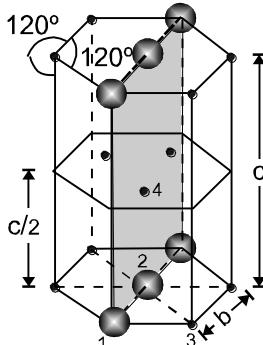


(A) AB

(B) A_5B_7 (C) A_7B_5

(D) None of these.

6. Calculate the perimeter of given plane in HCP unit cell (Given that radius of atoms = $R \text{ \AA}$).

(A) $6.437 R$ (B) $15.32 R$ (C) $16 R$

(D) None of these

7. MgAl_2O_4 , is found in the Spinal structure in which O^{2-} ions constitute CCP lattice, Mg^{2+} ions occupy 1/8th of the Tetrahedral voids and Al^{3+} ions occupy 1/2 of the Octahedral voids.

Find the total +ve charge contained in one unit cell.

(A) +7/4 electronic charge

(B) +6 electronic charge

(C) +2 electronic charge

(D) +8 electronic charge

Section-2 : (One or More than one options correct Type)

This section contains 6 multipole choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE or MORE THAN ONE are correct.

8. Lead metal has a density of 11.34 g/cm^3 and crystallizes in a face-centered lattice. Choose the correct alternatives

(A) the volume of one unit cell is $1.214 \times 10^{-22} \text{ cm}^3$ (B) the volume of one unit cell is $1.214 \times 10^{-19} \text{ cm}^3$

(C) the atomic radius of lead is 175 pm

(D) the atomic radius of lead is 155.1 pm

9. Given that interionic distance in Na^+ , F^- crystal is 2.31\AA and $r_{\text{F}^-} = 1.36 \text{\AA}$, which of the following predictions will be right

(A) $r_{\text{Na}^+}/r_{\text{F}^-} \approx 0.7$ (B) coordination number of Na^+ = coordination number of $\text{F}^- = 6$ (C) Na^+ , F^- will have rock salt type crystal structure(D) effective nuclear charge for Na^+ and F^- are equal

10. Which of the following statement(s) for crystal having schottky defect is/are correct.

(A) Schottky defect arises due to absence of cations & anion from positions which they are expected to occupy.

(B) The density of crystal having schottky defect is smaller than that of perfect crystal.

(C) Schottky defect are more common in co-valent compound with higher co-ordination number.

(D) The crystal having schottky defect is electrically neutral as a whole.



11. For each of the following substances, identify the intermolecular force or forces that predominate. Using your knowledge of the relative strengths of the various forces, rank the substances in order of their normal boiling points. Al_2O_3 , F_2 , H_2O , Br_2 , ICl , NaCl

(A) $\text{F}_2 < \text{Br}_2 < \text{ICl}$

(B) $\text{H}_2\text{O} < \text{NaCl} < \text{Al}_2\text{O}_3$

(C) $\text{ICl} < \text{H}_2\text{O}$

(D) $\text{H}_2\text{O} < \text{ICl}$

12. The ZnS zinc blende structure is cubic. The unit cell may be described as a face-centered sulfide ion sublattice with zinc ions in the centers of alternating minicubes made by partitioning the main cube into 8 equal parts (as shown in fig.)

(a) How many nearest neighbors does each Zn^{2+} have?

(b) How many nearest neighbors does each S^{2-} have?

(c) What angle is made by the lines connecting any Zn^{2+} to any two of its nearest neighbors?

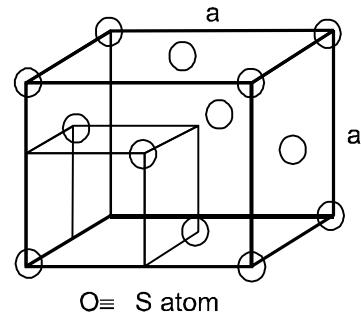
(d) What minimum r_+/r_- ratio is needed to avoid anion-anion contact, if closest cation-anion pairs are assumed to touch?

(A) C.N. of Zn^{2+} & S^{2-} = 4 & 4

(B) C.N. of Zn^{2+} & S^{2-} = 6 & 6

(C) $109^\circ 28'$

(D) $\frac{r_{\text{Zn}^{2+}}}{r_{\text{S}^{2-}}} = 0.225$



13. A metal (M), shows ABAB arrangement of atoms in solid state, then what is the relation between radius of atom (r) and edge length (a) and height (c) of HCP unit cell.

(A) $a = 2R$

(B) $c = \left(\sqrt{\frac{2}{3}}\right) 4r$

(C) $c = \left(\sqrt{\frac{3}{2}}\right) 4r$

(D) $a = (2\sqrt{2})r$

Section-3 : (One Integer Value Correct Type.)

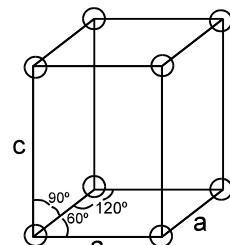
This section contains 5 questions. Each question, when worked out will result in one integer from 0 to 9 (both inclusive)

14. A mineral of iron contains an oxide containing 72.36% iron by mass and has a density of 5.2 g/cc. Its unit cell is cubic with edge length of 839 pm. What is the total number of atoms (ions) present in each unit cell? (Fe - 56, O-16)

15. Percentage of void space in AB solid having rock salt structure if $\frac{r_+}{r_-} = \frac{1}{2}$ having cation anion contact.

Given $\pi = 3.15$.

16. In an ionic solid $r_{(+)} = 1.6 \text{ \AA}$ and $r_{(-)} = 1.864 \text{ \AA}$. Use the radius ratio rule to determine the edge length of the cubic unit cell in \AA .



17. Ice crystallizes in a hexagonal lattice. At the low temperature at which the structure was determined, the lattice constants were $a = 4.53 \text{ \AA}$ and $c = 7.41 \text{ \AA}$ (as shown in fig.). How many H_2O molecules are contained in a unit cell? (Density of ice = 0.92 gm/cc)

18. A spinel is an important class of oxides consisting of two types of metal ions with the oxides ions arranged in CCP layers. The normal spinel has one-eighth of the tetrahedral holes occupied by one type of metal ion and one-half of the octahedral holes occupied by another type of metal ion. Such a spinel is formed by Zn^{2+} , Al^{3+} and O^{2-} with Zn^{2+} in the tetrahedral holes. If formula of the compound is $\text{Zn}_x\text{Al}_y\text{O}_z$, then find the value of $(x + y + z)$?



SECTION-4 : Comprehension Type (Only One options correct)

This section contains 1 paragraphs, each describing theory, experiments, data etc. 3 questions relate to the paragraph. Each question has only one correct answer among the four given options (A), (B), (C) and (D).

Paragraph for Questions 19 to 21

Two dimensional close packed structure can be generated by stacking the rows of close packed spheres. This can be done in two different ways.

- (I) Spheres. This can be done in two different ways.

The second row may be placed in contact with the first one, such that the spheres of the second row are exactly above those of first row. The spheres of the two rows are aligned vertically as well as horizontally.

If we call the first row as 'A' type of row, the second row being exactly same as the first one is also of 'A' type. Similarly, we may place more rows to obtain AAAA.... type arrangement.

(II) In this type, the second row may be placed above the first one in a staggered manner such that its spheres fit in depressions of first row. If the arrangement of spheres in the first row is called 'A' type, the one in the second row is different and may be called 'B' type. When the third row is placed adjacent to the second in staggered manner, its spheres are aligned with those of first layer. Hence this layer is also 'A' type. The spheres of similarly placed fourth row will be aligned with those of the second row ('B' type). Hence this arrangement is of ABAB.....type.

SECTION-5 : Matching List Type (Only One options correct)

This section contains 1 questions, each having two matching lists. Choices for the correct combination of elements from List-I and List-II are given as options (A), (B), (C) and (D) out of which one is correct

- 22.** Match list-I with list-II and select the correct answer by using the codes given below:

	List I (Shapes)		List II (Radius ratio)
P.	Planar triangle	1.	0.732
Q.	Square planar	2.	0.225
R.	Body centered cubic	3.	0.155
S.	Tetrahedral	4.	0.414

Code :

Code :	P	Q	R	S		P	Q	R	S	
(A)	3	4	1	2		(B)	3	2	1	4
(C)	2	1	4	3		(D)	1	3	4	2

Practice Test-2 (IIT-JEE (ADVANCED Pattern))

OBJECTIVE RESPONSE SHEET (ORS)

APSP Answers**PART – I**

- | | | | | | | | | | |
|------------|-----|------------|-----|------------|-----|------------|-------|------------|-----|
| 1. | (3) | 2. | (2) | 3. | (2) | 4. | (2) | 5. | (1) |
| 6. | (3) | 7. | (2) | 8. | (4) | 9. | (1) | 10. | (2) |
| 11. | (3) | 12. | (2) | 13. | (3) | 14. | (3) | 15. | (1) |
| 16. | (1) | 17. | (2) | 18. | (2) | 19. | (1) | 20. | (4) |
| 21. | 32 | 22. | 100 | 23. | 12 | 24. | 1.123 | 25. | 1 |

PART – II

- | | | | | | | | | | |
|------------|-----|------------|-----|------------|-----|------------|-----|------------|-----|
| 1. | (4) | 2. | (1) | 3. | (2) | 4. | (3) | 5. | (4) |
| 6. | (4) | 7. | (1) | 8. | (4) | 9. | (2) | 10. | (4) |
| 11. | (2) | 12. | (4) | 13. | (2) | 14. | (3) | 15. | (1) |
| 16. | (1) | 17. | (3) | 18. | (1) | | | | |

PART – III

- | | | | | | | | | | |
|------------|-----|------------|-----|------------|-----|------------|-----|------------|-----|
| 1. | (C) | 2. | (C) | 3. | (D) | 4. | (B) | 5. | (C) |
| 6. | (B) | 7. | (A) | 8. | (B) | 9. | (C) | 10. | (D) |
| 11. | (D) | 12. | (D) | 13. | (A) | 14. | (D) | 15. | (D) |
| 16. | (B) | 17. | (C) | 18. | (C) | 19. | (C) | 20. | (B) |
| 21. | (B) | 22. | (C) | 23. | (B) | 24. | (D) | 25. | (C) |
| 26. | (B) | 27. | (A) | 28. | (B) | | | | |

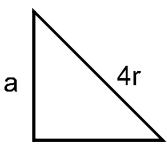
PART – IV

- | | | | | | | | | | |
|------------|-----------------------------|------------|------------|------------|------|------------|------|------------|-------|
| 1. | (D) | 2. | (B) | 3. | (C) | 4. | (B) | 5. | (D) |
| 6. | (B) | 7. | 3 | 8. | 62 | 9. | 8 | 10. | 3 |
| 11. | $\approx 65 \text{ g/cm}^3$ | 12. | $4(8 - 4)$ | 13. | (CD) | 14. | (BC) | 15. | (ABC) |

PART – V

- | | | | | | | | | | |
|------------|-------|------------|-------------------|------------|------|------------|-------------------|------------|-------|
| 1. | (B) | 2. | (A) | 3. | (A) | 4. | (A) | 5. | (A) |
| 6. | (D) | 7. | (D) | 8. | (AC) | 9. | (ABC) | 10. | (ABD) |
| 11. | (ABC) | 12. | (ACD) | 13. | (AB) | 14. | 56 | 15. | 30 |
| 16. | 4 | 17. | 4 water molecules | | | 18. | $7 = (1 + 2 + 4)$ | 19. | (B) |
| 20. | (B) | 21. | (D) | 22. | (A) | | | | |

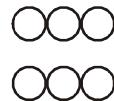
APSP Solutions**PART – I**

1. At corner = $\frac{1}{8}$ (for per atom)
 $\Rightarrow X_{\frac{1}{8}} Y$ (one X atom removed)
 $\Rightarrow X_{7/8} Y$
 $\Rightarrow X_7 Y_8$
2. When NaCl crystal is heated in sodium vapors, then it attains yellow colour. It is due to F-centres, which is electron trapped in anion vacancy created by Cl^- .
3. Packing efficiency of ccp is 74% so its best packing is cubic packing.
4. $2(r^+ + r^-) = a$ or $r^+ = x$ = radius of Na^+
 $2(x + y) = a$ $r^- = y$ = radius of Cl^-
5. Sr^{2+} are at the corners and face centre of the cubic arrangement.
6. Triclinic $a \neq b \neq c$
 $\alpha \neq \beta \neq \gamma$
7. Schottky defect occurs in electrovalent compound which has same bond size positive and negative ion.
8. For tetrahedral void r_+/r_- range will be $0.225 \leq \frac{r^+}{r^-} \leq 0.414$.
9. Malleability and ductility is tendency of metal ion layer slide over the other layer.
10. At corner = $\frac{1}{8} \times$ (for per atom) = $\frac{X}{8} \times 8$
At body center = $1 \times$ (for per atom) = Y
At face center = $\frac{1}{2} \times$ (for per atom) = $\frac{Z}{2} \times 6$
Simple ratio of all three XYZ_3
11. AgBr shows schottky and frenkel defect.
12. 
 $(4r)^2 = a^2 + a^2$
 $a = \frac{4}{\sqrt{2}} r$
13. In antifluorite structure anions form F.C.C. structure and cations occupy all tetrahedral voids.
14. CsCl have simple cubic structure. In this structure body diagonal of simple cube $\sqrt{3} a = 2 \times (r_{Cs^+} + r_{Cl^-})$
So interionic distance = $2 \times (r_{Cs^+} + r_{Cl^-})$
15. A at corner = $\frac{1}{8} \times 8 \times A = A$
B at face center = $\frac{1}{2} \times 6 \times B = 3B = AB_3$

16. $d = \frac{Z \times M}{N_A a^3} \Rightarrow N_A = \frac{4 \times 100}{10 \times (2 \times 10^{-8})^3} = 5 \times 10^{24}$ (here : 200 Pm = 2×10^{-8} cm.)

18. S^{2-} ion form fcc lattice

→ Zn^{+2} ion occupy alternate four tetrahedral void i.e.



19. Cubic system have three unit cell

(1) Simple cubic (2) F.C.C. (3) B.C.C

H_2O is a paramagnetic substance.

Graphit is a covalent solid in layer form. In these layer vanderwaal's forces present.

20. S_1 : edge length = $2(r_{Na^+} + r_{Cl^-})$

distance b/w Na^+ and Cl^- is less than edge length

S_2 : 4 triangular void.

S_3 : In Zns structure $4Zn^{+2}$ and $4s^{-2}$ present in each unit cell.

21. Packing efficiency = $\frac{2 \times \frac{4}{3} \pi R^3}{\left(\frac{4R}{\sqrt{3}}\right)^3} = \frac{\sqrt{3}\pi}{8} = 68\%$

vacent space = $100 - 68 = 32\%$

22. In 3D close packed structure for every 100 atoms it contain 100 octahedral voids.

23. C.N. of Cu^{2+} ion = 8

C.N. of F^- ion = 4

∴ C.N. of CaF_2 type structure is = 8 : 4

24. NaCl and KCl has octahedral structure

$$\frac{r_{Na^+}}{r_{Cl^-}} = 0.55 \text{ and } \frac{r_{K^+}}{r_{Cl^-}} = 0.74$$

In octahedral edge length = $r_{cation} + r_{anion}$

$$\frac{r_{Na^+} + r_{Cl^-}}{r_{Cl^-}} = 1.55 \quad \dots\dots(1)$$

$$\frac{r_{K^+} + r_{Cl^-}}{r_{Cl^-}} = 1.74 \quad \dots\dots(2)$$

a = edge length of KCl octahedral.

a = $r_{K^+} + r_{Cl^-}$

b = edge length of NaCl octahedral

b = $r_{Na^+} + r_{Cl^-}$

$$\frac{a}{b} = \frac{r_{K^+} + r_{Cl^-}}{r_{Na^+} + r_{Cl^-}} = \frac{1.74}{1.55} = 1.123$$

PART – II

1. BCC - points are at corners and one in the center of the unit cell.

$$\text{Number of atoms per unit cell} = 8 \times \frac{1}{8} + 1 = 2$$

FCC - Points are at the corners and also center of the six faces of each cell.

$$\text{Number of atoms per unit cell} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4.$$

2. mass (m) = density × volume = 1.00 g

Mol. wt. (M) of NaCl = 23 + 15.5 = 58.5

Number of unit cells present in a cube shaped crystal of NaCl of

$$\text{mass } 1.00 \text{ g} = \frac{\rho \times a^3 \times N_A}{M \times Z} = \frac{m \times N_A}{M \times Z} = \frac{1 \times 6.023 \times 10^{23}}{58.5 \times 4}$$

(In NaCl each unit cells has 4 NaCl units. Hence Z = 4)

$$\therefore \text{Number of unit cells} = 0.02573 \times 10^{23} = 2.57 \times 10^{21} \text{ unit cells.}$$

3. When an atom or ion is missing from its normal lattice site, a lattice vacancy is created. This defect is known as Schottky defect. Here equal number of Na^+ and Cl^- ions are missing from their regular lattice position in the crystal. So it is Schottky defect.

4. Number of A ions per unit cell = $\frac{1}{8} \times 8 = 1$

Number of B ions per unit cell = $\frac{1}{2} \times 6 = 3$ Empirical formula = AB_3 .

5. In case of a face-centered cubic structure, since four atoms are present in a unit cell, hence volume.

$$V = 4 \left(\frac{4}{3} \pi r^3 \right) = \frac{16}{3} \pi r^3$$

6. According to question : Number of Y atom in ccp unit cell = 4

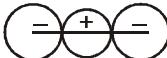
$$\text{Number of X atom in ccp unit cell} = 8 \times \frac{2}{3} = \frac{16}{13}$$

Formula of compound = $\text{X}_{16/3}\text{Y}_4 = \text{X}_{16}\text{Y}_{12} = \text{X}_4\text{Y}_3$

7. In fcc unit cell $4r = \sqrt{2}a$ [r = radius of Cu atom, a = edge length]

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

$$r = \frac{\sqrt{2} \times 361}{4} = 127 \text{ pm.}$$

8.  $2 \times 110 + 2 \times r_- = 508$

$2r_- = 288$

$r_- = 144 \text{ pm}$

9. Packing fraction of CCP = $\frac{\pi}{3\sqrt{2}}$ = 0.74 \Rightarrow 74%

\therefore Percentage of free space in CCP = 100 - 74 = 26%

Packing fraction of BCC = $\frac{\pi\sqrt{3}}{8}$ = 0.68 \Rightarrow 68%

\therefore Percentage of free space in BCC = 100 - 68 = 32%

10. A $\frac{1}{8 \times 1}$ B $\frac{1}{5 \times \frac{1}{2}}$

Formula of compound A_2B_5 .

11. FCC lattice

$a = 361 \text{ pm}$

$a\sqrt{2} = 4r$

$$r = \frac{361 \times \sqrt{2}}{4} = 127.6 \approx 128 \text{ pm.}$$

12. For BCC structure $\sqrt{3} a = 4r$ $r = \frac{\sqrt{3}}{4} a = \frac{\sqrt{3}}{4} \times 351 = 152 \text{ pm.}$

13. $M_{0.98}O$

Consider one mole of the oxide.

Moles of M = 0.98, Moles of O^{2-} = 1Let moles of M^{3+} = x

$$\Rightarrow \text{Moles of } M^{2+} = 0.98 - x$$

⇒ Doing charge balance

$$(0.98 - x) \times 2 + 3x - 2 = 0$$

$$\Rightarrow 1.96 - 2x + 3x - 2 = 0$$

$$\Rightarrow x = 0.04$$

$$\Rightarrow \% \text{ of } M^{3+} = \frac{0.04}{0.98} \times 100 = 4.08\%$$

14. In CsCl, Cl^- lie at corners of simple cube and Cs^+ at the body centre.

$$\text{Hence, along the body diagonal, } Cs^+ \text{ & } Cl^- \text{ touch each other so } \frac{\sqrt{3}a}{2} = r_{Cs^+} + r_{Cl^-}$$

$$15. R = \frac{\sqrt{3}}{4} a = 1.86 \text{ \AA}$$

16. NCERT based (Solid state).

17. For FCC, $\sqrt{2}a = 4R$

$$\text{So, } 2R = \frac{a}{\sqrt{2}}$$

18. Frenkel Defect.

PART – IV

$$1. \text{ Common Volume} = \left(\frac{a}{2}\right)^3 = \frac{a^3}{8} \quad [\therefore \text{Common vol is a cube of edge length } \frac{a}{2}]$$

2. Only tetrahedral, since there is one tetrahedral voids just above the atom & one just below the atom.

3. Unit cell is face centered cubic so coordination number is 12.

4. $Cu_4 \quad Ag_3 \quad Au$ \downarrow \downarrow \downarrow Froms c.c.p., $\frac{3}{8}$ th of tetrahedral voids, $\frac{1}{4}$ of octahedral voids [\therefore No. of O^- voids = 4] $z = 4$, [\therefore No. of T^- voids = 8].

$$5. (r_{Rb^+} + r_{Cl^-}) + (r_{K^+} + r_{Br^-}) - (r_{K^+} + r_{Cl^-}) = (r_{Rb^+} + r_{Br^-})$$

$$3.285 + 3.293 - 3.139 = 3.439.$$

6. These are isomorphous.

$$7. \text{ Number of atoms in 2D unit cells} = \frac{1}{3} \times 6 + 1 \times 1 = 3.$$

$$8. \text{ Volume of one atom of Ar} = \frac{4}{3} \pi r^3$$

$$\text{Also, number of atoms in 1.65 g or one mL} = \frac{1.65}{40} \times 6.023 \times 10^{23}$$

 \therefore Total volume of all atoms of Ar in solid state

$$= \frac{4}{3} \pi r^3 \times \frac{1.65}{40} \times 6.023 \times 10^{23} = \frac{4}{3} \times \frac{22}{7} \times (1.54 \times 10^{-8})^3 \times \frac{1.65}{40} \times 6.023 \times 10^{23} = 0.380 \text{ cm}^3$$

Volume of solid argon = 1 cm^3

$$\therefore \% \text{ empty space} = \frac{[1 - 0.380]}{1} \times 100 = 62\%$$

10. $3 \times \frac{1}{2} + \frac{1}{6} \times 6 + \frac{1}{2} \times 1 = 3$

11. No. of Mg^{2+} per unit cell = 8 [At corners] $\times \frac{1}{8} = 1$

No. of Ti per unit cell = 1 [body center] $\times \frac{1}{1} = 1$

No. of O per unit cell = 6 [Face center] $\times \frac{1}{2} = 3$

So formula = MgTiO_3

Atom are removed along face diagonal

No. of Mg^{2+} = 6 [At corner] $\times \frac{1}{8} = \frac{6}{8} = \frac{3}{4}$

No. of Ti per unit cell = 1 [Body center] $\times \frac{1}{1} = 1$

No. of O per unit cell = 5 [Face center] $\times \frac{1}{2} = \frac{5}{2}$

So formula of compound = $\text{Mg}_{\frac{3}{4}}\text{TiO}_{\frac{5}{2}}$

Formula mass = $24 \times \frac{3}{4} + 48 + 16 \times \frac{5}{2} = 18 + 48 + 40 = 106 \text{ amu}$

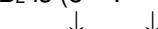
As corner ion are touching so $a = 2 r_{\text{Mg}^{2+}} = 2 \times 0.7 = 1.4 \text{ \AA}$

$$d = \frac{\text{mass}}{\text{Volume}} = \frac{106 \times 1.67 \times 10^{-24}}{(1.4)^3 \times 10^{-24}} \text{ g/cm}^3 = 64.5 \text{ g/cm}^3 \approx 65 \text{ g/cm}^3$$

12. It is fluorite (CaF_2) structure. Since formula is AB_2

\Rightarrow No. of B atoms is twice the no. of A atoms. Hence B occupies all the tetrahedral voids (100%).

AB_2 is (8 : 4) compound (Fluorite Structure Compound)



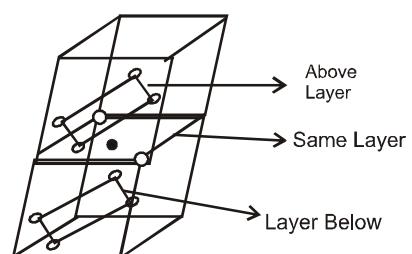
C.N. of A C.N. of B.

FCC can be viewed in two following ways -

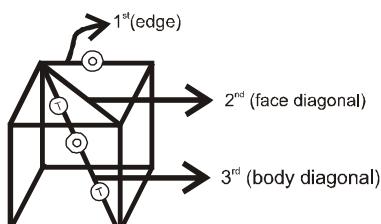
(i) Planes along the faces (and parallel to it) of the unit cell.

14. \Rightarrow Each atom touches 4 in same layer, 4 in layer above and 4 in layer below it.

(ii) Planes along closest packed spheres \rightarrow each atom touches 6 atom in same layer, 3 in layer above and 3 in layer below it.



15.



PART – V

1. Coordination number of square packing pattern is 4.
2. No. of X atom per unit cell = $7 \times \frac{1}{8} = \frac{7}{8}$
No. of Y atom per unit cell = $6 \times \frac{1}{2} = 3$
 \therefore Formula = $X_{7/8} Y_3$ or $X_7 Y_{24}$.
4. According to figure, it shows a simple cubic lattice. Now observe the center atom, its has 6 nearest neighbours
5. In new arrangement, A particles = $\left(\frac{1}{8} \times 8 + \frac{1}{2} \times 6\right) - \left(\frac{1}{8} \times 4 + \frac{1}{2} \times 2\right) = \frac{5}{2}$
& B particles = $\left(\frac{1}{4} \times 12 + 1\right) - \left(1 + \frac{1}{4} \times 2\right) = \frac{5}{2}$
So, formula is AB
6. Perimeter of plane is = $2C + 8R = \frac{2 \times 4\sqrt{2}R}{3} + 8R = 11.77 R$
7. Total positive charge = Charge on Mg^{2+} + Charge on Al^{3+} = $\frac{1}{8} \times 8 \times 2 + \frac{1}{2} \times 4 \times 3 = 8$ electronic charge.
8. Density = $\frac{Z \times M}{N_A \times \text{volume}}$
so, Volume = $\frac{4 \times 207}{6.02 \times 10^{23} \times 11.34} = 1.213 \times 10^{-22} \text{ cm}^3$; $4r = a\sqrt{2}$
 $r = \frac{4.95 \times 10^{-8} \times \sqrt{2}}{4} = 175 \text{ pm}$
Volume = $a^3 = 1.213 \times 10^{-22}$
so, $a = (1.213 \times 10^{-24})^{1/3}$
 $a = 4.95 \times 10^{-8} \text{ cm.}$
9. Na^+ & F^- are isoelectronic hence they will have same screening const (s) but not the effective nuclear charge.
 $\therefore r_{Na^+}/r_{F^-} \approx 0.7$ (coordination = 6, rock salt structure)
10. Schottky defect is only observed in ionic compound.
11. Al_2O_3 – ionic Br_2 – vanderwaal F_2 – vanderwaal
 ICl – dipole dipole H_2O – dipole - dipole (H-bonding) $NaCl$ – ionic,
 $F_2 < Br_2 < ICl < H_2O < NaCl < Al_2O_3$
12. (a) As each Zn^{2+} ion is present in tetrahedral void. So it is coordination number is = 4.
(b) Similarly S^{2-} ion have coordination number = 4.
(c) As Zn^{2+} ion is present in tetrahedral void that's why line's connecting any two nearest neighbour and Zn^{2+} have angle = $109^\circ 28'$.
(d) For tetrahedral voids radius ratio is $\frac{r_{Zn^{2+}}}{r_{S^{2-}}} = 0.225$.
13. $a = 2R, c = \sqrt{\frac{2}{3}} 2a = \sqrt{\frac{2}{3}} 4r$

14. $\frac{72.36}{56}$ 'Fe', $\frac{27.64}{16}$ 'O' \Rightarrow 1.292 'Fe', 1.7275 'O'

Hence proportion is 1 : 1.33; So Empirical formula is Fe_3O_4 , Empirical formula mass = 232 amu
Now if there are x formula units in the unit cell

$$5.2 = \frac{x(232)}{\frac{6.02 \times 10^{23}}{(8.39 \times 10^{-8})^3}} \Rightarrow x = 7.9688$$

Hence number of ions in the unit cell = 56

15. $r_+ + r_- = \frac{a}{2} \Rightarrow \frac{3r_-}{2} = \frac{a}{2}; r_- = \frac{a}{3}$ and $r_+ = \frac{a}{6}$

$$\text{Packing fraction} = \frac{4 \times \frac{4}{3} \pi (r_+^3 + r_-^3)}{a^3} = \frac{4 \times \frac{4}{3} \pi \left[\left(\frac{a}{6}\right)^3 + \left(\frac{a}{3}\right)^3 \right]}{a^3} = 0.7.$$

Percentage void = 30%.

16. $\frac{r_+}{r_-} = \frac{1.6}{1.864} = 0.858$

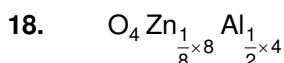
So, it is CsCl type unit cell

$$\text{So } \sqrt{3} a = 2(r_+ + r_-)$$

$$\text{So } a = \frac{2(1.864 + 1.6)}{\sqrt{3}} \text{ \AA} = 2 \times 2 \text{ \AA} = 4 \text{ \AA}$$

17. $d = \frac{Z \times M}{N_0 \times \text{Volume}}$ $\Rightarrow 0.92 = \frac{Z \times 18}{6.02 \times 10^{23} \left[\frac{6\sqrt{3}a^2}{4} \times c \right]}$

$$\Rightarrow 0.92 = \frac{Z \times 18}{6.02 \times 10^{23} \left[\frac{6\sqrt{3}}{4} \times (4.53)^2 \times 7.41 \times 10^{-24} \right]} \Rightarrow Z = 4.$$



So, formula is ZnAl_2O_4 .

22.

Radius ratio	Types of structure	Coordination No.
$r_+/r_- < 0.155$	linear void	2
$0.155 \leq r_+/r_- < 0.225$	triangular void	3
$0.225 \leq r_+/r_- < 0.414$	tetrahedral void	4
$0.414 \leq r_+/r_- < 0.732$	octahedral void	6
$0.732 \leq r_+/r_- < 1$	cubical void	8